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. For this purpose it is necessary to formulate reactions and write 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.

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 lattice sites in the metal and oxygen sublattices must be maintained, even if the total number of sites may increae or decrease during the reaction. These rules may be summarised as follows:

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.[1]

Electroneutrality

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 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 or 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.

Ratios of regular lattice sites.

The ratio(s) of the number of regular cation and anion lattice 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_2O_3 the ratio of regular cation to anion sites is 2:3, and if 3 oxygen sites are created in M_2O_3 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 is discussed below, 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 lattice sites may change in a defect reaction, and therefore, the defect equation may include the formation or annihilation of lattice sites as long as the proper ratios are maintained.

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[1] 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).

It should be noted that no sites are created in the formation of electronic defects.[2]

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 crystallite sizes for which the number of surface atoms is insignificant 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 a later chapter.)

Examples of defect equations

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.

It should be noted that both the stoichiometric and nonstoichiometric defect structures may prevail in the same compound, depending on the activities (partial pressures) of the components in the compound.

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 – instrinsic 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

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[2] One may choose to operate with sites – or energy levels - for electronic defects, and one must then take into account the emty levels of the conduction band and the occupied levels of the valence band.

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 lattice 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 lattice sites within the crystal, M_M and O_O, one must also take into account that the formation of the Schottky pair results in the formation of two new lattice sites, and the overall equation may thus be written

$$M_M + O_O = v_M^{//} + v_O^{\bullet\bullet} + M_M + O_O \tag{2.1}$$

However, in this equation M_M and O_O on both sides may be cancelled, and the net equation therefore becomes

$$0 = v_M^{//} + v_O^{\bullet\bullet} \tag{2.2}$$

where 0 (nil) designates a perfect crystal.

In Eqs. 2.1 and 2.2 it is assumed that doubly charged vacancies predominate and that neutral and singly charged vacancies can be neglected. The equations could have been written in more detailed steps starting with the formation of neutral vacancies and the subsequent, consecutive ionisation of these to singly and doubly charged vacancies.

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 lattice sites are created in the process. If, for the sake of illustration, the interstitial ion

and the resulting vacancy are assumed to be doubly charged, the formation of a Frenkel defect pair may be written

$$M_M = v_M^{//} + M_i^{\bullet\bullet} \tag{2.3}$$

A corresponding equation may be written for the formation of an anion Frenkel defect pair. This latter defect situation is also often termed an anti-Frenkel defect structure.

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

$$0 = e^{/} + h^{\bullet} \tag{2.4}$$

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

$$e^x = e^{/} + h^{\bullet} \tag{2.5}$$

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

$$e_v^x + h_c^x = e_c^{/} + h_v^{\bullet} \tag{2.6}$$

but both the two latter reactions represent levels of detail that we normally need not consider.

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

$$2Fe_{Fe}^x = Fe_{Fe}^{/} + Fe_{Fe}^{\bullet} \tag{2.7}$$

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:

$$Fe_{Fe}^x + Ti_{Ti}^x = Fe_{Fe}^\bullet + Ti_{Ti}^/ \qquad\qquad (2.8)$$

Nonstoichiometry

The ratio of cation to anion lattice 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, complementary electronic defects 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 (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

$$MO_2(s) = MO_{2-x}(s) + \tfrac{x}{2}O_2(g) \qquad\qquad (2.9)$$

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. No change in the number of lattice sites takes place. This defect reaction may be written

$$O_O^x = v_O^x + \tfrac{1}{2}O_2(g) \tag{2.10}$$

In this equation it is assumed that the oxygen vacancy is neutral, i.e. the two electrons of the O^{2-} ion are associated with the vacancy or its immediate neighbourhood and the vacancy has zero effective charge. 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. Correspondingly, the oxygen vacancy acts as a donor and becomes singly and doubly charged:

$$v_O^x = v_O^{\bullet} + e^{/} \tag{2.11}$$

$$v_O^{\bullet} = v_O^{\bullet\bullet} + e^{/} \tag{2.12}$$

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

$$O_O^x = v_O^{\bullet\bullet} + 2e^{/} + \tfrac{1}{2}O_2(g) \tag{2.13}$$

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

$$O_O^x + 2M_M^x = v_O^{\bullet\bullet} + 2M_M^{/} + \tfrac{1}{2}O_2(g) \tag{2.14}$$

If this takes place in the oxide MO_2 the valence of the M atoms then partly reduce from +4 to +3 when the oxide becomes non-stoichiometric (MO_{1-x}).

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 lattice site is annihilated in this process, two oxygen lattice 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

$$M_M^x + 2O_O^x = M_i^x + O_2(g) \tag{2.15}$$

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

$$M_i^x = M_i^\bullet + e^/ \text{, etc.} \tag{2.16}$$

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.

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 insterstitials in MO can be formed in equilibrium with the metal vapour:

$$M(g) = M_i^{\bullet\bullet} + 2e^/ \tag{2.17}$$

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 lattice sites and therefore an equivalent number of new metal lattice sites - which are vacant - is also formed:

$$\tfrac{1}{2}O_2(g) = v_M^x + O_O^x \tag{2.18}$$

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;

$$v_M^x = v_M^{//} + 2h^\bullet \tag{2.19}$$

The formation of electron holes may alternatively be expressed in terms of valence defects:

$$v_M^x + 2M_M^x = v_M^{//} + 2M_M^\bullet \tag{2.20}$$

This correspondingly means that the valence for some M atoms changes from +2 for to +3.

The metal vacancy, whether it is effectively neutral (electrons missing from its neighbourhood) or ionized (electrons supplied from the rest of the crystal) it 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

$$\tfrac{1}{2}O_2(g) = O_i^x \tag{2.21}$$

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

$$\tfrac{1}{2}O_2(g) = O_i^{//} + 2h^\bullet \qquad\qquad (2.22)$$

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, respectively one less or one too many valence electrons, 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:

$$B_{Si}^x = B_{Si}^{/} + h^\bullet \qquad\qquad (2.23)$$

$$P_{Si}^x = P_{Si}^\bullet + e^{/} \qquad\qquad (2.24)$$

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:

$$Li_{Ni}^x = Li_{Ni}^{/} + h^\bullet \qquad\qquad (2.25)$$

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.

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 $M_{1-y}O$.

Let us assume that the parent oxide is metal-deficient $M_{1-y}O$ and that the majority point defects in $M_{1-y}O$ 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 $M_{1-y}O$. 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 $M_{1-y}O$, 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

$$Mh_2O_3 = 2Mh_M^{\bullet} + v_{Mi}^{//} + 3O_O^x \tag{2.26}$$

and thus the dissolution of Mh_2O_3 in $M_{1-y}O$ 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:

$$Mh_2O_3 + 2h^{\bullet} = 2Mh_M^{\bullet} + 2O_O^x + \tfrac{1}{2}O_2(g) \tag{2.27}$$
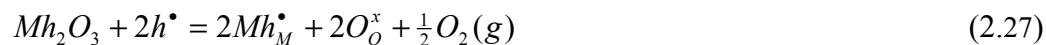
When the dissolution of Mh_2O_3 is written in this way, the equation emphasises that the concentration of electron holes is reduced. However, as the concentration of metal vacancies and electron holes are interrelated, it should be emphasised that both

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 $M_{1-y}O$. Let us alternatively consider what takes place when a lower valent dopant oxide, Ml_2O, is added to $M_{1-y}O$. If the Ml^+ ions dissolve substitutionally in $M_{1-y}O$, 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
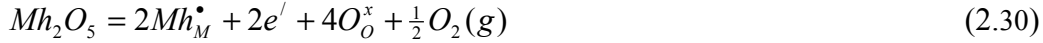
$$Ml_2O + \tfrac{1}{2}O_2(g) = 2Ml_M^{/} + 2h^\bullet + 2O_O^x \tag{2.28}$$

$$Ml_2O + v_M^{//} = 2Ml_M^{/} + O_O^x \tag{2.29}$$
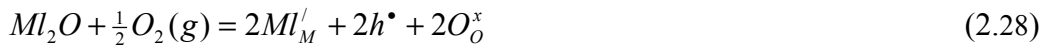
Thus, the addition of Ml_2O to $M_{1-y}O$ has the opposite effect of addition of Mh_2O_3; it increases the concentration of electron holes and decreases the concentration of metal vacancies. One may note that the first of the two reactions is an oxidation and thus involves uptake of oxygen, while the 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-x}

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

When the dopant oxide is higher valent, e.g. Mh$_2$O$_5$, 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

$$Mh_2O_5 = 2Mh_M^{\bullet} + 2e^{/} + 4O_O^x + \tfrac{1}{2}O_2(g) \tag{2.30}$$

$$Mh_2O_5 + v_O^{\bullet\bullet} = 2Mh_M^{\bullet} + 5O_O^x \tag{2.31}$$

Thus when MO$_{2-x}$ is doped with a higher valent oxides Mh$_2$O$_5$ the concentration of electrons is increased and the concentration of oxygen vacancies is decreased.

When the same oxide, MO$_{2-x}$, is doped with a lower valent oxide, Ml$_2$O$_3$, the negative effective charge of the dissolved atoms $Ml_M^{/}$ is compensated by annihilation of electrons or formation of oxygen vacancies:

$$Mh_2O_3 + 2e^{/} + \tfrac{1}{2}O_2(g) = 2Ml_M^{/} + 4O_O^x \tag{2.32}$$

$$Mh_2O_3 = 2Ml_M^{/} + v_O^{\bullet\bullet} + 3O_O^x \tag{2.33}$$

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:

$$Y_2O_3 = 2Y_{Zr}^{/} + v_O^{\bullet\bullet} + 3O_O^x \tag{2.34}$$

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.
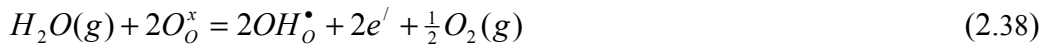
Foreign anions in oxides

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

$$O_O^x + H_2S(g) = S_O^x + H_2O(g) \tag{2.35}$$

$$3O_O^x + 2NH_3(g) = 2N_O^/ + v_O^{\bullet\bullet} + 3H_2O(g) \tag{2.36}$$
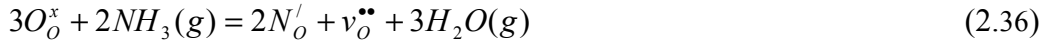
Dissolution of hydrogen in metal oxides

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 lattice sites and thereby form hydroxide ions on normal oxygen sites, $OH_O^{\bullet}$. We may thus for instance write the dissolution reaction

$$H_2 + 2O_O^x = 2OH_O^{\bullet} + 2e^/ \tag{2.37}$$

or

$$H_2O(g) + 2O_O^x = 2OH_O^{\bullet} + 2e^/ + \tfrac{1}{2}O_2(g) \tag{2.38}$$

in which case the protons dissolved are charge compensated by the formation of defect electrons. Of course, 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.

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.

In terms of defect chemistry the dissolved proton, located on a normal oxygen 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).

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

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 lattice 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:

$$0 = v_{Ca}^{//} + v_{Ti}^{////} + 3v_O^{\bullet\bullet} \tag{2.39}$$

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

$$\tfrac{3}{2}O_2(g) = v_{Ca}^{//} + v_{Ti}^{////} + 3O_O^x + 6h^\bullet \tag{2.40}$$

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 oxygen 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 fomation 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 $CaTiO_3$, 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 ABO_3, we may at very high temperatures (e.g., during sintering) see a preferential evaporation of the A component:

$$A_A^x + O_O^x = v_A^{//} + v_O^{\bullet\bullet} + AO(g) \tag{2.41}$$

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

$$A_A^x + \tfrac{1}{2}O_2(g) = v_A^{//} + 2h^{\bullet} + AO(s) \tag{2.42}$$

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 $LaScO_3$ with Ca substituting for La, we go for a composition $La_{1-x}Ca_xScO_3$. In order to see how we write the doping reaction in this case we first just look at the trivial normal synthesis:

$$\tfrac{1}{2}La_2O_3 + \tfrac{1}{2}Sc_2O_2 = La_{La}^x + Sc_{Sc}^x + 3O_O^x \tag{2.43}$$
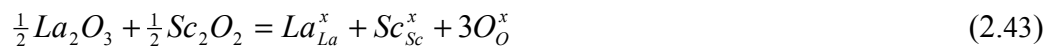
Accordingly, we then write the defect reaction for the doping in the way that we let there be Sc_2O_3 reserved for the CaO:

$$CaO + \tfrac{1}{2}Sc_2O_3 = Ca_{La}^{/} + Sc_{Sc}^x + \tfrac{5}{2}O_O^x + \tfrac{1}{2}v_O^{\bullet\bullet} \tag{2.44}$$
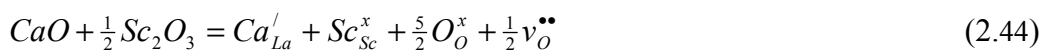
Summary

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 lattice sites, but are allowed to increase or decrease the total number of lattice 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 ions 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.

Further reading

Most of this chapter is based on standard textbooks in defect chemistry, see Further reading in Chapter 1.

For introduction to hydrogen defects, see e.g.:

Norby, T., *Hydrogen Defects in Inorganic Solids*, in Studies in Inorganic Chemistry, **9**; Selected Topics in High Temperature Chemistry: Defect Chemistry of Solids (A.G. Andersen, Ø. Johannesen, eds.), Elsevier, Amsterdam, 1989, 101-142.

References

None at this stage.

Exercises

The excercises 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 MO_2.
3. Write a reaction for the formation of Schottky defects in Cu_2O.
4. Write a defect reaction for the formation of anion Frenkel defects in MO.
5. Write a defect reaction for the formation of anion Frenkel defects in CaF_2.
6. Write a defect reaction for a charge transfer between the cation and anion in CeO_2. Write the same process as an intrinsic ionisation assuming delocalised electronic defects.
7. Write a defect reaction for the formation of fully ionised oxygen vacancies and electrons when oxygen is lost in the reaction $M_2O_3 = M_2O_{3-x} + x/2\ O_2(g)$.
8. Write defect reactions for the direct formation of fully ionised metal interstitials in MO, M_2O_3, and MO_2.
9. Write defect reactions for the direct formation of fully ionised metal vacancies in MO, M_2O_3, and MO_2.
10. Write defect reactions for formation of sodium vacancies in 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 defect reactions for dissolution of CaO into the oxide ZrO_{1-x}
13. Write defect reactions for dissolution of MfO into $M_{2-x}O_3$ when we assume that the foreign metal Mf is small and therefore dissolves interstitially.

14. Write defect reactions for dissolution of CaO substitutionally into the anion-Frenkel dominated Y_2O_3.

15. Write defect reactions for dissolution of ZrO_2 substitutionally into the anion-Frenkel dominated Y_2O_3.

16. Write defect reactions for dissolution of CaF_2 into CaO, assuming that F^- dissolves substitutionally and that CaO is dominated by Schottky defects in the pure, undoped state.

17. Write a defect reaction for dissolution of protons in an oxide with water vapour as source and with oxygen interstitials as compensating defects.

18. Write defect reactions for dissolution of protons in an oxide $M_{1-x}O$ with water vapour as source.

19. Consider an oxide M_2O_3 which is acceptor-doped by dissolving the oxide MlO. The dopants are compensated by oxygen vacancies. Write a defect reaction for the dissolution of MlO. 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 MlO in the presence of water vapour and without forming oxygen vacancies. Can the latter reaction be constructed as a sum of the two previous reactions?

20. Hydride ions 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 defect reactions for formation of A-site Frenkel, B-site Frenkel, and anion Frenkel disorders in a perovskite ABO_3 (assuming both cations are trivalent).

22. Write a defect reaction for the formation of Schottky disorder in spinel $MgAl_2O_4$.

23. Suggest a defect reaction for formation of Schottky-type disorder in $LaMnO_3$ when it is assumed that cation vacancies are formed in the La sublattice only.

24. Write a defect reaction for dissolution of Sc_2O_3 in $CaTiO_3$ during synthesis, assuming that the Sc enter on Ti sites and that they form acceptors compensated by oxygen vacancies.