

3. Defect equilibria

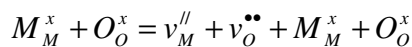
Introduction

After having learned to formulate defect reactions in a compound, we now turn our interest towards the equilibrium relations for those reactions. These correlate the equilibrium concentrations of the different defects with temperature, activities (e.g. partial pressures) of the components in the compound, and other parameters which affect the defect structure. 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. Thus, the defect equilibria may be treated in terms of the thermodynamics of chemical reactions and solutions.

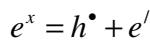
As examples of defect equilibria, mostly known from the preceding chapter, we may use the formation of a vacancy in an elemental solid;

$$E_E = v_E + E_E$$

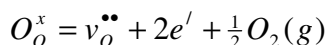
or the formation of a Schottky pair in MO, that we here choose to write;



or the excitation of electronic defects, that we here choose to write;



or the formation of oxygen deficiency;



From any starting point (given concentrations of reactants and products), a reaction may proceed to the right (forward) or left (backward). The proceeding of a reaction in some direction will be accompanied by changes in the internal energy U of the system. The change is called ΔU . At constant pressure (which we most normally consider) the change in energy is given by the change in enthalpy, H ; ΔH . There will also be a change in the disorder (chaos) of the system, expressed by the entropy S . The entropy change is denoted ΔS .

The first and second law of thermodynamics state that in an isolated system³ the energy is constant and the entropy can only increase or remain constant. These laws are empirical – we cannot prove them, just experience them. Equilibrium thermodynamics in closed systems – that we shall now consider – is one such experience. The isolated system of the Universe or a closed thermobottle are not

³ An isolated system is a system that exchanges neither mass nor heat with its surroundings. The Universe is believed to be such a system. A closed insulated thermobottle is a good example of a practically isolated system.

very practical laboratories or process containers for our purpose. We want to consider a closed system⁴, i.e. one that keeps the chemicals inside but exchanges heat. From a textbook in thermodynamics you may learn how the 1st and 2nd laws of thermodynamics predict that any process or reaction in a closed system will proceed spontaneously (voluntarily) only as long as $T\Delta S > \Delta H$, that is, as long as $\Delta H - T\Delta S < 0$. You may say that the effect of disorder must overcome the energy cost in the closed system for the process to run by itself.

For this purpose we see that the enthalpy H of a system can be split into Gibbs (free) energy G and the energy given by the entropy and temperature: $H = G + TS$. The change in the Gibbs (free) energy by a chemical reaction is thus given by

$$dG = dH - TdS \quad (3.1)$$

and, as stated above, a reaction proceeds as long as $dG < 0$. If $dG > 0$, it will proceed backwards to make $dG < 0$. *A reaction reaches equilibrium at $dG = 0$.* This extremely important conclusion we can use to understand and calculate chemical equilibria.⁵

A reaction at equilibrium does in fact not mean that it has stopped, but that the forward and backward reactions run equally fast. We will later on consider equilibrium thermodynamics also from the viewpoint of the mass-action. This will allow us to use the equilibrium constant, the main new tool of this chapter, plus provide more insight to help understand chemical equilibrium.

The creation of single, unassociated point defects in an elemental, crystalline solid increases the internal energy of the system and the enthalpy of the defect formation is positive. But the configurational entropy of the system also increases, and the equilibrium concentration of the defects will be reached when the Gibbs energy of the system is at minimum. Thermodynamically, point defects will thus always be present in a crystal above 0 K.

All types of defects will in principle be formed. However, the free energies of formation of the different types and systems of defects can have widely different values, and correspondingly it is often found that certain defects predominate in a particular solid. The relative concentrations of the different types of defects will be a function a temperature and other variables. Thus, defect equilibria with large positive enthalpy of formation, for instance, which are not favoured at low temperatures, may become important at high temperatures.

⁴ A closed system is one where the mass (chemical entities) of the system is confined, but where energy (heat) can be exchanged with the surroundings. The expression for the Gibbs energy arises as a result of the definition of entropy and of the first law of thermodynamics which preserves the total energy of the system and the surroundings.

⁵ It has been said that chemists have the ability to accept its applicability and to use it for a lifetime often without ever really understanding its derivation or basics. My experience is that physicists have the tendency to reject it and to be unable to use it for the same reasons.

Point defects and equilibrium in an elemental solid - a simple statistical thermodynamic approach

Before considering the thermodynamics of defect formation and of defect reactions in compounds such as metal oxides and the corresponding use of the law of mass action, the simpler case of formation of one type of defect in an elemental solid will be treated by means of statistical thermodynamics.

Consider a perfect crystal of an elemental solid E with N atoms as starting material. Let n_v vacancies be formed according to the defect-chemical reaction



where E_E is an E-atom on an E-site and v_E is a vacant E-site. The vacancies are formed by moving an E-atom from an E-site in the bulk to the surface of the crystal. The total number of sites then becomes $N+n_v$. The change in Gibbs energy can be expressed in terms of the enthalpy of formation of each vacancy, ΔH , and the entropy associated with the formation of the n_v defects, ΔS .

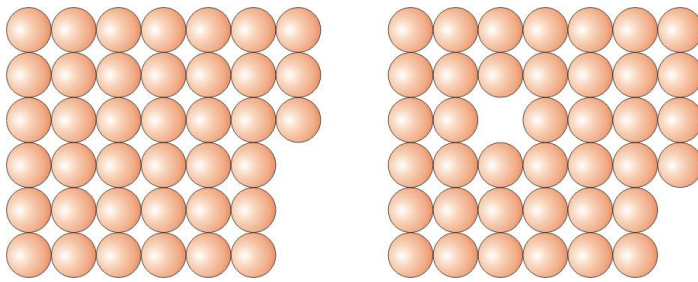


Figure 3-1. Left: Elemental solid consisting of 39 atoms on 30 sites (in the 2-dimensional picture of it). Right: 39 atoms and one vacancy, spread over 40 sites.

The enthalpy change on forming n_v vacancies is thus $n_v\Delta H$. It expresses the energy cost associated with creating a new, empty site.

The entropy change can be divided into two parts: A *vibrational entropy* change, ΔS_{vib} , reflects the entropy created by vibrations associated with *each* new vacancy. A *configurational entropy*, ΔS_{conf} , arises from the distribution of n vacancies among $N+n_v$ sites.

The vibrational entropy change is associated with the vibrations in the neighbourhood of each vacancy, and the total vibrational entropy change is thus proportional to the number of vacancies, $n_v\Delta S_{vib}$. The change in Gibbs free energy associated with the formation of n_v vacancies may accordingly be written

$$\Delta G = n_v\Delta H - T\Delta S = n_v\Delta H - T(n_v\Delta S_{vib} + \Delta S_{conf}) = n_v(\Delta H - T\Delta S_{vib}) - T\Delta S_{conf} \quad (3.3)$$

It may be noted that we have assumed that ΔH and ΔS_{vib} are constant, i.e. independent of defect concentrations. This may only be expected to hold true for small concentrations of defects, where defect-defect-interactions are negligible. Boltzmann was the first to propose that the configurational entropy (of mixing) can be expressed in terms of the thermodynamic probability, W , by the relation

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$$S_{conf} = k \ln W \quad (3.4)$$

where k is Boltzmann's constant. The thermodynamic probability W represents in this case the number of distinguishable ways whereby n_v vacancies may be distributed on $N+n_v$ lattice sites and is given as

$$W = \frac{(N + n_v)!}{N!n_v!} \quad (3.5)$$

We recognise that for the perfect crystal $n_v=0$ so that $W=1$ and $S_{conf}=0$. As the number of vacancies increases, S_{conf} increases and we have $\Delta S_{conf} = S_{conf}$.

For large numbers of N and n_v , which is typical for real crystals, Stirling's approximation ($\ln x! = x \ln x - x$ for $x \gg 1$) may be applied, whereby Eq. (3.5) takes the form

$$\Delta S_{conf} = k \left(N \ln \frac{N + n_v}{N} + n_v \ln \frac{N + n_v}{n_v} \right) \quad (3.6)$$

By insertion into the expression for the change in free energy Eq. (3.3) we get

$$\Delta G = n_v (\Delta H_v - T \Delta S_{vib}) - kT \left(N \ln \frac{N + n_v}{N} + n_v \ln \frac{N + n_v}{n_v} \right) \quad (3.7)$$

The changes in enthalpy, entropy, and Gibbs energy are illustrated in Figure 3-2.

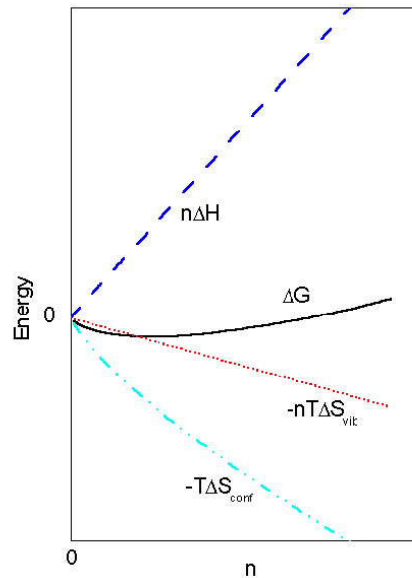


Figure 3-2. Example of the variation in enthalpy, vibrational and configurational entropy, and Gibbs energy with the concentration of vacancies in an elemental solid.

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At equilibrium G and thus ΔG will be at a minimum with respect to n_v , i.e. $d\Delta G/dn_v = 0$;

$$\frac{d\Delta G}{dn_v} = \Delta H - T\Delta S_{vib} + kT \ln \frac{n_v}{N + n_v} = 0 \quad (3.8)$$

The term $\frac{n_v}{N + n_v}$ represents the fraction of the total number of sites which are vacant and is through rearrangement given by

$$\frac{n_v}{N + n_v} = \exp\left(\frac{\Delta S_{vib}}{k}\right) \exp\left(\frac{-\Delta H}{kT}\right) \quad (3.9)$$

Since the formation of the vacancies is written $E_E = v_E + E_E$, the equilibrium constant may, following the law of mass action, be written

$$K = a_{v_E} = X_{v_E} = \frac{n_v}{N + n_v} = \exp\left(\frac{\Delta S_{vib}}{k}\right) \exp\left(\frac{-\Delta H}{kT}\right) \quad (3.10)$$

a_{v_E} is the activity and $X_{v_E} = \frac{n_v}{N + n_v}$ represents the site fraction of vacancies in the crystal.

ΔS_{vib} in the expressions above represents the vibrational entropy change and ΔH the enthalpy change per vacancy. If one wants to express the same properties per mole of vacancies, k must be substituted by the gas constant $R = N_A k$ where N_A is Avogadro's number. Relations corresponding to Eq. (3.10) may be derived for other types of point defects.

At any temperature $T > 0$ all solids will following Eq. (3.10) contain point defects. In the example above we have shown that the equilibrium constant, containing defect activities as site fractions, is given by an enthalpy change and an entropy term which constitutes the vibrational entropy change as one goes from the reactants to the products. It does *not* contain the (configurational) entropy change.

This applies to chemical reactions and their equilibrium constants in general. Furthermore, it illustrates that the vibrational entropy change enters without other contributions if the equilibrium constant is expressed properly, as activities. Each activity is unitless, that is, it is some concentration divided by the concentration in the standard, reference state. For defects, activities are given as site fractions. When activities properly use standard states as reference, the enthalpy and vibrational entropy changes are called standard enthalpy and entropy changes, ΔH^0 and ΔS^0 , respectively.

We may combine the standard enthalpy and entropy changes into a standard Gibbs energy change:

$$K = \exp\left(\frac{\Delta S_{vib}^0}{R}\right) \exp\left(\frac{-\Delta H^0}{RT}\right) = \exp\left(\frac{-\Delta G^0}{RT}\right) \quad (3.11)$$

We will see later that this standard Gibbs energy change is the Gibbs energy change we have when the reaction proceeds with all reactants and products in their standard reference state (activity of unity). It is not the same as the variable Gibbs energy change calculated for the progression of the defect formation reaction earlier.

What happened to the configurational entropy? Should it not be part of the entropy that balances the reaction at equilibrium? And what is K ? Look at Eq. (3.11). The right hand side tells us via the standard enthalpy, entropy, and Gibbs energy changes how much the reaction wants to proceed *when all reactants and products are in their standard states*. If $\Delta G^0 < 0$ it is a favourable reaction. K is the quotient of all product activities over all reactant activities when equilibrium is attained. In other words, K tells us how much the activities have to deviate from the standard state in order to balance the force from ΔG^0 to drive the reaction forward ($\Delta G^0 < 0$, $K > 1$) or backward ($\Delta G^0 > 0$, $K < 1$). One may thus say that the configurational entropy is in the K .

In our example of the elemental solid, the equilibrium quotient K contained only the activity of the product, the site fraction of vacancies.

What were the standard states in our example? For atoms, it is a site fraction of 1, i.e. the perfect crystal is the standard state. For the vacancies it is also a site fraction of 1, i.e. an empty crystal! This exemplifies that standard states of defects are virtual.

Thermodynamics of chemical reactions

As a basis for the subsequent considerations of thermodynamics of defect equilibria the following section provides a brief review of some general aspects of thermodynamics of chemical reactions.

In treating chemical reactions and systems consisting of two or more constituents, it is convenient to introduce the concept of partial molar thermodynamic quantities. As regards equilibria, the partial molar Gibbs energy is particularly important. The partial molar Gibbs energy is commonly termed the chemical potential and written μ_i . The physical significance of a partial molar property is the increase in the value of that property resulting from the addition of 1 mole of that constituent to such a large quantity of the system that its composition remains essentially unchanged. If a system consists of $n_1 + n_2 + \dots + n_i$ moles of constituents 1, 2, ... and i , the partial molar free energy for the "i"th constituent is given by

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_1,n_2,\dots} \quad (3.12)$$

The Gibbs energy of a system is in terms of chemical potentials of the constituents given by

$$G = n_1\mu_1 + n_2\mu_2 + \dots + n_i\mu_i \quad (3.13)$$

When a chemical reaction takes place, the numbers of various constituents change, and dG changes correspondingly. For an open system (i.e. where we may add or remove heat and mass) at constant temperature and pressure, dG is given by

$$dG_{T,p} = \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_i dn_i \quad (3.14)$$

At equilibrium we have

$$dG_{T,p} = \sum_i \mu_i dn_i = 0 \quad (3.15)$$

It may also be shown that under equilibrium conditions

$$n_1 d\mu_1 + n_2 d\mu_2 + \dots + n_i d\mu_i = 0 \quad (3.16)$$

This equation is one form of the Gibbs-Duhem equation.

In a chemical reaction, e.g.



the change in Gibbs energy is given by the difference in the total free energy in the final and initial state

$$\Delta G = c\mu_C + d\mu_D - (a\mu_A + b\mu_B) \quad (3.18)$$

The chemical potential of the constituent "i" in the mixture can be written

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (3.19)$$

where a_i is the activity of constituent "i" in the mixture and μ_i^0 is the chemical potential of constituent "i" at a chosen standard state of unit activity.

The activity of pure solids or liquids is usually taken as unity at atmospheric pressure (1 bar or 10^5 Pa), while for gases the activity is unity when the partial pressure of the gas constituent is 1 bar.

In solutions the activity may be equated with the mole fraction, X_i , in ideal solutions:

$$a_i = X_i \quad (3.20)$$

In non-ideal solutions the activity is related to the mole fraction through the activity coefficient, γ_i ,

$$a_i = \gamma_i X_i \quad (3.21)$$

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γ_i is thus equal to unity in ideal solutions. It may be noted that in a system consisting of several phases, the condition of equilibrium implies that the chemical potential of constituent "i" is the same in all phases.

If one introduces the expression for the chemical potential in Eq. (3.19) into Eq. (3.18) it follows that ΔG for the reaction in Eq. (3.17) is given by

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (3.22)$$

where $\Delta G^0 = c\mu_C^0 + d\mu_D^0 - (a\mu_A^0 + b\mu_B^0)$ represents the change in Gibbs energy in the standard state, i.e. at unit activities. ΔG^0 is a constant under specified standard states. At equilibrium $\Delta G = 0$ such that

$$\Delta G^0 = -RT \ln \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{equilibrium} \quad (3.23)$$

where the quotient at equilibrium is called the equilibrium coefficient, K :

$$\left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{equilibrium} = K \quad (3.24)$$

K is termed the equilibrium coefficient as it relates the ratio of activities of products and reactants when equilibrium has been attained at a given temperature. It takes a constant value at any given temperature and is thus also often called the equilibrium constant. ΔG^0 may as in Eq. (3.1) be expressed in terms of the standard enthalpy change, ΔH^0 , and entropy change, ΔS^0 , such that

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K \quad (3.25)$$

This may be rewritten in the form

$$K = K^0 \exp\left(-\frac{\Delta H^0}{RT}\right) = \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \quad (3.26)$$

Thus, we have arrived at the same type of expression for the equilibrium constant as we did in our initial example from statistical thermodynamics. From that, we know that the entropy term contained in $K^0 = \exp(\Delta S^0/R)$ contains the change in vibrational entropy terms between the reactants and products in their standard states, and that it does not contain the configurational entropy change involved by the system when the activities are different from the standard states.

From the equation above we see that the temperature dependence of K is given by

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H^0}{R} \quad (3.27)$$

and that a plot of $\ln K$ vs $1/T$ (van 't Hoff plot) will give $\Delta S^0/R$ as the intercept and $-\Delta H^0/R$ as the slope.

This general treatment is applicable to any ideal solutions whether these are gaseous, liquid, or solid, and it applies also to defect chemistry as we have exemplified initially.

Thermodynamics and point defects

Equilibrium thermodynamics may as stated above be applied to defect reactions. However, before so doing it is of interest to consider the thermodynamic properties of the individual point defects.

Virtual chemical potentials of point defects

The regular atoms on their normal sites and the point defects occupy particular sites in the crystal structure and these have been termed structural elements by Kröger, Stieltjes, and Vink (1959) (see also Kröger (1964)). As discussed in Chapter 2, the rules for writing defect reactions require that a definite ratio of sites is maintained due to the restraint of the crystal structure of the compounds. Thus if a normal site of one of the constituents in a binary compound MO is created or annihilated, a normal site of the other constituent must simultaneously be created or annihilated.

As discussed above the chemical potential of a constituent represents the differential of the Gibbs energy with respect to the amount of the constituent when the pressure, temperature and the amounts of all other constituents are kept constant. When a structure element is created, the number of complementary structure elements can not be kept constant due to the requirement of a definite site ratio, and it is therefore not possible to assign a true chemical potential to a structure element. However, Kröger *et al.* showed that one may get around this difficulty by assigning a virtual chemical potential ζ (zeta) to each separate structure element and that the virtual chemical potential behaves like a true chemical potential and may be related in a similar way to activity:

$$\zeta_i = \zeta_i^0 + RT \ln a_i \quad (3.28)$$

The virtual potential differs from the true chemical potential by an undefined constant which is incorporated in ζ^0 . For this reason the absolute value of the virtual chemical potential can not be determined experimentally.

In real changes in crystals where the site ratio is maintained and complementary structure elements (or building units) are created or annihilated, the undefined constants in the virtual chemical potential of each separate structure element cancel out, and the overall change is characterised by real changes in

Gibbs free energies; $dG_i = d\mu_i = d\zeta_i = dRT\ln a_i$. At constant temperature and with ideal conditions (small concentrations of defects), a change in activity corresponds to the change in concentration, and we have $dG_i = d\mu_i = RTd\ln a_i = RTd\ln(c_i/c_0) = RTd\ln c_i$.

Kröger *et al.* pointed out that a similar treatment applies to aqueous electrolytes.

As we have mentioned before, we have not only the problem of measuring true chemical potentials μ of defects and other structure elements, we also have the problem of establishing or even imagining the standard state of site fraction of unity: For oxygen vacancies in a simple oxide this would for instance mean a crystal where all oxide ions are missing, i.e. a crystal with only cations.

Ideal and non-ideal models

As described in the preceding section the defect reactions and equilibria can be described as chemical reactions and treated in terms of the law of mass action. It is emphasised that the equilibrium constants relate activities of the structure elements involved in the defect reaction, but under ideal conditions and when the structure elements can be assumed to be randomly distributed over the available sites, the activities equal the concentrations of the structure elements. This is a valid assumption for very dilute solutions. However, for larger defect concentrations interactions take place between the defects, etc. and in principle activities should be used instead of concentrations.

The interactions between charged defects may be accounted for by using the Debye-Hückel theory in analogy with the interactions of ions in aqueous solutions. This requires knowledge of the relative dielectric constant, the smallest distance between charged defects, and other parameters for the solid. Debye-Hückel corrections have, for instance, been worked out and tested for cation vacancy defects in metal-deficient Co_{1-x}O and Ni_{1-x}O . At infinite dilution the metal vacancies can be considered to have two negative charges, v_{Co}'' , and the equivalent number of electron holes is assumed to be randomly distributed in the oxide. With an increasing concentration of point defects and electron holes, there will be an increasing association of the metal vacancies (with two effective negative charges) and the positively charged electron holes. In these terms, the metal vacancies can be considered surrounded by a cloud of electron holes. This results in a deviation from a random distribution of electron holes and a corresponding deviation from the ideal solution model. For the case of Co_{1-x}O the Debye-Hückel correction can explain the increasing deviation from ideality with increasing defect concentration. However, this model in its present form does not satisfactorily explain various electrical conductivity results for Co_{1-x}O and so far apparently fails to give a full description of the defect structure and defect-dependent properties of the oxide.

An alternative approach is to consider that the association of defects leads to the formation of new "associated" defect species. These "new" defects are, in turn, treated in terms of the ideal solution models. Specifically, in the case of metal vacancies in, for instance, Co_{1-x}O and Ni_{1-x}O it is assumed that the metal

vacancies with two effective charges become associated with one electron hole to give a metal vacancy with one negative effective charge, v_{Co}' , as has already been described in Chapter 2. At this stage this simple approach appears to give an equally consistent description of the defect structure and defect-dependent properties of $Co_{1-x}O$ as the much more complicated Debye-Hückel model. However, it is to be expected that future developments will provide a more detailed understanding of defect interactions and how they influence defect-dependent properties of inorganic compounds.

Despite its shortcomings the ideal solution approach will be used in this book in treating defect equilibria. Defect interactions will generally be treated by assuming the formation of associated defects as is, for instance, exemplified above for the formation of singly charged metal vacancies through the association of an electron hole with a doubly charged metal vacancy. Furthermore, the defect equilibria will be treated using the law of mass action.

Concentrations of the structure elements may be expressed in many units. In semiconductor physics it is common to express the concentrations in number per cm^3 . This has the disadvantage, however, that when two compounds with different molecular (packing) densities contain the same number of defects per cm^3 , the number of defects per molecular unit is different in the two compounds, and *vice versa*. Furthermore, the molecular unit size (packing density, or unit cell parameters) of a compound changes as a function of its nonstoichiometry and temperature, and in this case the unit of defects per cm^3 does not unequivocally reflect the relative defect concentration per molecular unit or atom site under different conditions.

In the following, concentration will in most cases be expressed as the number of defects or atoms per molecular unit or site, i.e. in molar or site fractions, while we for some purposes need to use the number of defects per cm^3 . As mentioned before, the value of the equilibrium constant depends on the units of concentration that are employed, but it is a simple matter to convert the values of the equilibrium constant from one system to another.

Examples of defect equilibria in pure, stoichiometric metal oxides

In this section we will see how we write defect reactions for selected simple cases of combinations of defects, express the equilibrium constants, and combine this with an electroneutrality condition to express the concentration of dominating defects as a function of temperature and activities. We will when possible stay with proper statistical thermodynamics, such that entropy changes in the defect reaction can be interpreted as a change in the vibrational entropy from reactants to products in their standard states. Approximations will be implemented in order to visualise the simplicity of the method.

Schottky defects

As a first illustration let us consider the defect equilibrium for Schottky defects in the oxide MO and where the metal and oxygen vacancies are doubly charged. The defect equation for their formation is given in Chapter 2 as

$$0 = v_O^{\bullet\bullet} + v_M^{\prime\prime} \quad (3.29)$$

The corresponding defect equilibrium may at low defect concentrations be written

$$K_S = X_{v_O^{\bullet\bullet}} X_{v_M^{\prime\prime}} = \frac{[v_O^{\bullet\bullet}][v_M^{\prime\prime}]}{[O][M]} \quad (3.30)$$

where K_S is the equilibrium constant for a Schottky defect pair, X represent site fractions, and square brackets express concentrations of species. [O] and [M] represent the concentration of oxygen and metal sites, respectively.

If we let square brackets express concentration in mole fraction (i.e. the number of moles of the species per mole of MO), then [O] = [M] = 1, and then

$$K_S = [v_O^{\bullet\bullet}][v_M^{\prime\prime}] \quad (3.31)$$

When the concentrations of the defects are expressed in site fractions, or properly converted to mole fractions as here, K_S is related to the standard Gibbs energy change ΔG_S^0 , enthalpy change ΔH_S^0 , and entropy change ΔS_S^0 , of formation of pairs of doubly charged Schottky defects:

$$K_S = [v_O^{\bullet\bullet}][v_M^{\prime\prime}] = \exp\left(-\frac{\Delta G_S^0}{RT}\right) = \exp\left(\frac{\Delta S_S^0}{R}\right) \exp\left(-\frac{\Delta H_S^0}{RT}\right) \quad (3.32)$$

It may be useful to repeat that the entropy change ΔS_S^0 does not include the configurational entropy changes associated with the formation of the defects, but only the change in vibrational entropy associated with the vacancies formed.

When the Schottky pair dominates the defect structure, we may see from the reaction equation or from the electroneutrality condition that in MO the concentrations of the metal and oxygen vacancies are equal:

$$[v_O^{\bullet\bullet}] = [v_M^{\prime\prime}] \quad (3.33)$$

Insertion into the preceding equation yields

$$[v_O^{\bullet\bullet}] = [v_M^{\prime\prime}] = K_S^{1/2} = \exp\left(\frac{\Delta S_S^0}{2R}\right) \exp\left(\frac{-\Delta H_S^0}{2RT}\right) \quad (3.34)$$

Under these conditions the defect concentrations are only dependent on the temperature; they are independent of the activities of the components M and O₂. The slope in a van 't Hoff plot of $\ln[v_O^{\bullet\bullet}]$ or $\ln[v_M^{\prime\prime}]$ vs $1/T$ would be $-\Delta H_S^0/2R$, see

Figure 3-3. The factor 2 results from the square root of the equilibrium constant, in turn resulting from the fact that there are *two* defects created, in comparison with the one we got in the element used as example earlier.

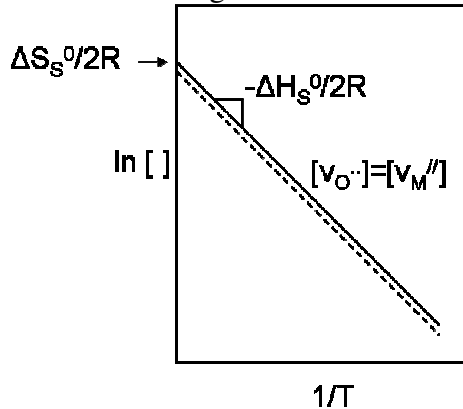


Figure 3-3. van 't Hoff plot of the logarithm of defect concentrations vs inverse absolute temperature yields intercept and slope related to the standard entropy and enthalpy, respectively, of the defect formation reaction, divided by the number of defects formed and R .

It may be useful to note that the procedure we have applied is to write down the defect reaction and the mass action law expression for its equilibrium constant, and the prevailing electroneutrality condition. Thus, we have two independent equations for the two unknowns (provided that either K_S or all of ΔS_S^0 , ΔH_S^0 , and T are known).

Frenkel defect pairs

In our next example we consider Frenkel defect pairs in MO. If, for the sake of illustration, the Frenkel defects in MO are assumed to be doubly charged, the defect equation for their formation is given as



It may be noted that a vacant interstitial site has been included to keep track of the sites where the interstitials are going. The corresponding defect equilibrium is written as

$$K_F = \frac{X_{v_M^{//}} X_{M_i^{••}}}{X_{M_M^x} X_{v_i^x}} = \frac{[v_M^{//}] [M_i^{••}]}{[M] [i]} = \frac{[v_M^{//}] [M_i^{••}]}{[M_M^x] [v_i^x]} \quad (3.36)$$

If there is one interstitial site per MO, and if the defect concentrations are small such that $[M_M^x] = [v_i^x] = 1$, we obtain simply

$$K_F = [M_i^{••}] [v_M^{//}] \quad (3.37)$$

If Frenkel defects predominate in the pure stoichiometric compound, the concentrations of interstitial cation and vacancies are then equal, and we obtain:

$$[M_i^{\bullet\bullet}] = [v_M^{\prime\prime}] = K_F^{1/2} = \exp\left(\frac{\Delta S_F^0}{2R}\right) \exp\left(\frac{-\Delta H_F^0}{2RT}\right) \quad (3.38)$$

where ΔS_F^0 and ΔH_F^0 are the standard entropy and enthalpy changes of formation of Frenkel defect pairs. Under these conditions the concentration of the Frenkel defect pairs is independent of the activities of the metal and oxygen components.

Intrinsic ionisation of electrons

For many oxides, and particularly when considering defect structure situations close to stoichiometry, it is essential to take into account the intrinsic ionisation of electrons. This can include localised defects (valence defects) or delocalised defects (valence band and conduction band).

In the case of valence defects, the ionisation of a pure binary metal oxide M_aO_b may typically be assigned to mixed valency of the metal and thus be written as

$$2M_M^x = M_M^{\prime} + M_M^{\bullet} \quad (3.39)$$

The equilibrium constant may then be expressed as site fractions, which in our case immediately simplifies into an expression containing only volume or molar concentrations:

$$K_i = \frac{[M_M^{\bullet}][M_M^{\prime}]}{[M_M^x]^2} \quad (3.40)$$

If this intrinsic ionisation dominates the defect structure, we have

$$[M_M^{\bullet}] = [M_M^{\prime}] \quad (3.41)$$

Insertion into the equilibrium constant yields

$$[M_M^{\bullet}] = [M_M^{\prime}] = [M_M^x] K_i^{1/2} = [M_M^x] \exp\left(\frac{\Delta S_i^0}{2R}\right) \exp\left(\frac{-\Delta H_i^0}{2RT}\right) \quad (3.42)$$

In the case of delocalised electrons we write the ionisation reaction

$$0 = e^{\prime} + h^{\bullet} \quad (3.43)$$

If we describe this as a chemical reaction, the product of the activities of the electrons and holes should remain constant at a given temperature. However,

electrons and holes in the band model do not occupy sites, but energy states, and thus the activity might be represented as the fraction of concentration over density of states:

$$K_i = a_{e'} a_{h^\bullet} = \frac{[e']}{N_C} \frac{[h^\bullet]}{N_V} = \frac{n}{N_C} \frac{p}{N_V} \quad (3.44)$$

where K_i is the equilibrium coefficient and n and p denote the concentrations of electrons and holes, respectively. N_C and N_V denote the density of states in the conduction band and valence band edges, respectively. If we apply statistical thermodynamics to this we might assign K_i to standard Gibbs energy, entropy and enthalpy changes:

$$K_i = \frac{n}{N_C} \frac{p}{N_V} = \exp \frac{-\Delta G_i^0}{RT} = K_{0,i} \exp \frac{-\Delta H_i^0}{RT} = \exp \frac{\Delta S_i^0}{R} \exp \frac{-\Delta H_i^0}{RT} \quad (3.45)$$

However, the use of entropy is not commonly adopted for reactions involving band electrons and holes, as the concept of the standard states, that would imply $n=N_C$ and $p=N_V$, are not commonly accepted. In physics, one instead uses simply⁶

$$K'_i = [e'] [h^\bullet] = n p = N_C N_V \exp \frac{-E_g}{RT} \quad (3.46)$$

where E_g is the band gap. We see from this that $K'_i = N_C N_V K_i$ and that the band gap would correspond to the standard Gibbs energy change of the intrinsic ionisation reaction. The prime on this K'_i and others to follow is used here to denote an equilibrium coefficient that has been multiplied with densities of state such that it gets units (e.g. m^{-6} or cm^{-6} as here) and cannot be directly related to an entropy.

Our brief discussion of electronic ionisation as seen from both defect chemical and physics perspectives may seem confusing, and is in fact not well resolved in textbooks or in the literature. This should not prevent us from coming out with a simple conclusion: The product np is *constant* at any given temperature, and its variation with temperature is roughly given by the band gap, E_g .

If the concentrations of electrons and electron holes predominate, then the electroneutrality condition is $n = p$ and insertion into the equilibrium coefficient yields

⁶ 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 per mole electrons. This is a trivial conversion (factor $1 \text{ eV} = 96485 \text{ J/mol} = 96.485 \text{ kJ/mol}$).

$$n = p = (K_i')^{1/2} = (N_C N_V)^{1/2} \exp\left(\frac{-E_g}{2RT}\right) \quad (3.47)$$

The density of states is often – under certain assumptions – approximated as

$$N_C = \left(\frac{8\pi m_e^* kT}{h^2}\right)^{3/2} \quad \text{and} \quad N_V = \left(\frac{8\pi m_h^* kT}{h^2}\right)^{3/2} \quad (3.48)$$

where the constants have their usual meanings, and m_e^* and m_h^* are the effective masses of electrons and holes, respectively. Effective masses are sometimes known, or may be to a first approximation be set equal to the rest mass of electrons, whereby N_C and N_V may be estimated. It may be noted that they have units of m^{-3} and that they contain temperature dependencies of $T^{3/2}$.

Intrinsic ionization of electrons and holes is, for instance, concluded to dominate the defect structure of Fe_2O_3 and Cr_2O_3 at high temperatures.

Defect equilibria in nonstoichiometric oxides

Here, we will employ mainly the same methodology as in the preceding section, but when delocalised defect electrons and holes are introduced we cannot stay strictly with statistical thermodynamics and the equilibrium thermodynamics cannot be related in the same simple manner to the change in vibrational entropy any longer.

Oxygen deficient oxides

In oxides with oxygen deficit, the predominant defects are oxygen vacancies. If these are fully ionised (doubly charged), and if the electronic defects are localised as valency defects, their formation reaction can be written:



The corresponding equilibrium coefficient shall be expressed in terms of activities. Writing these as site fractions for the defects, and as partial pressure for the gas species (the division by the standard state of 1 bar is omitted for simplicity) we get

$$K_{vO} = \frac{X_{v_O^{\bullet\bullet}} X_{M_M'}^2}{X_{O_O^x} X_{M_M^x}^2} p_{O_2}^{1/2} = \frac{[v_O^{\bullet\bullet}][M_M']^2}{[O_O^x][M_M^x]^2} p_{O_2}^{1/2} \quad (3.50)$$

3. Defect equilibria

If these oxygen vacancies and the compensating electronic valence defects are the predominating defects in the oxygen deficient oxide, the principle of electroneutrality requires that

$$[M'_M] = 2[v_o^{\bullet\bullet}] \quad (3.51)$$

By insertion, and assuming the oxide is MO and that $[M'_M] = [O_o^x] = 1$ (small defect concentrations) we then obtain:

$$[M'_M] = 2[v_o^{\bullet\bullet}] = (2K_{vo})^{1/3} p_{O_2}^{-1/6} = 2^{1/3} \exp\left(\frac{\Delta S_{vo}^0}{3R}\right) \exp\left(\frac{-\Delta H_{vo}^0}{3RT}\right) p_{O_2}^{-1/6} \quad (3.52)$$

This shows that the concentrations of the dominating defects (defect electrons and oxygen vacancies) increase with decreasing oxygen partial pressure. It furthermore shows the relation between defect concentrations and entropy and enthalpy changes of the defect reaction. The factor 3 that enters results from the formation of 3 defects in the defect reaction.

Now, let us do the same treatment, but for an oxide where defect electrons are delocalised in the conduction band. The formation of oxygen vacancies is then written:



The equilibrium coefficient should be

$$K_{vo} = \frac{a_{v_o^{\bullet\bullet}} a_{e'}^2 a_{O_2(g)}^{1/2}}{a_{O_o^x}} = \frac{[v_o^{\bullet\bullet}] \left(\frac{n}{N_c}\right)^2 \left(\frac{p_{O_2}}{p_{O_2}^0}\right)^{1/2}}{\frac{[O_o^x]}{[O]}} = \frac{[v_o^{\bullet\bullet}] \left(\frac{n}{N_c}\right)^2 \left(\frac{p_{O_2}}{p_{O_2}^0}\right)^{1/2}}{[O]} \quad (3.54)$$

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

$$K'_{vo} = [v_o^{\bullet\bullet}] n^2 p_{O_2}^{1/2} \quad (3.55)$$

This means that $K'_{vo} = N_c^2 K_{vo}$ and that the expression is valid for small concentrations of defects.

If these oxygen vacancies and the compensating electrons are the predominating defects in the oxygen deficient oxide, the principle of electroneutrality requires that

$$n = 2[v_o^{\bullet\bullet}] \quad (3.56)$$

By insertion we then obtain:

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$$n = 2[v_o^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6} = (2K'_{0,vO})^{1/3} \exp\left(-\frac{\Delta H_{vO}^0}{3RT}\right) p_{O_2}^{-1/6} \quad (3.57)$$

and deliberately use a pre-exponential K'_0 instead of an entropy change. Otherwise, the solution is the same as in the case with localised valence defects for the electrons.

A plot of $\log n$ or $\log[v_o^{\bullet\bullet}]$ vs $\log p_{O_2}$ (at constant temperature) will give straight lines with a slope of $-1/6$. Such plots are called Brouwer diagrams, and they are commonly used to illustrate schematically the behaviour of defect concentrations under simplified limiting cases of dominating defects.

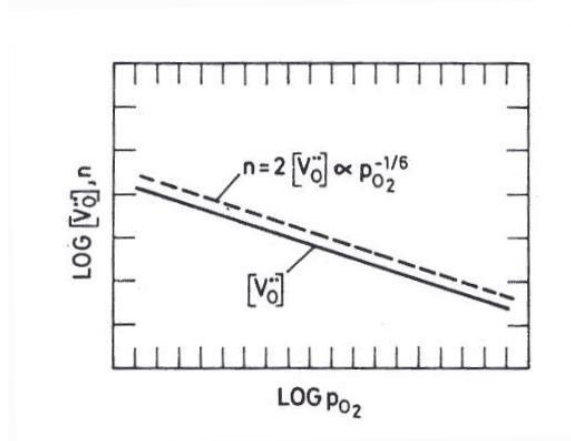


Figure 3-4. Brouwer diagram for $n = 2[v_o^{\bullet\bullet}]$ as the electroneutrality condition.

If we want to investigate the more complex situation of involving neutral and partially ionised oxygen vacancies and the excitation of the trapped electrons (described in Chapter 2) we start by writing down the stepwise reactions and their corresponding equilibria:



$$K_{vOx} = \frac{[v_o^x]}{[O_o^x]} p_{O_2}^{1/2} \quad (3.59)$$



$$K'_{vO1} = \frac{[v_o^\bullet]}{[v_o^x]} n \quad (3.61)$$



$$K'_{vO2} = \frac{[v_o^{\bullet\bullet}]}{[v_o^\bullet]} n \quad (3.63)$$

where K_{vOx} , K'_{vO1} , and K'_{vO2} are the respective equilibrium constants. Now the principle of electroneutrality requires that

$$n = [v_O^\bullet] + 2[v_O^{\bullet\bullet}] \quad (3.64)$$

The concentrations of the electrons and the neutral, singly, and doubly charged oxygen vacancies are related through the equations above, and by combination expressions for each of the defects may be obtained. The electron concentration is given by

$$n^3 = K_{vOx} K'_{vO1} (2K'_{vO2} + n) p_{O_2}^{-1/2} \quad (3.65)$$

This equation has two limiting conditions.

If $n \ll 2K'_{vO2}$, then

$$n = 2[v_O^{\bullet\bullet}] = (2K_{vOx} K'_{vO1} K'_{vO2})^{1/3} p_{O_2}^{-1/6} \quad (3.66)$$

Under these conditions the concentrations of electrons and oxygen vacancies are relatively small, the doubly charged vacancies are the predominating oxygen vacancies, and the concentrations of electrons and these oxygen vacancies are proportional to $p_{O_2}^{-1/6}$. Of course, this situation corresponds to the simple case presented initially for the doubly charged vacancies, and obviously $K_{vOx} K'_{vO1} K'_{vO2} = K'_{vO}$.

If, on the other hand, $n \gg 2K'_{vO2}$, then

$$n = [v_O^\bullet] = (K_{vOx} K'_{vO1})^{1/2} p_{O_2}^{-1/4} \quad (3.67)$$

Under these conditions the concentration of electrons is relatively large, and the predominant oxygen vacancies are then singly charged. Furthermore, the concentrations of electrons and oxygen vacancies are then proportional to $p_{O_2}^{-1/4}$.

A general tendency similar to that of oxygen deficient oxides applies to metal deficient oxides; in the oxide $M_{1-x}O$ the metal vacancies are doubly charged at very small deviations from stoichiometry and tend to become singly charged with increasing nonstoichiometry.

It may be noted that the neutral oxygen vacancies are not affected by charged defects, nor do they affect the electroneutrality.

Oxide with excess metal

We will as an example consider the formation of fully ionised interstitial metal ions and complementary electrons in an oxide with excess metal $M_{2+x}O_3$. The equation for the formation of interstitial metal ions with three effective positive charges and three complementary electrons is given by



The corresponding defect equilibrium is given by

$$K_{Mi}^I = [M_i^{\bullet\bullet\bullet}] n^3 p_{O_2}^{3/4} [O_o^x]^{-3/2} [M_M^x]^{-1} \quad (3.69)$$

where K_{Mi}^I is the equilibrium constant. If these defects are the predominating ones, and we as before assume small defect concentrations, the electroneutrality condition and the oxygen pressure dependence of the interstitial metal ions and the electrons is

$$3[M_i^{\bullet\bullet\bullet}] = n = (3K_{Mi}^I)^{1/4} p_{O_2}^{-3/16} \quad (3.70)$$

Thus, also in this case the concentration of the defects increases with decreasing oxygen activity and is now proportional to $p_{O_2}^{-3/16}$. This oxygen pressure dependence is different from that for formation of singly as well as doubly charged oxygen vacancies. In such a case it would thus in principle be possible to decide from measurements of electron concentration (e.g. via electrical conductivity) or of nonstoichiometry as a function of oxygen activity whether the predominating defects are triply charged interstitial metal ions or oxygen vacancies with one or two charges.

Had the metal interstitials predominantly been doubly charged in the oxide $M_{2+x}O_3$, a $p_{O_2}^{-1/4}$ dependence would have been the result, and additional studies of defect-dependent properties (e.g. self-diffusion of metal or oxygen) would be needed to distinguish this situation from that of singly charged oxygen vacancies.

It may be noted that it is not only the absolute number of charges on a defect that determines the p_{O_2} dependence, but also the difference between the actual charge and the charge given by the nominal valence of the atoms involved. Thus, in the oxide MO (or $M_{1+x}O$) doubly charged metal interstitials will give a $p_{O_2}^{-1/6}$ dependence of the defect concentrations (as opposed to the case above) and in this case be indistinguishable from doubly charged oxygen vacancies.

Simultaneous presence of oxygen vacancies and interstitial metal ions

In an oxide M_aO_b where the ratio of metal to oxygen is larger than the stoichiometric ratio a:b it is *a priori* difficult to predict whether interstitial metal ions or oxygen vacancies predominate. In principle both types of defects may be important, at least in certain regions of nonstoichiometry. In the following, let us consider a case where it may be necessary to take into account the simultaneous presence of interstitial metal ions and oxygen vacancies.

Consider an oxide with a stoichiometric composition MO_2 . Let us further assume for the sake of illustration that when the oxide is nonstoichiometric the important point defects are doubly charged oxygen vacancies and doubly charged interstitial metal ions. (It may be noted that the metal interstitials are not fully

3. Defect equilibria

ionised in this case.) The composition of the nonstoichiometric oxide may accordingly be written $M_{1+y}O_{2-y}$.

The defect equations for the formation of these two types of defects are written

$$O_o^x = v_o^{\bullet\bullet} + 2e' + \frac{1}{2}O_2(g) \quad (3.71)$$

$$2O_o^x + M_M^x = M_i^{\bullet\bullet} + 2e' + O_2(g) \quad (3.72)$$

The corresponding defect equilibria (assuming $[M_M]$ and $[O_O]$ to be equal to unity) then become

$$K'_{vo} = [v_o^{\bullet\bullet}]n^2 p_{O_2}^{1/2} [O_o^x]^{-1} \quad (3.73)$$

$$K'_{Mi2} = [M_i^{\bullet\bullet}]n^2 p_{O_2} [O_o^x]^{-2} [M_M^x]^{-1} \quad (3.74)$$

The electroneutrality condition is given by

$$n = 2[v_o^{\bullet\bullet}] + 2[M_i^{\bullet\bullet}] \quad (3.75)$$

Two limiting conditions may be considered:

When $[v_o^{\bullet\bullet}] \gg [M_i^{\bullet\bullet}]$ then

$$n = 2[v_o^{\bullet\bullet}] = (2K'_{vo})^{1/3} p_{O_2}^{-1/6} \quad (3.76)$$

as obtained also earlier for the same conditions. By inserting this relationship for n into the equilibrium constant for formation of the minority defects, metal interstitials, we obtain

$$[M_i^{\bullet\bullet}] = K'_{Mi2} (2K'_{vo})^{-2/3} p_{O_2}^{-2/3} \quad (3.77)$$

Under these conditions the minority concentration of metal interstitials, $[M_i^{\bullet\bullet}]$, increases rapidly with decreasing oxygen partial pressure, more rapidly than the two dominating defects, and may eventually catch up with them and become dominating at the expense of oxygen vacancies, as illustrated in the figure below.

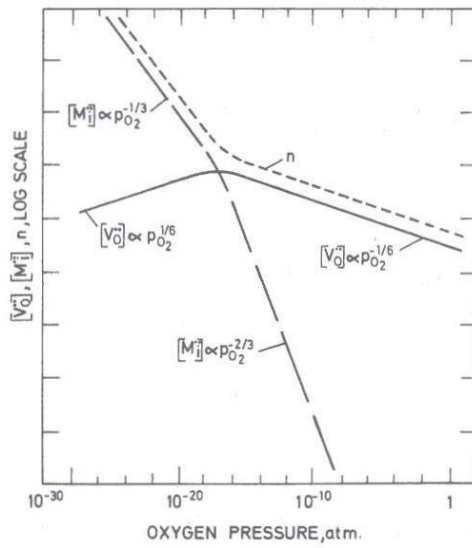


Figure 3-5. Schematic presentation defect concentrations as a function of oxygen pressure in an oxide MO_2 containing both doubly charged oxygen vacancies and doubly charged interstitial metal ions, compensated by electrons.

When, as the other limiting case, $[M_i^{\bullet\bullet}] \gg [v_o^{\bullet\bullet}]$ then

$$n = 2[M_i^{\bullet\bullet}] = (2K_{Mi2}^I)^{1/3} p_{O_2}^{-1/3} \quad (3.78)$$

By inserting this relationship for n into the equilibrium constant for formation of the minority defect, oxygen vacancies, we obtain

$$[v_o^{\bullet\bullet}] = K_{vO}^I (2K_{Mi2}^I)^{-2/3} p_{O_2}^{1/6} \quad (3.79)$$

It may be noted that under these conditions the concentration of oxygen vacancies *increases* with the oxygen pressure, as shown in the figure.

The overall situation may be illustrated schematically as shown in Fig.3.3, in which the concentrations of the three defects are plotted as a function of the partial pressure of oxygen. In this diagram it is assumed that $[v_o^{\bullet\bullet}]$ is 10^5 times larger than $[M_i^{\bullet\bullet}]$ at 1 atm O_2 , and with this assumption it is seen that the interstitial cations will predominate at a partial pressure below about 10^{-17} atm. Many oxides with high melting points are stable over large oxygen pressure ranges and it is not improbable that this hypothetical situation, with oxygen vacancies predominating at high partial pressures of oxygen (and small deviations from stoichiometry) and interstitial cations predominating at low partial pressures (relatively large deviations from stoichiometry) may generally apply to oxygen deficient oxides at elevated temperatures. In actual cases more than one ionisation state of the defects may of course also have to be considered.

In this section we have employed and illustrated a very important sequence of actions often used to solve ideal situations in defect chemistry, but also implicitly used in traditional aqueous and other chemistry. We write down the sequence of operations in a numbered list for clarity:

3. Defect equilibria

1. Write down the full electroneutrality condition containing all charged defects of interest.
2. Write down a number of independent chemical reactions and corresponding equilibrium constant expressions – if you have n defects you need normally $n-1$ such equilibria. The n 'th expression is the electroneutrality itself.
3. Decide one set (normally a pair) of dominating charged defects, and simplify the electroneutrality condition to this limiting situation.
4. Insert this limiting condition into an appropriately chosen defect equilibrium to obtain the expression for the concentration of the two dominating defects. (Normally, simplifications such as assuming small defect concentrations are made here.)
5. Insert the obtained expression into another equilibrium expression and solve to obtain an expression of the concentration of a minority defect.
6. Extrapolate to see which minority defect comes up to become dominating as conditions change. Then repeat from step 3 until all defects have been dealt with under all simplified defect situations.

On the basis of such an exercise one may construct schematic diagrams of how defect pairs dominate defect structures and how minority defects behave and eventually take over. Transition zones are *not* solved explicitly in this way and are thus often drawn sharp and schematically. Logarithmic depictions are common, and such plots are then called Brouwer diagrams.

Metal-deficient oxide

The reactions and defect equilibria for the formation of single, unassociated neutral metal vacancies and the subsequent excitation of electron holes in MO may for small defect concentrations be written



$$K_{vMx} = [v_M^x][O_O^x]p_{O_2}^{-1/2} \quad (3.81)$$

$$v_M^x = v_M' + h^\bullet \quad (3.82)$$

$$K_{vM1}' = \frac{[v_M']}{[v_M^x]}p \quad (3.83)$$

$$v_M' = v_M'' + h^\bullet \quad (3.84)$$

$$K'_{vM2} = \frac{[v_M'']}{[v_M']} p \quad (3.85)$$

where K_{vMx} , K'_{vM1} , and K'_{vM2} are the equilibrium constants for the respective defect equilibria.

When the metal vacancies and their complementary electron holes are the predominating defects, the electroneutrality condition reads

$$p = [v_M'] + 2[v_M''] \quad (3.86)$$

Through combinations of the equilibrium constant expressions and electroneutrality above, the concentration of the separate point defects and electronic defects can be evaluated. In an oxide $M_{1-x}O$ this leads to relationships similar to that for oxygen vacancies with the exception that the concentrations of electron holes and metal vacancies always increase with increasing oxygen pressure. The concentration of electron holes is, for instance, determined by the expression

$$p^3 = K_{vMx} K'_{vM1} (2K'_{vM2} + p) p_{O_2}^{1/2} \quad (3.87)$$

As regards the electron holes two limiting conditions may be considered:

At low concentrations of electron holes (small deviations from stoichiometry; $p \ll K'_{vM2}$) we have

$$p = (2K_{vMx} K'_{vM1} K'_{vM2})^{1/3} p_{O_2}^{1/6} \quad (3.88)$$

At high concentrations of electron holes ($p \gg K'_{vM2}$) we obtain

$$p = (K_{vMx} K'_{vM1})^{1/2} p_{O_2}^{1/4} \quad (3.89)$$

The oxygen pressure dependence of the concentration of electron holes and the total concentration of the charged metal vacancies (deviation from stoichiometry) correspondingly changes from $p_{O_2}^{1/6}$ to $p_{O_2}^{1/4}$ with increasing deviation from stoichiometry.

Metal oxides with excess oxygen.

The defect equilibria involving the formation of interstitial oxygen atoms or ions in oxides with excess oxygen may be set up following the same treatment as applied to the other defects which have been dealt with above. The concentration of interstitial oxygen species increases with p_{O_2} , and the formation of charged oxygen interstitials is accompanied by the formation of electron holes.

Examples of defect structures involving both oxygen deficiency and excess

In the preceding examples of defect structures in non-stoichiometric oxides it has been assumed that the oxides either have an oxygen deficit (or excess metal) or excess oxygen (or metal deficit). In many oxides the predominating defect may change from one type to another depending on the oxygen activity. As an illustration of such a defect structure situation a hypothetical case will be considered where an oxide predominantly contains oxygen vacancies at reduced oxygen activities and interstitial oxide ions at high oxygen activities. In an intermediate region the oxide will be stoichiometric or close to stoichiometric. Some oxides with the fluorite structure exhibit such a defect structure, e.g. $\text{UO}_{2\pm x}$.

For the sake of simplicity in illustrating such a defect structure situation it will be assumed that both the interstitial oxide ions and the oxygen vacancies are doubly charged. In this case it will then be necessary to consider the following equilibria, for the formation of oxygen vacancies, oxygen interstitials, electrons and holes, and for anion Frenkel pairs:

$$K'_{vO} = [v_O^{\bullet\bullet}] n^2 p_{O_2}^{1/2} \quad (3.90)$$

$$K'_{Oi} = [O_i^{\prime\prime}] p^2 p_{O_2}^{-1/2} \quad (3.91)$$

$$K'_i = np \quad (3.92)$$

$$K_{AF} = [O_i^{\prime\prime}] [v_O^{\bullet\bullet}] \quad (3.93)$$

In these equilibria we have assumed small defect concentrations such that the concentrations of normal lattice sites and empty interstitial sites have been assumed constant and equal to unity and thus omitted from the expressions.

It should be noted that the defect equilibria are interrelated, and through a combination of the equations it may be shown that $K'_i K_{AF}^2 = K'_{vO} K'_{Oi}$. Thus, only three out of the four equilibria are sufficient to describe the defect structure of the oxide.

The full electroneutrality condition is given by

$$2[v_O^{\bullet\bullet}] + p = 2[O_i^{\prime\prime}] + n \quad (3.94)$$

We will explore the defect structure of the oxide by considering limiting conditions and follow the procedure listed before to construct Brouwer diagrams.

Oxygen deficit.

At large oxygen deficit the following approximation may be made

$$n = 2[v_O^{\bullet\bullet}] \gg 2[O_i^{\prime\prime}], p \quad (3.95)$$

We first insert this into the appropriate equilibrium to find the concentrations of the dominating defects in the usual manner:

$$n = 2[v_O^{\bullet\bullet}] = (2K'_{vO})^{1/3} p_{O_2}^{-1/6} \quad (3.96)$$

and then insert this into other equilibria to find the concentrations of the minority defects. By inserting the expression for the concentration of vacancies into the anion Frenkel equilibrium, we obtain for the concentration of interstitials:

$$[O_i^{\bullet\bullet}] = 2^{2/3} K_{AF} (K'_{vO})^{-1/3} p_{O_2}^{1/6} \quad (3.97)$$

By inserting the expression for the concentration of electrons into the intrinsic electronic equilibrium, we obtain for the concentration of holes:

$$p = K'_i (2K'_{vO})^{-1/3} p_{O_2}^{1/6} \quad (3.98)$$

Oxygen excess

For relatively large excess oxygen, that is, when

$$p = 2[O_i^{\prime\prime}] \gg 2[v_O^{\bullet\bullet}], n \quad (3.99)$$

we may in a manner analogous to the preceding case, derive the following relations:

$$p = 2[O_i^{\prime\prime}] = (2K'_{Oi})^{1/3} p_{O_2}^{1/6} \quad (3.100)$$

$$[v_O^{\bullet\bullet}] = 2^{2/3} K_{AF} (K'_{Oi})^{-1/3} p_{O_2}^{-1/6} \quad (3.101)$$

$$n = K'_i (2K'_{Oi})^{-1/3} p_{O_2}^{-1/6} \quad (3.102)$$

Stoichiometric condition

At or close to stoichiometry two alternative limiting conditions must be considered, namely dominance by intrinsic electronic ionisation or by anion Frenkel disorder.

If intrinsic ionisation of electrons predominates, and thus

$$p = n = (K'_i)^{1/2} \gg 2[O_i^{\prime\prime}], 2[v_O^{\bullet\bullet}] \quad (3.103)$$

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The concentrations of electrons and electron holes (n and p) are then independent of oxygen pressure. The point defect concentrations are obtained by insertion of the expression for the concentrations of the electronic defects into the appropriate equilibria, and we obtain:

$$[V_o^{\bullet\bullet}] = \frac{K'_{vo}}{K'_i} p_{O_2}^{-1/2} \quad (3.104)$$

$$[O_i^{\prime\prime}] = K'_{oi} K'_i p_{O_2}^{1/2} \quad (3.105)$$

A Brouwer diagram illustrating this case of stoichiometric condition, along with oxygen deficit and excess, is shown below.

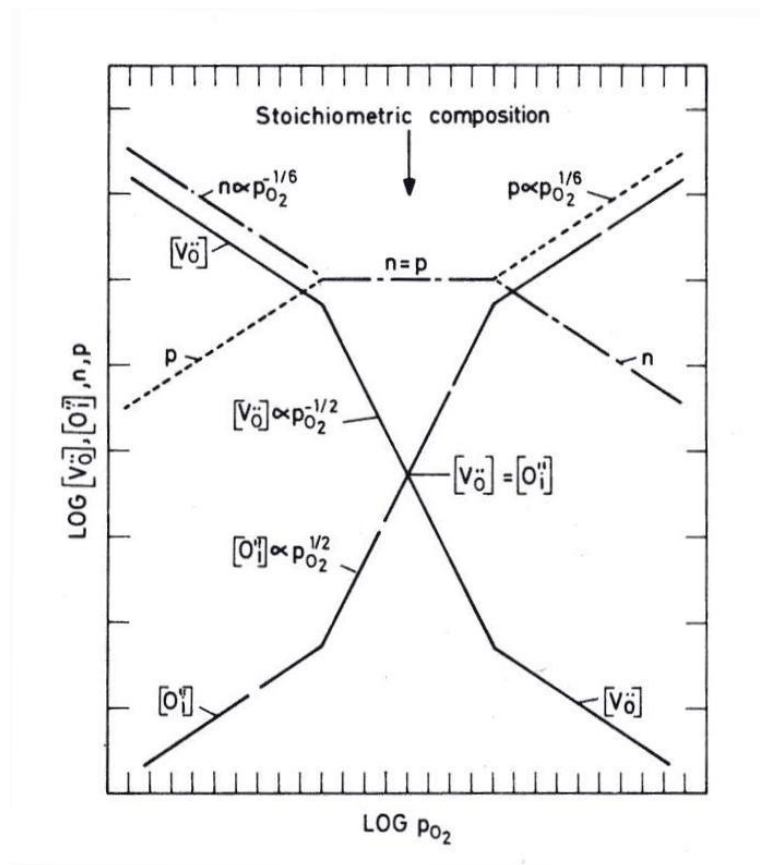


Figure 3-6. Schematic presentation of oxygen point defects and electronic defects as a function of oxygen pressure in an oxide which depending on the partial pressure of oxygen may have an excess or deficit of oxygen. Intrinsic electronic excitation is assumed to predominate at stoichiometric composition.

If, on the other hand, anion Frenkel disorder predominates under stoichiometric conditions, and thus

$$[O_i^{\prime\prime}] = [V_o^{\bullet\bullet}] = K_{AF}^{1/2} \gg \frac{p}{2}, \frac{n}{2} = \frac{(K'_i)^{1/2}}{2} \quad (3.106)$$

3. Defect equilibria

then $[O_i^{//}]$ and $[V_O^{**}]$ are independent of the partial pressure of oxygen, while the concentrations of electronic defects are given by

$$n = (K_{vO}^I)^{1/2} K_{AF}^{-1/4} p_{O_2}^{-1/4} \quad (3.107)$$

$$p = (K_{oI}^I)^{1/2} K_{AF}^{-1/4} p_{O_2}^{1/4} \quad (3.108)$$

A Brouwer diagram illustrating this case of stoichiometric condition, along with oxygen deficit and excess, is shown below.

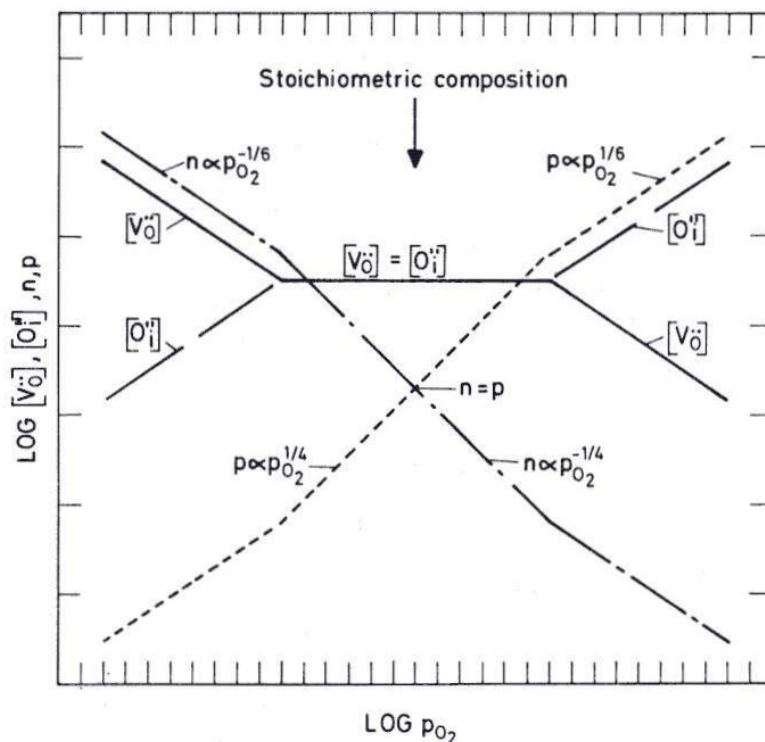


Figure 3-7. Schematic presentation of the concentration of oxygen point defects and electronic defects as a function of oxygen pressure. Oxygen defects are assumed to predominate at stoichiometric composition.

From the diagrams we can conclude that at low oxygen activities the oxide has oxygen deficiency and will be an electronic n-type conductor, because the mobility of the electrons is always much higher than that of oxygen vacancies. At high oxygen partial pressures the oxide will correspondingly have oxygen excess and be a p-type electronic conductor. At intermediate oxygen activities it may be a mixed n- and p-type electronic conductor in the case of intrinsic electronic disorder, while it may exhibit ionic or mixed ionic/electronic conduction in the case of anion Frenkel disorder.

Similar diagrams and analyses may be made for many other combinations of non-stoichiometric and stoichiometric defect situations of pure (undoped) oxides and other ionic compounds.

Summary

Chemical reactions for defects can be formulated and treated using the mass-action law. As for other chemical reactions, equilibrium constants can be defined in terms of the activities of the defects and other species. Under the normal constrictions we can approximate activities with concentrations of defects and partial pressures of gases. The equilibrium constants can also be expressed in terms of the standard Gibbs energy change of the reaction, which in turn is a function of the standard entropy and enthalpy changes.

We have seen that the standard entropy change of the standard Gibbs energy change contains only vibrational terms of the standard states provided that the configurational terms are properly handled in expressing the equilibrium conditions. This is often possible in defect idealised defect chemistry since we can apply classical statistical thermodynamics. However, for non-classical defects such as delocalised electrons and holes this approach is less meaningful, and the entropy change may then be interpreted in a less straightforward manner. We have introduced the use of a prime (as in K') to denote equilibrium constants that are not expressed according to statistical thermodynamics and where the entropy change in the Gibbs energy change may have other than vibrational contributions.

The mass action expressions can be combined with the full or limited cases of the electroneutrality condition to obtain exact or approximate (limiting case) expressions for the concentration of defects. Such concentrations are typically a function of the oxygen partial pressure and temperature. It is common to illustrate defect structures for oxides by plotting log defect concentrations vs log p_{O_2} (Brouwer diagrams) or ln or log defect concentrations vs $1/T$ (van 't Hoff plots). We have shown these principles and techniques through examples of intrinsic ionic and electronic disorder, various types of nonstoichiometry and variable ionisation of point defects.

We have restricted our treatment to simple cases and made simplifications where possible. Assumption of small defect concentrations have allowed the assumptions that the concentrations of normal lattice atoms and empty interstitial sites are constant, with activities equal to unity. (Larger defect concentrations can to a first approximation be taken into account by including mass and site balances into the expressions used to solve the defect structure.)

Literature

Kröger, F.A. (1964) *The Chemistry of Imperfect Crystals*, North-Holland, Amsterdam, and Wiley, New York.

Kröger, F.A., Stieltjes, F.H. and Vink, H.J. (1959), *Philips Res. Rept.* **14**, 557.

Problems

1. Do the insertion of Stirling's approximation and the derivation that leads up to the relation between equilibrium constant and entropy and enthalpy changes for the elemental reaction $E_E = v_E + E_E$ (Eqs. 3.3 and onwards).
2. Write the reaction for formation of Schottky defects in MO_2 and find an expression for the defect concentrations as a function of the equilibrium constant and thermodynamic parameters and temperature. Note in particular how the solution deviates from the one obtained for the oxide MO treated in the text.
3. In the case of cation Frenkel defects in MO we assumed in the text that we had one interstitial site per MO . Derive the expression for the defect concentrations if the structure consists of fcc close-packed O ions, with M ions on each octahedral hole, and with interstitial sites on all tetrahedral holes (Hint: consult Chapter 1). Does it deviate from Eq. (3.38)?
4. For a defect situation in an oxide dominated by doubly charged oxygen vacancies and electrons, sketch the van 't Hoff plot (Log defect concentration vs $1/T$) and a double-logarithmic plot of defect concentrations vs p_{O_2} (Brouwer diagram).
5. Consider a metal oxide MO_{1-y} dominated by singly and doubly charged oxygen vacancies. Suggest a condition that expresses the changeover from dominance of one to dominance of the other.
6. Consider a metal oxide $M_{2-x}O_3$ dominated by doubly and triply charged metal vacancies. Suggest a condition that expresses the changeover from dominance of the doubly charged to dominance of the triply charged.
7. Find a general expression for m in the $[e'] \propto p_{O_2}^m$ relationship for oxides MO_b with non-stoichiometry dominated by fully ionised metal interstitials. (Hint: Find m as a function of b). Use this to find m in the case of M_2O , MO , M_2O_3 , MO_2 , M_2O_5 and MO_3 .
8. Find a general expression for m (as a function of the valency z of the cation) in the $[h'] \propto p_{O_2}^m$ relationship for binary oxides with non-stoichiometry dominated by fully ionised metal vacancies. Use this to find m in the case of M_2O_3 .
9. Sketch a full Brouwer diagram (log defect concentrations vs log p_{O_2}) for an oxide M_2O_3 dominated by fully ionised oxygen and metal vacancies at under- and overstoichiometry, respectively. Assume that Schottky defects predominate close to stoichiometric conditions. (The main goal in this and following Problems is to obtain and illustrate the p_{O_2} -dependencies. Use the rules we listed for such constructions of Brouwer diagrams.)
10. Sketch a full Brouwer diagram (log defect concentrations vs log p_{O_2}) for an oxide MO_2 dominated by fully ionised oxygen and metal vacancies at under- and overstoichiometry, respectively. Assume that intrinsic electronic equilibrium predominates close to stoichiometric conditions.
11. Sketch a full Brouwer diagram (log defect concentrations vs log p_{O_2}) for an oxide ABO_3 dominated by fully ionised oxygen and metal vacancies at under- and overstoichiometry, respectively. Assume that Schottky defects

3. Defect equilibria

predominate close to stoichiometric conditions. You may assume that both cations are trivalent, but discuss also the effect it would have if A was divalent and B tetravalent.

12. Sketch a full Brouwer diagram (\log defect concentrations vs $\log p_{O_2}$) for an oxide AB_2O_4 dominated by fully ionised metal interstitials and vacancies at under- and overstoichiometry, respectively. Assume that Frenkel defects predominate close to stoichiometric conditions. You may assume that A is divalent and B trivalent.
13. In the text we considered an oxide MO_2 that had oxygen deficiency by both fully charged oxygen vacancies and doubly charged metal interstitials. Figure 3-5 illustrating the case was drawn assuming that the ratio between the concentrations of the two defects was 10^5 at 1 atm p_{O_2} . Calculate the exact p_{O_2} at which the concentrations are equal.

Answers and hints to selected Problems, Ch. 3

1. -
2. -
3. -
4. Hint: Use Eq. (3.57)
5. Condition for changeover: $2[v_{\text{O}}^{\bullet\bullet}] = [v_{\text{O}}^{\bullet}]$
6. -
7.for MO $m = -1/6$, for M_2O_3 $m = -3/16$
8. $+3/16$
9. Hint: Use rules on page 3-23. Diagram should appear similar to Figure 3-6 and Figure 3-7 but with different slopes. These exercises take time, but are important to master reasonably well.
10. -
11. -
12. -
13. -