

Dissolution of Protons in Oxides

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The paper gives a brief introduction to protonic defects and their chemistry, thermodynamics and transport in oxides. The temperature dependence of the equilibrium concentration of protons is illustrated and compared for different acceptor-doped oxides. The difficulties of saturating as well as emptying the oxides of protons are discussed. In order to illustrate the possibility of lattice relaxation of defects, a conceptual study is made of a case where the enthalpy of dissolution of protons (water) at the cost of oxygen vacancies is assumed dependent on the concentration of vacancies. It is shown how this changes the behaviour of hydration curves vs temperature and water vapour pressure. Finally, a discussion is given on the water uptake in heavily oxygen deficient oxides; how water uptake may affect order-disorder in the oxygen sublattice and eventually lead to defective, disordered or ordered oxyhydroxides or hydroxides of potential interest as intermediate temperature proton conductors.

Key words : Protons, Water vapour, Enthalpy of defect equilibria, Lattice relaxation, BaCeO₃, Ba_nCaNb₂O₉

I. Introduction

Incorporation, migration and effects of protonic defects in oxides were seldomly observed and described until the discovery around 1980 of utilisable protonic conduction in acceptor-doped alkaline earth cerate and zirconate perovskites.¹⁾ Since then a large number of studies have focused on this group of oxides. The basic mechanisms and principles governing the incorporation and transport of protons in these materials are gaining acceptance, and our understanding of them is reaching a level where we to some extent can predict experimental observations and reproduce them with computer simulations. The large experimental base for acceptor-doped SrCeO₃ and BaCeO₃ in particular allows us to apply more detailed understanding and analysis than previously, but it also shows that there are a number of pitfalls and difficulties involved in measurements as well as in interpretation. New classes of complex oxygen deficient perovskites such as Ba₃Ca_{1+x}Nb_{2-x}O_{9-3x/2}²⁾ and Ba₂Y SnO_{6.5}³⁾ have recently been shown to take up water and exhibit high proton conductivities. They are attracting or will attract similar attention as the traditional II-IV perovskites mentioned above, and will need detailed models and analyses of the incorporation of protons. This paper outlines the traditional defect chemistry of protons in oxides and tries to point out examples of how this can and must be developed further, especially when dealing with heavily doped or inherently oxygen deficient oxides able to take up substantial amounts of protons or water.

There is presently also a development in the detail of understanding how protons migrate in oxides and what factors determine their mobility. However, few experi-

mental studies report true, equilibrium, partial proton conductivities. This reflects difficulties connected with determination of protonic transport numbers and with establishing equilibrium concentrations of protons. We will touch upon some of these problems, but not go in detail on proton diffusion and migration (for more detail here, as well as for many of the aspects to follow, see, for instance, refs. 4 and 5).

II. Conductivity, concentration, mobility and diffusivity of protons

The conductivity of protons is proportional to their charge e , concentration c_{H^+} (in cm⁻³) and mobility μ_{H^+} (in cm²/Vs):

$$\sigma_{\text{H}^+} = e c_{\text{H}^+} \mu_{\text{H}^+}^0 T^{-1} \exp(-\Delta H_{\text{m,H}^+}/kT) \quad (1)$$

where the $\Delta H_{\text{m,H}^+}$ is the migration enthalpy and the T⁻¹ term arises from the Nernst-Einstein relationship between mobility and diffusivity D_{H^+} :

$$\mu_{\text{H}^+} = (e/kT) D_{\text{H}^+} = (e/kT) D_{\text{H}^+}^0 \exp(\Delta H_{\text{m,H}^+}/kT) \quad (2)$$

When protons compensate an acceptor dopant the concentration may be constant, but otherwise it varies with temperature and ambient atmosphere. The conductivity or flux of protons through a material thus generally contains terms related to concentration as well as mobility. Ideally, the mobility and diffusivity are independent of the concentration, and it is thus convenient to treat concentration and transport separately. Here we shall concentrate on the concentration terms, but multiply by the mobility when we discuss conductivity.

III. Hydrogen species and defects

Elemental hydrogen is usually dealt with as molecules H_2 or atoms H, and can be imagined to be atoms also when dissolved in some metals or taking part in covalent molecules.

Upon formation of compounds with elements of higher electropositivity hydrogen tends to attract an electron, increase in size and become a hydride ion, H^- . The hydride ion takes on regular lattice positions, and such metal hydrides form ionic (salt-like) solids.

With sufficiently electronegative elements, on the other hand, the hydrogen atom loses its electron and becomes a proton, H^+ . The proton has the uniquely small ionic radius of a bare nucleus. In such compounds the protons cannot occupy a lattice or normal interstitial site, but are always embedded in the electron cloud of the electronegative element; the anion. If the element is oxygen, as in oxides, hydroxides, sulfates, phosphates etc., the proton will then locally be present as a hydroxide group, OH^- , and we may alternatively refer to the proton by the hydroxide group.

The proton in a hydroxide group will be trapped in the electron cloud; it can only escape by jumping to another ion's electron cloud. This can take place if the two anions are structurally close enough, or during momentary overlap of the two electron clouds due to thermal vibrations.

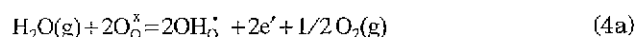
Many materials will contain stoichiometric amounts of protons (hydroxide ions) which then have regular crystallographic sites. Examples comprise basic hydroxides such as NaOH or $Y(OH)_3$, oxyhydroxides such as $YOOH$, and acidic materials such as $CsHSO_4$ (which could be viewed as $CsSO_3(OH)$). In all of these, proton transport is accomplished by thermally excited defects such as proton vacancies (vacant proton sites on hydroxide ions) or proton interstitials (oxygen ions with a proton). Alternatively, transport can be accomplished by partial occupancy (several equivalent proton sites on different oxygen ions, populated by a smaller number of protons). The high-temperature superprotonic polymorph of $CsHSO_4$ is a model material for the latter mechanism.

Materials nominally without hydrogen at all, such as oxides, will contain only defect protons, i.e., hydroxide defects. When this hydroxide sits on a normal oxygen site, the protonic defect may in Kröger-Vink notation be written OH_o^{\cdot} (the subscript $_o$ denotes the oxygen site and the superscript \cdot denotes positive effective charge). If we consider the oxygen in the hydroxide as structurally normal, and only view the proton as the defect, we may use the analogous notation H_i for simplicity (or to indicate that the protons migrate as lone protons).

The dissolution of protons in oxides can be written with many types of charge compensation. If we first disregard point defects, and only consider electronic defects, and use hydrogen as source, we get;



or, equivalently, with water vapour as source;



where superscripts \cdot and $'$ denote neutral and negative effective charge, respectively. The mass action expression for Eq. 4a is, assuming ideal conditions (small concentrations of defects and ideal gases):

$$K_4 = \exp(\Delta S_4/R) \exp(-\Delta H_4/RT) \\ = [OH_o^{\cdot}]^2 [O_o^{\cdot}]^{-2} [e']^2 p(O_2)^{1/2} p(H_2O)^{-1} \quad (4b)$$

where the symbols contained in brackets denote site fraction. Eqs. 3 and 4 are related through the gas phase equilibrium



The concentration of protons will in general be a function of $p(H_2O)$ (or $p(H_2)$), $p(O_2)$, doping and temperature.

When protons are minority defects, the concentration of electrons is independent of $p(H_2)$ and $p(H_2O)$ in Eqs. 3 and 4 (at constant $p(O_2)$). Under these conditions mass action evaluations of Eqs. 3 and 4 show that

$$[OH_o^{\cdot}] \propto p(H_2)^{1/2} \propto p(H_2O)^{1/2} \text{ (for constant } p(O_2)) \quad (6)$$

The square root dependency contained herein is often referred to as Sievert's law behaviour.

At sufficiently high $p(H_2O)$ and $p(H_2)$, protons may dissolve in sufficient quantities to become the dominant positive defects. If Eq. 3 (or 4) is representative for the dominant defect reaction and thus electrons are the major compensating species, the material is effectively reduced by hydrogen (or water). The simplified electroneutrality condition becomes

$$[OH_o^{\cdot}] c_o = [e'] c_{e,c} \quad (7)$$

where the c_o and $c_{e,c}$ denote density of oxygen sites and conduction band states, respectively, while $[OH_o^{\cdot}]$ and $[e']$ denote fraction of such sites occupied by hydroxide and defect electrons. (The use of site fractions and density of sites or states are both used, so that their relation is evident: Site fractions must be used in the mass action expressions in order to express equilibrium constants correctly in terms of entropy (e.g. Eq. 4b) while densities must enter the electroneutrality.) Combination of Eqs. 4b and 7 yields

$$[OH_o^{\cdot}] = [e'] c_{e,c} / c_o = K_4^{1/4} (c_o / c_{e,c})^{-1/2} p(O_2)^{-1/8} p(H_2O)^{1/4} \quad (8)$$

Dominant concentrations of protons compensated by electrons have been reported for ZnO^6 and $YBa_2Cu_3O_6^7$ where the electrons may be taken to represent the reduced species Zn^+ and Cu^+ .

At higher oxygen activities and for oxides with less reducibility, protons may dissolve instead through simultaneous creation of and charge compensation by oxygen

interstitials or metal vacancies. The former situation may be likely for relatively open oxygen sublattices like in brownmillerites, pyrochlores or cubic rare earth sesquioxides, while we must anticipate that the latter prevails in structures with more close-packed oxygen sublattices such as perovskites. While the compensation of protons by electrons represents reduction (incorporation of hydrogen), the compensation of protons by oxygen interstitials or metal vacancies instead represents an increase in both hydrogen and oxygen content. The reaction can be seen as incorporation of water; the material is partly hydrated. We shall return to such situations in a later section, but first discuss doped oxides.

IV. Doped oxides

Doping with metal cations of higher valence than the host cations (donor-doping) will force the concentration of protons down, and their role will decrease. We will thus not discuss such cases further than just mentioning that donor-doping is an efficient way of decreasing the number, the conductivity, and thus the flux of protons in oxides; donor-doped oxides become efficient hydrogen barriers.

Doping with a substitutional lower-valent cation (acceptor), on the other hand, increases the concentration of positive defects, including protons. If protons are dominating defects in the undoped oxide, they may remain so under acceptor doping, compensating the effectively negative charge of the acceptors. The doping may thus take the concentration of protons to considerable levels, e.g. several mole-% in acceptor doped perovskites. Materials in this group do in some cases exhibit proton conductivities high enough for use in fuel cells at a few hundred centigrades.

Let us analyse the behaviour of protons in acceptor doped oxides in some more detail, with special reference to perovskites. The oxides under interest will at sufficiently high temperatures and dry conditions compensate the acceptors by oxygen vacancies, such that the simplified electroneutrality condition becomes $[Ml_M] c_M = 2 [V_O] c_O = \text{constant}$. Here Ml is used to denote the lower valent metal, and M to denote the host metal.

When protons are minority defects in the acceptor doped oxide, their concentration increases with decreasing temperature and with increasing water vapour partial pressure (Eq. 6). Protons eventually become the dominating defects compensating the acceptors, with limiting electroneutrality $[Ml_M] c_M = [OH_O] c_O = \text{constant}$.

To properly model the change in defect structure, we need to use an electroneutrality condition containing both vacancies and protons:

$$[Ml_M] c_M = 2[V_O] c_O + [OH_O] c_O = \text{constant} \quad (9)$$

The equilibrium and competition between oxygen vacancies and protons can be expressed as



$$K_{10} = \exp(\Delta S_{10}/R) \exp(-\Delta H_{10}/RT) \\ = [OH_O^{\cdot}]^2 [V_O]^{-1} [O_O^{\times}]^{-1} p(H_2O)^{-1} \quad (10b)$$

We may insert Eq. 9 into Eq. 10b and utilise $[O_O^{\times}] + [V_O] + [OH_O^{\cdot}] = 1$ to obtain a solution for $[OH_O^{\cdot}]$ as a function of $p(H_2O)$, K_{10} , and $[Ml_M] c_M$:

$$[OH_O^{\cdot}] = 1/4 K_{10} p(H_2O) \{-1 + [1 + 8[Ml_M] c_M c_O^{-1} K_{10}^{-1} p(H_2O)^{-1}]^{1/2}\} \quad (11)$$

This solution is given under the simplifying assumption that $[O_O^{\times}] \approx 1 \gg [V_O] + [OH_O^{\cdot}]$, i.e. it is valid only for small or modest acceptor levels. $[V_O]$ can be calculated by inserting the result of Eq. 11 back into Eq. 9.

It is of interest to look at how $[OH_O^{\cdot}]$ and $[V_O]$ vary as a function of temperature and $p(H_2O)$ for selected cases. We choose to use $[Ml_M] c_M / c_O = 0.1$. This corresponds, for instance, to a perovskite which is 30% acceptor substituted on one of the cation sites, or to a binary sesquioxide with 15% cation acceptor substituents. Depending on the conditions this may be compensated by 5% vacancies or 10% protons (as hydroxide) in the oxygen sublattice.

In order to calculate the defect concentrations of this system we need to know K_{10} , preferably as a function of temperature through knowledge of ΔS_{10} and ΔH_{10} , and we will do this using examples and literature values compiled in ref. 8.

ΔS_{10} is commonly found to be in the range -120 ± 40 J/mol-K, likely to be dominated by the entropy of the consumed water vapour (188.7 J/mol-K) in the course of reaction 10. Equation 11 does, with these values of ΔS_{10} , the above said doping level, and wet atmospheres ($p(H_2O) = 0.03$ atm) give values for $[OH_O^{\cdot}]$ (site fraction) at infinitely high temperatures of the order of 10^{-5} (independent of ΔH_{10}), as evident for the selected oxides in Fig. 1.

ΔH_{10} determines how the proton concentration changes with temperature. ΔH_{10} has always been found to be negative, reflecting that the annihilation of the oxygen vacancy gives us more energy back than we need to atomise water and incorporate the protons in the oxide. There appear to be systematic trends in the variation of ΔH_{10} among oxides,⁹ relating to the bond strength (promotes annihilation of oxygen vacancy), probably basicity¹⁰ (promoting proton binding) and possibly other factors.

The negative value of ΔH_{10} means that the concentration of protons will increase with decreasing temperature and eventually become dominant and constant, given by the acceptor level and suppressing the concentration of oxygen vacancies. Fig. 1 shows this for selected oxides with widely different values of ΔH_{10} ; -202 kJ/mol (Y_2O_3), -172 kJ/mol ($BaCeO_3$), -79 kJ/mol ($Ba_3CaNb_2O_9$), and -43 kJ/mol ($SrTiO_3$). The ΔH_{10} values are in many cases uncertain and mostly obtained for heavily acceptor doped samples. In the four cases, protons become more dominant than oxygen vacancies below temperatures of roughly 1050, 750, 350, and 100°C,

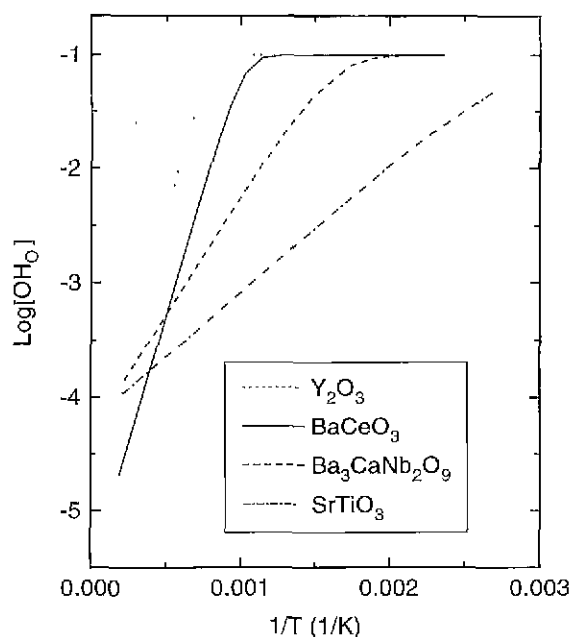


Fig. 1. $\text{Log}[\text{OH}_0^-]$ (site fraction) vs $1/T$ for selected oxides using data compiled in Ref. [8]. $p(\text{H}_2\text{O})=0.03$ atm. Oxides assumed doped corresponding to $2[\text{V}_0^{++}]+[\text{OH}_0^-]=0.1$.

respectively. Consequently, acceptor doped Y_2O_3 and similar cubic rare earth sesquioxides like Er_2O_3 are proton conductors to very high temperatures in the presence of water vapour and then exhibit only minor contributions of oxygen vacancy conduction. Acceptor-doped SrTiO_3 and similar alkaline earth titanates (CaTiO_3 and BaTiO_3) on the other hand possess mainly oxygen ion conduction and no significant proton conduction. BaCeO_3 represents an intermediate case and shifts from a proton conductor at relatively low temperatures to an oxygen ion conductor at high temperatures. The same is expected for $\text{Ba}_3\text{CaNb}_2\text{O}_9$, in which the acceptor-doping is done by a higher-than-stoichiometric Ca:Nb ratio; the material is a proton conductor up to at least 600°C , but the onset of oxygen ion conduction needs to be clarified in this case.

Fig. 2 illustrates concentrations of protons as a function of temperature under wet and dry conditions. Dry is taken to be 30 ppm of water ($p(\text{H}_2\text{O})=30 \times 10^{-6}$ atm) as found to be representative for even the driest gas when it passes through a single-walled ceramic cell at elevated temperature.¹⁰ Wet is, as before, taken to be $p(\text{H}_2\text{O})=0.03$ atm. Such a plot can be used to deduce how low a temperature we need to saturate the material with protons in wet atmospheres and how high the temperature needs to be to empty the material of protons in dry atmospheres. In wet atmospheres the doped BaCeO_3 would essentially be saturated with water at below 500°C , while in dry atmospheres it would be 99% emptied of water at above some 850°C . The non-stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$ requires as low as 200°C to achieve complete saturation with water in wet atmosphere and 450°C to

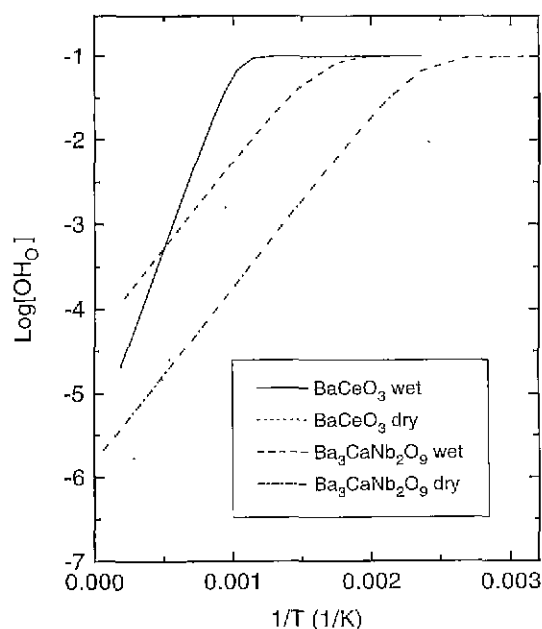


Fig. 2. $\text{Log}[\text{OH}_0^-]$ vs $1/T$ using data compiled in Ref. [8]. $p(\text{H}_2\text{O})=0.03$ atm (wet) and 30×10^{-6} atm (dry). Oxides doped corresponding to $2[\text{V}_0^{++}]+[\text{OH}_0^-]=0.1$.

empty the material of water in dry atmospheres.

From this it appears that it is especially difficult to saturate materials which have small absolute ΔH_{10} values; the temperatures required are too low for practical equilibration. This may possibly explain some of the apparent discrepancies between nominal doping level and limit of water uptake, although some observations undoubtedly reflect real discrepancies due to e.g. un-deliberate counter-doping (dopants distributed over more than one cation site).¹⁰

A complication may arise if the protons are present in concentrations above the availability of lowest-energy sites and thus may distribute themselves over more than one type of sites. This can, for instance, happen when protons are preferably trapped close to acceptors with high effective charge, such that the acceptors are present in a smaller number than the protons. Then the protonation and deprotonation may occur in two regions of temperature/ $p(\text{H}_2\text{O})$ or at least spread over a larger span in T and $p(\text{H}_2\text{O})$.

V. Proton conductivities

Fig. 3 shows calculated equilibrium proton conductivities in selected oxides as a function of inverse temperature. The proton concentrations are the same as in Fig. 1, but estimated mobilities are used to calculate the conductivities (activation enthalpies for mobilities taken from literature data compiled in Ref. [8], preexponentials partly taken directly from literature, partly chosen to make the conductivities confer with typical values in the

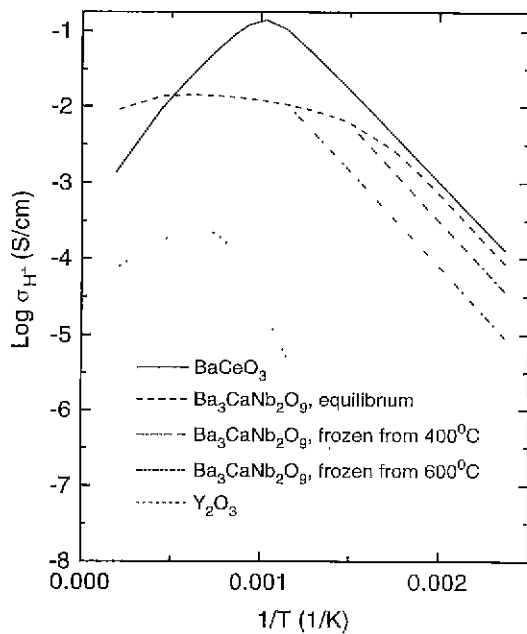


Fig. 3. Log partial proton conductivity vs $1/T$ using data in Ref. [8]. $p(\text{H}_2\text{O})=0.03$ atm. Oxides doped corresponding to $2[\text{V}_\text{O}^\bullet] + [\text{OH}_\text{O}^-] = 0.1$. More details in text.

literature).

The changeover in defect structure, as described above, gives the curves a bend. When $\Delta H_{10}/2$ is larger than the activation enthalpy $\Delta H_{\text{m,H}^+}$, the proton conductivity in fact goes through a maximum and decreases with increasing temperature, as evident for BaCeO_3 and Y_2O_3 in the figure. Changeovers in proton conductivity (and other partial conductivities) vs $1/T$ is the basis for extraction of ΔH_{10} and $\Delta H_{\text{m,H}^+}$ from conductivity data.⁹⁾

The materials included in Fig. 3 are fairly pure proton conductors at low temperatures. With increasing temperature, other conductivity contributions invariably take over, whether the proton conductivity starts decreasing or not. In acceptor doped materials this is normally oxygen vacancy conduction due to the increasing concentration of vacancies and their higher activation enthalpy than for protons. At high $p(\text{O}_2)$ also p-type conduction often becomes dominant at high temperatures. It is thus imperative that studies of proton conduction and other types of conduction are founded on measurements of transport numbers, so as to represent true partial conductivities. This can be done by, for instance, mass transport measurements, emf-measurements on concentration cells, or deconvolution of total conductivity over a range of temperatures and partial pressures. In the case of mixed proton/oxygen ion/electronic conductors these methods may involve complicated control systems for independent control of and variation in partial pressures of oxygen, water vapour and/or hydrogen. However, such apparatus and methodologies have been described and applied.^{9,12)}

In order to overcome the problems of transport num-

bers in mixed conductor regimes, many investigators measure proton transport in low temperature regimes where the proton concentration is frozen at a high level and the material is essentially a pure proton conductor. In this case the temperature dependency reflects only the migration enthalpy of the protons, and such studies have given useful insight into proton migration and isotope effects of this in various oxides.⁵⁾

But in some cases such samples are probably frozen from temperatures too high to give a saturated proton concentration, and the subsequent conductivity curves at lower temperatures may yield conductivities lower than the ones that would have been obtained under true equilibrium conditions, where the proton concentration is allowed to increase further with lowering the temperature. An illustration of this is included in Fig. 3 in the case of non-stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$: The equilibrium proton conductivity was calculated from literature data of ΔS_{10} , ΔH_{10} , and $\Delta H_{\text{m,H}^+}$ plus an empirically chosen mobility preexponential. If the sample was frozen from 600 or 400°C, the proton conductivity would follow straight lines from those points (slope reflecting only $\Delta H_{\text{m,H}^+}$). The sample frozen at 600° would at lower temperatures have conductivities approximately 10 times lower than the equilibrium value, and the sample frozen at 400°C would exhibit around half of the equilibrium conductivity, as shown in Fig. 3.

Non-stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$ has recently been demonstrated as an electrolyte in a lab-scale fuel cell.¹³⁾ At 600°C the cell performance reflected a proton conductivity higher than 10^{-2} S/cm, and it is interesting to note that according to Fig. 3, the proton conductivity is fairly independent of temperature in this region: It would not increase much by increasing the temperature nor diminish much by going down to 500°C (performance of course dependent also on overcoming slower kinetics of the electrodes).

VI. Concentration dependent defect formation enthalpies.

In the examples used to illustrate how we go from oxygen vacancies to protons as the positive acceptor-compensating defects, we have assumed that ΔS_{10} and ΔH_{10} are constant, independent of temperature and concentration of the defects. This may be representative for an idealised, dilute solution case.

In this situation the small concentration of defects allows each defect to decrease its energy by relaxing the lattice surrounding it over a relatively large volume. As we increase the number of defects, the energy of each defect eventually increases as the average distance between defects becomes smaller than the radius of the relaxed sphere around each defect; the defect relaxation becomes impossible.

This can be probed by lattice calculations, and pre-

liminary modeling on BaCeO_3 indicates that creation of oxygen vacancies requires much more energy when the material is heavily acceptor doped and contains already many vacancies, than when it is undoped and contains no vacancies.¹⁴ Awaiting more calculations let us assume that this is mainly connected with the vacancies themselves, not the dopant ions. Let us assume that also protons impose smaller strains on the lattice, relax over effectively smaller distances and that this thus changes less with proton content. Under these assumptions, only the changing energy of oxygen vacancies affects ΔH_{10} as we go from vacancy to proton dominated situations. The preliminary lattice simulation for BaCeO_3 gives ΔH_{10} close to the experimental value of -172 kJ/mol ⁷ for an Y-doped oxide compensated with oxygen vacancies. As the concentration of vacancies is decreased, the calculation gives a less negative number. Thus, ΔH_{10} and, in turn, K_{10} change as a function of vacancy and proton content and are not constant during changes in temperature, $p(\text{H}_2\text{O})$, or doping level. We will illustrate this by an example where we rather arbitrarily let ΔH_{10} vary linearly from -172 to -130 kJ/mol when $[\text{V}_\text{O}^{\bullet\bullet}]$ (site fraction) goes from 0.05 to 0 . We calculate $[\text{OH}_\text{O}^-]$ using Eq. 11, but when ΔH_{10} and in turn K_{10} depend on the result, a numerical solution (e.g. using simple iterations) becomes necessary. Fig. 4 shows how $[\text{OH}_\text{O}^-]$ now varies as a function of $1/T$, and compares this with classical cases where ΔH_{10} is held constant at the end values and at an average value of -151 kJ/mol . The curve shape is different from any of the three.

Fig. 5 shows the same effect in a plot of $\log[\text{OH}_\text{O}^-]$ vs $\log p(\text{H}_2\text{O})$ at 600°C .

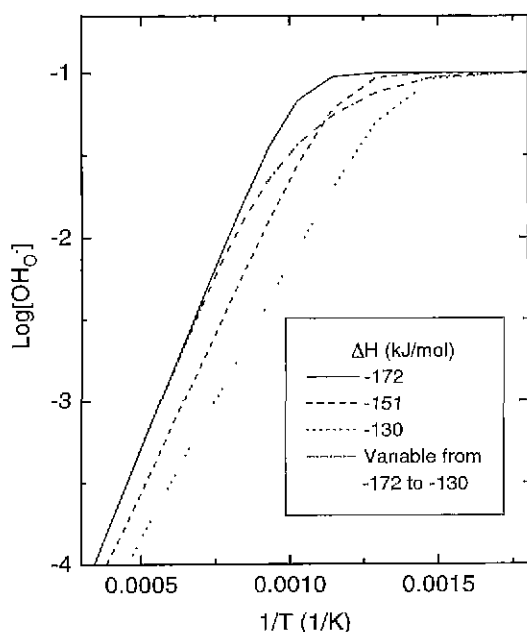


Fig. 4. $\text{Log}[\text{OH}_\text{O}^-]$ (site fraction) vs $1/T$ at $p(\text{H}_2\text{O})=0.03 \text{ atm}$ and using various ΔH_{10} (see text). Oxide assumed doped corresponding to $2[\text{V}_\text{O}^{\bullet\bullet}] + [\text{OH}_\text{O}^-] = 0.1$.

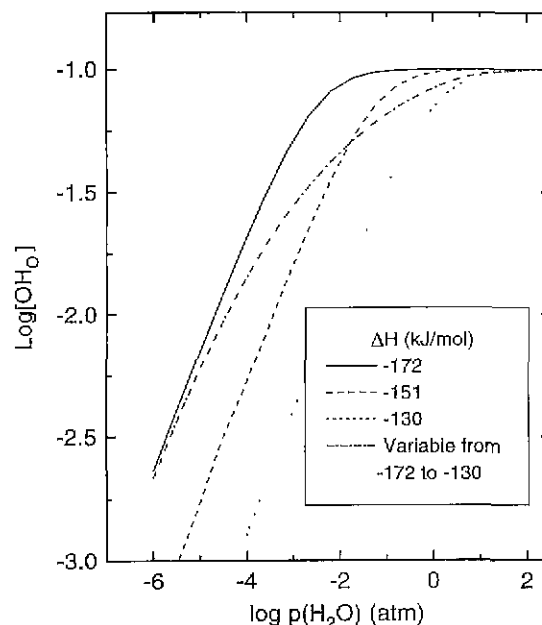


Fig. 5. $\text{Log}[\text{OH}_\text{O}^-]$ (site fraction) vs $p(\text{H}_2\text{O})$ at 600°C using various ΔH_{10} (see text). Oxide assumed doped corresponding to $2[\text{V}_\text{O}^{\bullet\bullet}] + [\text{OH}_\text{O}^-] = 0.1$.

When Eq. 10 is driven to the right by increasing $p(\text{H}_2\text{O})$ or decreasing temperature, the concentration of oxygen vacancies becomes smaller and ΔH_{10} becomes less negative. This drives the reaction to the left, and eventually the system may come to equilibrium. However, if we try to impose too large dependencies of ΔH_{10} on vacancy concentration, we fail to find an equilibrium situation (calculations do not converge), and the solid solution would be thermodynamically unstable.

The exercise above is done with many assumptions and arbitrarily chosen input values, with no claim to reflect the real situation in BaCeO_3 or any other material. However, it illustrates the possibility of e.g. water uptake or conductivity curves which deviate from ideal behaviour, affecting for instance how we curve-fit dependencies of measured properties and, in turn, assign thermodynamic parameters to them.

It should be mentioned that the ideas implemented above are not entirely new; they have for instance been postulated before by Kreuer *et al.*¹⁰ for doped BaCeO_3 (although their treatment, unlike ours, appears to suggest that vacancy relaxation may give different limiting proton (water) contents). In a recent paper the same group has pursued variable thermodynamic parameters further.¹⁶ They confirmed experimentally that the values of ΔH_{10} (and also ΔS_{10}) become more negative with increased Y-content in $\text{BaCe}_{1-x}\text{Y}_x\text{O}_3$. They assign this to the increased basicity of Y^{3+} compared with Ce^{4+} . One may note that this implies a variation of the thermodynamic parameters with Y-content as such, while we in this paper have chosen to relate them to the actual oxygen

vacancy concentration, such that the parameters change with conditions (T and $p(\text{H}_2\text{O})$) for one and the same Y-content. Although ours is merely a conceptual study, it is interesting to note that a temperature dependency of ΔH_{10} which agrees qualitatively with our model was noted in an early study of doped SrCeO_3 .¹⁶⁾

VII. Dissolution of water in oxides with crystallographically empty oxygen sites

We have discussed the complete filling of oxygen vacancy defects with oxygen from water. If we continue to increase the water vapour pressure, the concentration of protons will remain constant, given by the acceptor doping, over a range of $p(\text{H}_2\text{O})$. Under these conditions, however, the concentration of negatively charged defects such as oxygen interstitials, metal vacancies and electrons increases (while the concentration of positively charged defects decreases). Eventually, one of the negative defects may become dominating and continue to increase accompanied by an increase in the proton concentration, as touched upon earlier in this paper.

Here we will look closer at such a situation for an oxide with structurally vacant oxygen sites; sometimes referred to as structural vacancies, $V_{\text{S}_i}^{\cdot}$. In many cases they can be regarded as ordered oxygen vacancies. This situation is interesting for several reasons: Oxygen interstitials must be assumed relatively favourable in such materials, they relate to the acceptor doped materials by having ordered rather than disordered vacancies, and we get interesting situations when we eventually fill all of the vacant sites.

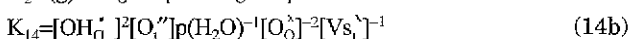
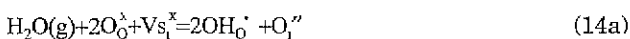
The situation to be described may for instance be applicable to cubic rare earth sesquioxides or pyrochlore oxides (oxygen deficient fluorite type structures), brownmillerites, or complex perovskites like $\text{YBa}_2\text{Cu}_3\text{O}_6$ and many others. They will have in common a tendency of dissolving interstitial oxygen according to:



where we for the sake of illustration have included the vacant interstitial site in the reaction. If we combine this with Eq. 3 and with the intrinsic ionisation of electrons:



we obtain for the incorporation of water as protons and oxygen interstitials:



where $K_{14} = K_3 K_{12} K_{13}^{-2}$ so that $\Delta H_{14} = \Delta H_3 + \Delta H_{12} - 2\Delta H_{13}$, referring to the equilibrium constants and enthalpies of the reactions above. When the dominating electroneutrality is $[\text{OH}_0^{\cdot}] = 2[\text{O}_i^{\cdot\cdot}]$ and $[\text{O}_i^{\cdot\cdot}] \ll [V_{\text{S}_i}^{\cdot}]$ we get the sim-

plified case:

$$[\text{OH}_0^{\cdot}] = 2[\text{O}_i^{\cdot\cdot}] = 2^{-1/3} K_{14}^{1/3} p(\text{H}_2\text{O})^{1/3} \quad (15)$$

We would thus be interested in the values of ΔS_{14} and ΔH_{14} which determine K_{14} and, in turn, the ability to dissolve water in such systems.

We may as a first approximation assume that ΔS_{14} can be of the same order of magnitude as ΔS_{10} (-120 ± 40 J/mol-K) based on the same consumption of water vapour in both reactions, and thus calculate estimates of the defect concentration.

The enthalpy ΔH_{14} will comprise the atomisation of water, the incorporation and ionisation of one oxygen interstitial and two protons, minus twice the bandgap. (One might also develop relations involving the oxygen Frenkel defect pair formation enthalpy, the enthalpy of ordering of vacancies, and ΔH_{10} .) Water uptake in brownmillerite $\text{Ba}_2\text{In}_2\text{O}_5$ (low-temperature, ordered) has been found to yield an enthalpy, interpretable as ΔH_{14} , of -87 kJ/mol.¹⁷⁾ Data on Y_2O_3 have suggested that ΔH_{14} also here has a relatively small, negative value.¹⁸⁾ Negative values for ΔH_{14} makes the concentration of the defect couple in Eq. 15 increase with decreasing temperature.

The concentration of defects increases with $p(\text{H}_2\text{O})^{1/3}$ and at high water vapour pressures we may find ourselves filling all the available interstitial sites. The end product is in principle a material with complete oxygen sublattice (without the structural vacancies) and with a high concentration of disordered protons (as hydroxide ions). Thus, we have changed a "perfect", ordered oxide into an effectively acceptor-doped (or self-doped) oxide with disordered protonic defects.

Along the way, it is likely that the vacant oxygen sites, becoming fewer and fewer, will give up the ordering, so that in the midst of hydration the material undergoes an order-disorder transition.

On the other hand the protons may themselves order at some point; we would then call the new phase an oxyhydroxide. If this happens before the oxygen sublattice is full, we would have a defective oxyhydroxide, having oxygen vacancies and proton vacancies (oxygen ions without protons at the site of a hydroxide group; $\text{O}_{\text{OH}}^{\cdot}$). It may along this line perhaps be viable to search for proton conductors with oxyhydroxides as starting point. In these materials it may then be interesting with acceptor-doping to promote proton interstitials, as well as donor doping to promote proton vacancies.

Incorporation of water into inherently oxygen deficient oxides has been studied for a number of rare earth oxides. Indications of dominance by a situation such as Equation 15 have been reported for nominally undoped Y_2O_3 , but normally these oxides are dominated by protons compensating acceptor-doping.^{15,19)} Protons have recently been studied in pyrochlore oxides, but also here they compensate acceptor dopants.¹⁹⁾ More convincing are reports of protonation/hydration, filling to a large extent

the oxygen deficiencies, in materials such as $\text{Ba}_2\text{YSnO}_{5.5}$ (which becomes a decent proton conductor)³⁾ and $\text{YBa}_2\text{Cu}_3\text{O}_6$.⁴⁾ Hydration of $\text{Ba}_2\text{In}_2\text{O}_5$ at around 300°C has recently been reported to result in an exothermic transition into a material with a composition given as $\text{Ba}_2\text{In}_2\text{O}_5 \cdot 1\text{H}_2\text{O}$.²⁰⁾

We have in this brief appetizer omitted the possibility of association between protons and oxygen interstitials, forming interstitial hydroxide defects. However, indications of such defects have not been reported to the author's knowledge. If these defects are mobile, they may identify themselves in emf measurements with water vapour concentration cells.¹²⁾ Furthermore, we have not discussed metal vacancies for compensating protons, but they of course open up a possibility of hydration of more close-packed structures, as mentioned earlier.

VIII. Concluding remarks

In the search for proton conductors at intermediate temperatures we most often deal with heavily acceptor doped or inherently oxygen deficient oxides. We have given the hydration of these a brief treatment, focusing on the problem of equilibration at low temperatures and of non-ideality in the thermodynamics of defect equilibria.

As the oxides involved take up water they may eventually become oxyhydroxides or hydroxides. However, the path through this process, as a function of cation composition and doping, temperature, $p(\text{H}_2\text{O})$ and $p(\text{O}_2)$, goes through a number of defect situations, order-disorder transitions and other phase transformations. We may have ordering in the oxygen and hydroxide (proton) as well as in the metal cation sublattices. Obviously, experimental as well as theoretical studies are needed to gain ability to navigate through and take advantage of these matters.

The incorporation of water in open structured oxides at moderate temperatures is an interesting and challenging route in our search for proton conductors. It also has an academic interest in that water may have a role in many order-disorder reactions in oxides at moderate temperatures. It is important to notice that in order to clarify this it is necessary to do in situ structural characterisation, with controlled $p(\text{H}_2\text{O})$ and at high temperature, since it will be difficult to hinder the ordering of protons by quenching.

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