APPROXIMATE SOLUTION FOR THE CONCENTRATIONS OF IMPERFECTIONS IN A PURE METAL OXIDE MO_y WITH SCHÖTTKY DISORDER

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ABSTRACT — A description of the defect structure of a pure metal oxide MO_y with Schöttky disorder in equilibrium with a surrounding oxygen gas phase is presented. Appropriate defect reactions are formulated and equilibrium concentrations of the different defects as a function of the ambient oxygen partial pressure are calculated using the Brouwer's method of approximation.

1 — INTRODUCTION

Many inorganic compounds above absolute zero are known to deviate from the ideal crystalline state and such deviations which may be attributed to lattice defects can occur in different ways and to varying degree. According to the Wagner-Schöttky statistical thermodynamic model (Wagner and Schöttky 1930), the structure and the chemistry of nonstoichiometric compounds can be interpreted in terms of lattice defects and this has led to the concept that all crystalline compounds are inherently nonstoichiometric to a greater or less degree. In a nonstoichiometric compound, generally only one type of point defect predominates and electrical neutrality in such a compound is maintained through the formation of an electronic or valence defect to every point defect.

A very common situation occurs predominantly in high temperature systems consisting of ionic oxides with a Schöttky

defect structure in equilibrium with the atmosphere defined by the oxygen pressure $P(O_2)$. The defects encountered in a MO$_y$ compound in such cases and their concentrations as a function of the oxygen partial pressure of the gas phase in equilibrium with the oxide determine a number of properties of (or processes in) the oxide such as mass transport, solid state reactions, gas-metal reactions, etc.; and if these defect-controlled properties or processes are to be interpreted, it is important that the defect concentrations are known. The derivation of expressions for the relevant defect concentrations as $f[P(O_2)]$ is to be the subject of this paper. The general character of the arguments and the way of presentation follows very much the lines of many available papers (Kröger 1974).

As a basis for those derivations, the remainder of this introduction briefly discusses the notation for description of point and electronic defects, and the effective charges of the defects.

In order to describe the point defects which are formed in pure crystals and to express their formation in terms of equations, different systems have been put forth by Schöttky (1959), Rees (1954), Kröger and Vink (1956, 1964), and others. The symbols and system used by Kröger and Vink will be employed in this paper, as this is being increasingly adopted in the literature.

The native point defects in an oxide MO$_y$ include M and O vacancies and M and O interstitial atoms or ions. Vacancies are written V with a subscript M or O referring to vacant metal or oxygen sites, respectively. Interstitial ions or sites are described with a sub i. Correspondingly, an unoccupied or vacant interstitial site is written V$_i$.

The point defects often occur in ionized form. In considering their charges, one may describe their actual charges or valence. However, it is generally more convenient in writing defect reactions to consider the charge on the defects relative to the perfect crystal. This relative charge is termed the effective charge of the defect.

In addition to the structural defects, crystals also contain electronic imperfections, i.e., electrons and holes, which are relatively free to move in the crystal. Free electrons and holes are usually indicated by e^l and h$^{\cdot}$, e and h standing for electron

and hole respectively, the aded dash and dot indicating the effective negative and positive charge.

More complex defect species may be encountered, for instance, from an association of two or more single point defects, valence defects, etc. In this paper, however, for the sake of simplicity, and because this actually applies to a great number of pure inorganic compounds at higher temperatures, we shall assume complete absence of association of imperfections. Therefore, for an oxide MO$_y$ with a Schöttky disorder, the only allowed oxygen vacancies will be written $V_O^{..}$, with two positive effective charges. That doubly charged oxygen vacancies predominate relatively to neutral or singly charged ones at high temperatures is a very well illustrated aspect in papers dealing with the individual oxides.

2 — CALCULATION OF DEFECT CONCENTRATIONS

If a simple MO$_y$ oxide contains simultaneously several of the imperfections referred in the previous section, their concentrations are interrelated. Since both the stoichiometric and nonstoichiometric defect structure situations may apply to the same binary metal oxide, depending on the oxygen partial pressure of the gas phase in equilibrium with the oxide, we will begin by considering a Schöttky defect structure situation in stoichiometric MO$_y$ oxides, and then, two defect structure situations in nonstoichiometric MO$_y$ oxides, in which predominate either oxygen or metal vacancies. It should be noted that the subscript y in the MO$_y$ formula may be equal to 1/2, 1, 3/2, 2, etc., depending on the valence of the metal associated with the oxygen component.

Stoichiometric MO$_y$ oxides. A stoichiometric compound MO$_y$ with Schöttky disorder contains y oxygen vacancies per metal vacancy. The overall formation of such a defect situation within the crystal involves the transfer of an equivalent number of cations and anions on regular lattice sites from the bulk to the surface. The overall defect equation may thus be written

$$0 = V_M^{2y\,|} + y\,V_O^{..}$$

where 0 designates a perfect crystal.

Applying equilibrium thermodynamics to this net reaction the corresponding defect equilibrium may, at low defect concentrations, be written

$$[V_O^{\cdot\cdot}]^y \, [V_M^{2y\,|}] = K_S$$

where K_S is the equilibrium constant. The square brackets indicate that the structure elements are expressed in terms of concentrations. It is obvious that the value of the equilibrium constant depends on the units of concentration employed, but it is a simple matter to convert values of the equilibrium constant from one system to another (Kröger 1974).

Oxygen-deficient MO$_{y-x}$ oxides. For the oxides treated in this paper interstitial defects are supposed to be absent, so the composition of a oxygen-deficient MO$_y$ oxide may be written MO$_{y-x}$, to emphasize that the defects represent a deficit of oxygen relative to the stoichiometric composition.

In these oxides, an oxygen vacancy is formed by the transfer of an oxygen atom on a normal site to the gaseous state, without any change in the number of sites. This defect reaction may be written
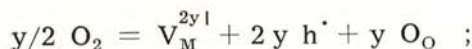
$$O_O = V_O^{\cdot\cdot} + 1/2 \, O_2 + 2 \, e^{|}$$
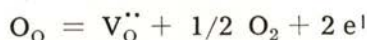
where O_O designates the oxygen ions on normal lattice sites. The defect equilibrium may accordingly be written

$$[V_O^{\cdot\cdot}] \, P(O_2)^{1/2} \, n^2 = K' \, [O_O]$$

where $n = [e^{|}]$ designates the concentration of electrons.

Metal-deficient M$_{1-x}$O$_y$ oxydes. In a metal-deficient MO$_y$ oxide a charged metal vacancy may be formed through the reaction of oxygen with the oxide

$$y/2 \, O_2 = V_M^{2y\,|} + 2 \, y \, h^{\cdot} + y \, O_O \quad ;$$

in this reaction both a cation and y anion sites are created in MO$_y$.

The defect equilibrium may, for small defect concentration, be written

$$[V_M^{2y\,|}] \, p^{2y} \, [O_O]^y = K'' \, P(O_2)^{y/2}$$

where $p = [h^{\cdot}]$ denotes the concentration of electron holes.

Intrinsic electronic equilibrium. This process, of thermal excitation of electrons from the valence band to the conduction band, can be formulated by the reaction

$$0 = e^| + h^{\cdot}$$

and leads to the following equilibrium concentration of electrons and holes

$$n\,p = K_i$$

Brouwer's method of approximation. Summarizing the preceding considerations, it can be stated that for a pure MO$_y$ crystal in equilibrium with its vapour phase, in which are present in the solid phase atoms M and O, ionized metal and oxygen vacancies, electrons, holes, and molecules O$_2$ only in the vapour phase, the following reactions and relations will hold:

$$0 = V_M^{2y\,|} + y\,V_O^{\cdot\cdot} \qquad\qquad [V_O^{\cdot\cdot}]^y\,[V_M^{2y\,|}] = K_S \qquad (1)$$

$$y/2\;O_2 = V_M^{2y\,|} + 2\,y\,h^{\cdot} + y\,O_o \qquad [V_M^{2y\,|}]\,p^{2y} = K\,P(O_2)^{y/2} \qquad (2)$$

$$0 = e^| + h^{\cdot} \qquad\qquad n\,p = K_i \qquad (3)$$

It should be noted that the formulations for nonstoichiometric MO$_{y-x}$ and M$_{1-x}$O$_y$ oxides are equivalent and, as a result, only the defect reaction (2) is taken into account at this stage.

Another basic requirement for treating defect equilibria and for evaluating defect concentrations in crystals is the electroneutrality condition. Therefore:

$$2\,y\,[V_M^{2y\,|}] + n = 2\,[V_O^{\cdot\cdot}] + p \qquad (4)$$

Since all the constants K are functions of temperature only, the four unknown concentrations n, p, $[V_O^{\cdot\cdot}]$ and $[V_M^{2y\,|}]$ can be calculated from relations (1)-(4). At any temperature the problem is completely determined. However an analytical solution is not possible; for instance eqs. (1)-(4) lead to a non-linear equation for the hole concentration p

$$p^{2y-1}\,[\,2\,K_S^{1/y}\,K^{-1/y}\,p^3\,P(O_2)^{-1/2} + p^2 - K_i\,] = 2\,y\,K\,P(O_2)^{y/2}\;.$$

Whereas precise calculation of all the concentrations is a rather tedious affair, approximate solutions are easily obtained if the neutrality condition is approximated by its dominant members; this method which is to be our next task, was first proposed by Brouwer (1954) for exactly this type of problem. The neutrality condition can be approximated in four ways: $n = 2 [V_O^{\cdot\cdot}]$; $n = p$; $[V_O^{\cdot\cdot}] = y [V_M^{2y\,|}]$; $p = 2y [V_M^{2y\,|}]$.

The first approximation holds at small values of the oxygen partial pressure, corresponding to the predomination of oxygen vacancies and the complementary electrons in the oxygen-deficient oxide. In this case (range I) the various concentrations are given by

$$n = 2^{1/3} (K_i K^{-1/2y} K_S^{1/2y})^{2/3} P(O_2)^{-1/6}$$

$$p = 2^{-1/3} (K_i K^{-1/2} K^{-1/2y} K_S^{1/2y})^{-2/3} P(O_2)^{1/6}$$

$$[V_O^{\cdot\cdot}] = 2^{-2/3} (K_i K^{-1/2y} K_S^{1/2y})^{2/3} P(O_2)^{-1/6}$$

$$[V_M^{2y\,|}] = 2^{2y/3} (K_i^{-y} K^{1/2} K_S)^{2/3} P(O_2)^{y/6}$$

(5)

Thus n and $[V_O^{\cdot\cdot}]$ will decrease with increasing oxygen pressure, and p and $[V_M^{2y\,|}]$ will increase with increasing oxygen pressure. This situation is typical of Ta_2O_5, V_2O_5, ZrO_2, etc., over at least a large part of their homogeneity ranges. The approximation $n = 2 [V_O^{\cdot\cdot}]$ is no longer valid when either p or $[V_M^{2y\,|}]$ become larger than $[V_O^{\cdot\cdot}]$ or n. Which of these two possibilities will occur depends on whether, in range I, $p >$ or $< [V_M^{2y\,|}]$; and this, in turn, depends on whether $K_i >$ or $< K_S$.

For $K_i > K_S$ we get a new range (II) in which the neutrality condition is governed by $n = p$. Under this condition

$$n = p = K_i^{1/2}$$

$$[V_O^{\cdot\cdot}] = K_i K^{-1/y} K_S^{1/y} P(O_2)^{-1/2}$$

$$[V_M^{2y\,|}] = K_i^{-y} K P(O_2)^{y/2}$$

(6)

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Thus $[V_O^{\cdot\cdot}]$ decreases and $[V_M^{2y\,|}]$ increases with $P(O_2)$, whereas n and p remain constant. This situation is particularly important for many oxides in which the intrinsic ionization is large and concentration of electron and holes according to eq. (3) predominates in the oxide (e.g. CaO-ZrO$_2$).

For $K_i < K_S$, n and p become smaller than $[V_M^{2y\,|}]$ and $[V_O^{\cdot\cdot}]$, respectively. In this case the electroneutrality condition can be approximated by $y\,[V_M^{2y\,|}] = [V_O^{\cdot\cdot}]$.

Under this condition (range III)

$$n = y^{-1/2(y+1)}\ K_i\ K^{-1/2y}\ K_S^{-1/2y(y+1)}\ P(O_2)^{-1/4}$$

$$p = y^{1/2(y+1)}\ K^{1/2y}\ K_S^{-1/2y(y+1)}\ P(O_2)^{1/4} \tag{7}$$

$$[V_O^{\cdot\cdot}] = y\,[V_M^{2y\,|}] = (y\,K_S)^{1/(y+1)}$$

In this range n decreases and p increases with increasing $P(O_2)$, whereas $[V_O^{\cdot\cdot}]$ and $[V_M^{2y\,|}]$ remain constant. This situation is typical of solid electrolytes in which the Schöttky defects predominate; a good example may be illustrated by pure thoria which exhibits predominant ionic conductivity at reduced oxygen pressures.

The last region holds at very high values of the oxygen pressure, corresponding to the predomination of metal vacancies and the complementary electron holes in the metal-deficient oxide. In this case (range IV) electroneutrality is governed by $2y\,[V_M^{2y\,|}] = p$, and the defect concentrations are given by

$$n = K_i\ K^{-1/(2y+1)}\ (2y)^{-1/(2y+1)}\ P(O_2)^{-y/2(2y+1)}$$

$$p = K^{1/(2y+1)}\ (2y)^{1/(2y+1)}\ P(O_2)^{y/2(2y+1)} \tag{8}$$

$$[V_O^{\cdot\cdot}] = K_S^{1/y}\ K^{-1/y(2y+1)}\ (2y)^{2/(2y+1)}\ P(O_2)^{-1/2(2y+1)}$$

$$[V_M^{2y\,|}] = K^{1/(2y+1)}\ (2y)^{-2y/(2y+1)}\ P(O_2)^{y/2(2y+1)}$$

These relations are similar to those for range I. Some examples of oxides which are metal-deficient at higher partial pressures of

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oxygen are V_2O_3, Cu_2O, NiO, etc. It should be noted that NiO is approximately stoichiometric at lower partial pressures of oxygen, which, as mentioned earlier, is in agreement with the fact that, depending on the oxygen gas pressure, different defect situations may apply to the same high-temperature oxide.

The advantages of the Brouwer's compensation mechanism, which is typical of all practical discussions about defect chemistry, become apparent when more intricate problems are described, in particular if solutions under a variety of circumstances are to be obtained, and graphical methods (logarithmic plots) can be used. In the present case, although the defect chemistry is quite simple, the discussion was facilitated by the approximation possibilities, leading to equations (5) to (8) which were readily derived.

REFERENCES

G. BROUWER, *Philips Res. Rep.*, **9**, 366 (1954).

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

F. A. KRÖGER, *"The Chemistry of Imperfect Crystals"*, vol. 2, North-Holland (1974).

F. A. KRÖGER and H. J. VINK, *"Solid State Physics"*, ed. by F. Seitz and D. Turnbull, vol. 3, 307, Academic Press, New York (1956).

A. G. REES, *"Chemistry of the Defect Solid State"*, Methuen, London (1954).

W. SCHÖTTKY, *"Halbleiterprobleme"*, ed. by W. Schöttky, vol. 4, 235, Vieweg und Sohn, Braunschweig (1959).

C. WAGNER and W. SCHÖTTKY, *Z. Physik. Chem.*, B. II, 163 (1930).