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Insights into the Mechanism of Electrochemical Ozone Production via Water Splitting on the Ni and Sb Doped SnO₂ Catalyst

Gregory Gibson,²,³ Ziyun Wangᵇ, Christopher Hardacreᵇ and Wen-Feng Linᵃ

The H₂O splitting mechanism is a very attractive alternative used in electrochemistry for the formation of O₂. The most efficient catalysts employed for this reaction at room temperature are SnO₂-based, in particular the Ni/Sb-SnO₂ catalyst. In order to investigate the H₂O splitting mechanism Density Functional Theory (DFT) was performed on a Ni/Sb-SnO₂ surface with oxygen vacancies. By calculating different SnO₂ facets, the (110) facet was deemed most stable, and further doped with Sb and Ni. On this surface, the H₂O splitting mechanism was modelled paying particular attention to the final two steps, the formation of O₂ and O₃. Previous studies on β-PbO₂ have shown that the final step in the reaction (the formation of O₃) occurs via an Eley-Rideal style interaction where surface O₂ desorbs before attacking surface O to form O₃. It is revealed that for Ni/Sb-SnO₂, although the overall reaction is the same the surface mechanism is different. The formation of O₂ is found to occur through a Langmuir-Hinshelwood mechanism as opposed to Eley-Rideal. In addition to this the relevant adsorption energies (Eₐdₙs), Gibb’s free energy (ΔGₐdₙs) and activation barriers (Eₐₗₚ₃ₙ₇₉) for the final two steps modelled in the gas phase have been shown; providing the basis for a tool to develop new materials with higher current efficiencies.

Introduction

In the last few decades, the treatment of wastewater via Advanced Oxidation Processes (AOP’s) using ozone (O₃) as the principal oxidant has been investigated.¹⁻⁵ O₃ is a strong oxidant, the second strongest after chlorine, with an oxidation potential of 2.07 V. For this reason, it is a viable option as a replacement for chlorine as a water disinfectant. When using O₃ as a disinfectant, the main advantage over chlorine is that few harmful by-products are produced whereas chlorine produces halogenated complexes on reaction. The applications of O₃ are not limited to water treatment as more recent studies outline its application in healthcare,⁶⁻⁷ sterilization,⁸⁻⁹ and chemical synthesis.¹⁰

The traditional method of generating O₃ is via a Cold Corona Discharge Reactor which occurs via the following reaction:

\[
\frac{3}{2} O_2 \rightarrow O_3 \quad \Delta H_{298}^{\text{f}} = 34.1 \text{kcal mol}^{-1} \quad (R1)
\]

In this process, O₂ passes through the reactor, where the O₂ molecules dissociate to O atoms before interacting with further O₂ to form O₃. Although a simple method, the O₃ is formed in the gas phase making it difficult for aqueous applications. The current efficiency (CE) tends to be low with values reported of between 2-7 %,¹¹ depending on the source of O₂.

A more promising method is to produce O₃ via the electrochemical process of water splitting known as Electrochemical Ozone Production (EOP). This is not a new process with previous work being carried out on various different anodes such as Pt,¹³,¹⁴ β-PbO₂,¹⁵⁻¹⁷ BDD,¹⁸,¹⁹ and Ni/Sb-SnO₂,²⁰⁻²² anode materials. The electrochemical splitting of water can occur through either a 4 or 6 step electron process shown in Reactions 2 and 3:

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23 \text{ V} \quad (R2)
\]

\[
3H_2O \rightarrow O_3 + 6H^+ + 6e^- \quad E^0 = 1.51 \text{ V} \quad (R3)
\]

Reactions (2) and (3) show the same H₂O splitting mechanism with different products. The formation of O₂ can be deemed thermodynamically favoured in comparison to O₃ as can be seen from the E° values. Therein lays the major challenge with O₂ production. One way of overcoming the thermodynamics is to develop a system which requires a large overpotential for O₂ formation. This, in turn, will result in a surface with partially inhibited sites for O₂ formation and thus O₃ formation will be promoted. Of the many systems tested, Ni/Sb-SnO₂ reports the best CE values with O₃ yields reported at between 30 % to upwards of 50 % under ambient conditions.²⁰⁻²²

The H₂O mechanism, although postulated by various groups, is still not well understood. Based on previous studies on β-PbO₂,²³ the motivation of this research was to understand how the mechanism for the formation of O₃ proceeds on different catalysts using Density Functional Theory (DFT) calculations.
For Ni/Sb-SnO$_2$, there are two mechanisms postulated based on either an O$_3$H intermediate or via direct O$_3$ formation. In this study the direct O$_3$ pathway is investigated. The Ni/Sb-SnO$_2$ catalyst is not one that has been studied using theoretical approaches before and thus little is known as to its preferred surface geometry. However, studies carried out by Batzill et al. on investigating SnO$_2$ showed that the (110) facet was the most stable and so was used as the initial starting geometry. After further doping with Sb and Ni, the level of surface oxidation was tested and the direct O$_3$ mechanism examined.

Theoretical Methods

Density Functional Theory (DFT)

All DFT calculations were carried out with a periodic slab model using the Vienna Ab-initio simulation programme (VASP). A combination of the Generalised Gradient Approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional was applied. The Projector Augmented Wave (PAW) method was utilized to describe the electron-ion interactions, and the plane wave basis expansion cut-off was set to 500 eV. All adsorption energies were optimised using the force-based conjugate gradient algorithm, whereas the transition states (TS) where located using the constrained minimization technique.

For the modelling of the Ni/Sb-SnO$_2$ surface, a stable SnO$_2$ facet must be generated before doping with Sb and Ni. The most stable SnO$_2$ surface facet was a (110) surface (Figure 2a). This was modelled as a (2 x 2) unit cell (6.37 Å x 6.70 Å) with a surface coverage of between 0.25 and 1 ML. The two-dimensional Brillouin integrations for each surface were sampled using k-points. The surfaces with a (2 x 2) unit cell were sampled using a 3 x 3 x 1 Monkhorst-Pack grid. Ni/Sb-SnO$_2$ was modelled using a periodic 4-layer model with the lower two layers fixed and the upper two layers relaxed. Slab separation was provided normal to the surface by use of a 15 Å vacuum region.

To dope the surface with Sb and Ni a simple yet robust approach was applied. An Sb atom has replaced each of the four surface Sn atoms simultaneously to determine on which site it is most stable. Again geometry optimization is carried out with the lower two layers fixed and the upper two layers relaxed (Figure 1b). To further dope the surface with Ni, the same approach for Sb was repeated. Each of the remaining Sn atoms is replaced with a Ni atom to determine the most stable arrangement across the top surface layer. Geometry optimization calculations are run again with the lower two layers fixed and upper two layers relaxed. Throughout each of these steps the slab separation will remain 15 Å. The Ni/Sb-SnO$_2$ catalyst was similar to the bulk SnO$_2$ (110) and thus the unit cell size was (2 x 2) with the k-point sampling being 3 x 3 x 1 (Figure 1c). All calculations for SnO$_2$, Sb-SnO$_2$ and Ni/Sb-SnO$_2$ were performed as spin-open.

In addition, the presence of surface defects or vacancies was examined. It is common when analysing a surface using experimental techniques that vacancies are detected. For this study an oxygen vacancy on the bridging site was introduced.

Surface Adsorption Calculations

The adsorption energy ($E_{ads}$) of the system was calculated using equation 1:

$$E_{ads} = E_{adsorbate on surface} - E_{surface} - E_{gas}$$ (1)

where $E_{adsorbate on surface}$ is the energy of the adsorbate on the surface, $E_{surface}$ is the energy of the surface and $E_{gas}$ is the energy of the corresponding adsorbing species in the gas phase. Equation 1 shows the more negative the adsorption energy is, the greater the adsorption to the surface. Each term in equation 1 must correspond to the same surface coverage, whether this is a pure metal or metal oxide.

Results and Discussion

Most Stable Surface Facet of SnO$_2$

In agreement with the study reported by Batzill et al., the (110) facet was calculated to be most stable and thus the doping with Sb and Ni was carried out on this facet (Figure 2a). It should be noted that although NiSn$_2$ is not stable under acidic conditions at the surface, this is reflected by the poor lifetimes for these anodes. Possible solutions to the problem of NiSn$_2$ instability is an on-going topic that we are currently studying through the addition of other dopants such as gold, and the results will be published in future papers. Batzill et al. also discussed the possibility of surface vacancies or defects, where it was suggested that the SnO$_2$ was especially susceptible to the presence of an oxygen vacancy (Figure 2b). By creating this vacancy, two cationic Sn sites form which act as Lewis acidic sites and consequently this site tends to be particularly reactive.

Figure 2a shows the most stable arrangement of Ni/Sb-SnO$_2$, with Sb occupying the bridged region and Ni occupying the top site region. The oxygen vacancy was modelled at different oxygen sites (Figure S1) and it was found that the preferred vacancy was the bridged oxygen close to the Sb as shown in Figure 2b. The results for the other sites tested are shown in the supplementary information (Tables S1-S3).
Surface Oxidants

Upon constructing a stable surface model, the degree of surface oxidation must be determined. As the mechanism being investigated involves the splitting of H₂O, surface oxidants from H₂O adsorption and activation can be calculated and a phase diagram constructed (Figure 3). In this model the Ni/Sb-SnO₂ has four possible active sites on the surface, two on the top-site and two on the bridging site (Figure S2). For this reason it is, therefore, possible to have a surface coverage of 0.25, 0.50, 0.75 and 1.00 ML.

Construction of Phase Diagrams

In order to construct a phase diagram the energy of each coverage must be calculated. Each calculation will yield an energy value, the free energy of reaction (ΔG_rxn). This free energy change can be calculated using equation 2:

$$\Delta G_{\text{rxn}} = \Delta E + \text{ZPE} - T\Delta S$$

(2)

where ΔE is the total energy of the system, ZPE is the zero-point energy, and TΔS is the entropy of the system which also includes the temperature. The free energy change of the system accounts for the zero-point energy and the associated entropy. Temperature is also factored into the free energy, along with the pH correction factor. As this experiment is carried out in an acidic electrolyte (0.5 M H₂SO₄), a pH correction factor (59.13 meV) is used which can be calculated using the following equation:

$$\Delta G(pH) = k_B T \ln 10(pH)$$

(3)

where pH is taken as 1, T as 298 K, and Boltzmann’s constant k_B is 1.38 x 10⁻²³ m² kg s⁻² K⁻¹.

After considering this, the standard free energy (ΔG°_rxn) for the formation of each species is the free energy change at 0 V vs SHE. It is the potential independent contribution to the free energy change for each reaction, therefore, U = 0 V. This comes from ΔG_rxn = ΔG°_rxn, where U is the applied potential. This is in essence the second part of constructing a phase diagram; determining the value of U at which ΔG_rxn is equal to zero, so the potential at which a reaction becomes thermodynamically favourable. To calculate U the following equation must be used:

$$\Delta G_{\text{rxn}} = \Delta G^0_{\text{rxn}} - eU$$

(4)

The e represents the charge of an electron (e= -1) giving the equation below:

$$\Delta G_{\text{rxn}} = \Delta G^0_{\text{rxn}} + U$$

(5)

In a phase diagram, a straight line is given for each oxidant at that specific coverage. This equation is in the form of y = mx + c where the gradient is 1. This form of the equations can be attributed to H formation, so if ΔG_rxn is set to zero then U = -ΔG°_rxn.

For OH formation, the gradient should be -1, so U = ΔG°_rxn and for O formation, U = 1/2ΔG°_rxn since two electrons are transferred.

Figure 2 (a) shows the SnO₂ (110) facet doped with Ni and Sb and (b) shows the same surface with an oxygen vacancy. The grey atoms are Sn, the purple is Sb, the blue is Ni and the green circle represents the vacant site.

The main surface oxidants expected are either OH, O or both. The reaction is an oxidation reaction and so corresponds to the loss of electrons and the release of a proton (steps 1 and 2). This proton is capable of surface adsorption (or site hopping) and so is also taken into account.

Figure 3 shows the phase diagram constructed for OH and O present on the Ni/Sb-SnO₂ anode. To interpret a phase diagram, both the lines representing OH and O are observed with the line that intersects the x-axis first considered the dominant surface oxidant. It can be clearly seen that the blue line (OH) intersects the x-axis at a lower potential than the red line (O).
At this crossing point (1.57 V), OH oxidation is dominant, and this is the case at anything above this potential. Surface H⁺ was also tested, but not included in the phase diagram as it was found to occur at a potential of -9.52 V, much lower than the experimental potential of 2.7 V. Considering this, it should be noted that although not included in the phase diagram, surface H⁺ does on occasion occur, with H⁺ hopping across surface sites between O atoms.

Mechanistic studies of O₃ formation on Ni/Sb-SnO₂

Based on previous results³³, the same method was applied to the Ni/Sb-SnO₂ catalyst to determine the correct mechanism for O₃ formation through the splitting of H₂O. How and the thermodynamics and kinetics are affected as a result. The mechanism investigated has four steps involving including the splitting of H₂O to form O₂ and ultimately O₃ through the interaction of O₂ and surface O as illustrated in reactions 4-7:

\[
\begin{align*}
H₂O & \rightarrow OH + H^{+} + e^- \quad (R4) \\
OH & \rightarrow O + H^{+} + e^- \quad (R5) \\
2O & \rightarrow O₂(ads) \rightarrow O₂ \\
O₂ + O & \rightarrow O₃(ads) \rightarrow O₃ \\
\end{align*}
\]

Steps 1 and 2 (reactions 4 + 5) involve the deprotonation to OH and O and should occur with ease after a potential is applied across the surface of the anode. For this reason the main focus of this study is reactions 6 and 7. Step 3 is the formation of O₂ (Figure 4) and step 4 is the formation of O₃ (Figure 5) from the O₂ formed in step 3 interacting with further surface O.

**Step 3 – The formation of O₂**

In step 3 two surface O atoms interact with each other to form O₂ (ads). The most stable site for this interaction was across a surface vacancy. This is better seen in reaction 8:

\[
2O \rightarrow O₂(ads) \rightarrow O₂ \\
\]

Reaction 8 shows that the two surface O atoms interact to form O₂ (ads), before desorbing to the gaseous phase. In order to continue to step 4, O₂ must remain adsorbed on the surface for long enough so that the formation of O₃ can occur. The degree to which the O₂ remains adsorbed will help in determining the overall current efficiency (CE). The longer the O₂ is adsorbed the greater the chance for interaction with surface O.

**Initial state of reaction (IS)**

From the phase diagram (Figure 3) the optimal coverage was determined to be 0.5 ML OH. The IS, two O (ads) atoms that have been formed by the deprotonation of OH. The optimized distance between these two O atoms was 3.38 Å. It is also of note to mention that one of the O atoms is adsorbed on the site with oxygen vacancy (more reactive site)³⁴.

**Transition State of Reaction (TS)**

In going from the IS to TS, an activation barrier (E_{act}) must be overcome. The lower the barrier, the easier the reaction will progress. The difference in energy between the TS and IS, i.e. the activation energy was calculated as 0.34 eV.

\[
E_{act}(O₂) = E_{TS} - E_{IS} = 0.34 \text{ eV} \\
\]

The E_{act} was calculated as 0.34 eV (Figure 4). Thermodynamically this progression should occur with ease. Coupled with the high experimental potential (2.7 V)³⁶, this results further suggests that the reaction will occur easily as the high potential will drive the reaction in the forward direction to completion forming O₃.

**Final State of Reaction (FS)**

The FS of the reaction is the formation of O₂. When both top site and bridging O are in close enough proximity to one another they will interact and O₂(ads) is formed. Experimentally, O₃ formation on Ni/Sb-SnO₂ shows a high CE suggesting a large proportion of the O₂ formed stays adsorbed to the surface, with a small proportion being desorbed. In order to determine the stability of O₂, the enthalpy of reaction (ΔG_{rxn}) between the IS and FS is calculated in equation 7:

\[
ΔG_{rxn} = E_{FS} - E_{IS} = -0.47 \text{ eV} \\
\]

The ΔG was calculated to be -0.47 eV. The FS is more stable than the IS and minimal O₂ decomposition should occur as a result. As well as the ΔG_{rxn}, the E_{ads} (O₂) was calculated to determine the stability of O₂ to the surface:

\[
E_{ads}(O₂) = E(\text{surface O₂}) - E(\text{clean surface}) - E(O₂) = -0.05 \text{ eV} \\
\]

The E_{ads}(O₂) was found to be -0.05 eV, with entropy considerations taken into account at 298 K. This adsorption is weak at -0.05 eV but should be noted that the reaction is run as gas phase whereas experimentally an aqueous electrolyte is employed; hence a H₂O stabilization effect³⁷ will occur, resulting in a more stable adsorption for O₂.

**Step 4 – The formation of O₃**

Step 4, the formation of O₃, occurs by interaction of surface O₂ formed from step 3 with further surface O obtained through the adsorption of OH:

\[
O₂ + O^+ \rightarrow O₃ \\
\]

**The adsorption of OH and subsequent deprotonation to O**

Experimentally, this reaction is carried out in aqueous electrolyte (0.5M H₂SO₄) with a large concentration of OH passing over the surface from the splitting of H₂O seen in reaction 4. As a result the adsorption of OH is calculated first.
After the most stable arrangement has been determined, this OH is deprotonated creating O\(^-\) (ads) needed for step 4. In this deprotonation the Gibbs free energy (\(\Delta G_{\text{rxn}}\)) can be calculated using equation 9:

\[
\Delta G_{\text{rxn}} = G(O) + G(H^+ + e^-) - G(OH) = 1.96 \text{ eV} \quad (9)
\]

Equation 9 shows the Gibbs free energy calculated for the deprotonation of OH being 1.96 eV. This suggests that a minimum potential of 1.96 V is required for the second deprotonation to take place. This is higher than the experimental onset potential, but within the electrochemical window of study, with a potential of 2.7 V applied for Ni/Sb-SnO\(_2\) \(^{36}\).

The reaction of O\(_2\) and O to form O\(_3\)

As found for step 3, step 4 will have an IS, TS and a FS. The IS in this step is O\(_2\) (ads) and O (ads). The TS is O\(_2\) (ads) and O (ads), but this time they are in closer proximity to one another. The FS is the formation of O\(_3\) (ads).

![Energy profile for step 3 of the mechanism](image)

\[E_{\text{act}}(O_3) = E_{TS} - E_{IS} = 0.77 \text{ eV} \quad (10)\]

The \(E_{\text{act}}\) associated with this step was found to be 0.77 eV. Although there is not a maximum value for the \(E_{\text{act}}\), the higher the barrier the slower the reaction. However, the rate of reaction with a lower \(E_{\text{act}}\) (less than 0.77 eV) would be expected to proceed at a faster rate. These calculations have been performed in the gas phase, whereas experimentally the reaction occurs in liquid phase (electrolyte solution). If this step had been run in the presence of H\(_2\)O across the surface, the barrier would be expected to be lower due to the water stabilisation effect\(^ {37}\). The potential for this reaction is 2.7 V. This is quite a high potential and will aid in driving the reaction to completion and should occur with ease.

Final State of Reaction (FS)

The FS of the reaction is the formation of surface O\(_3\) (ads). When surface O\(_2\) and O\(^-\) from the IS are close enough in proximity (less than 1.75 Å), they interact with each other to form surface O\(_3\) (ads). To determine the stability of O\(_3\) (ads), both the \(E_{\text{ads}}\) and \(\Delta G_{\text{ads}}\) are taken into account:

\[\Delta G_{\text{rxn}} = E_{FS} - E_{IS} = -0.05 \text{ eV} \quad (11)\]

The \(\Delta G\) change is small at -0.05 eV, suggesting a slightly more favourable FS (Figure 5). This agrees with what the thermodynamics suggest, that O\(_2\) is thermodynamically more stable than O\(_3\), and so the O\(_3\) will readily decompose back to O\(_2\) and O via the reverse process. This is why a high overpotential is required for O\(_2\) formation. Through this high overpotential, the O\(_2\) sites would be inhibited and thus promote O\(_3\) formation, hence stopping this decomposition As well as the \(\Delta G\), the \(E_{\text{ads}}\) (O\(_3\)) can be calculated to determine the stability of O\(_3\) on the surface:

\[E_{\text{ads}}(O_3) = E(\text{surface } O_3) - E(\text{clean surf.}) = E(O_3) - E(O_2) = -0.15 \text{ eV} \quad (12)\]

An \(E_{\text{ads}}\) (O\(_3\)) of -0.15 eV shows the adsorption energy taking into account entropy, highlighting the stability of O\(_3\) at 298 K. Figure 5 shows the reaction pathway for the formation of O\(_3\) through the interaction of surface O\(_2\) and O. The reaction is found to occur via a Langmuir-Hinshelwood mechanism where two species adsorb to the surface (O\(_2\) and O), the diffuse across the surface interacting with each other before desorbing as a molecule (O\(_3\)). This is interesting as the same mechanism run on β-PbO\(_2\) previously \(^ {23}\), showed that the formation of O\(_3\) preferred to occur via an Eley-Rideal mechanism where the O\(_2\) passes over the surface and interact with an adsorbed species forming O\(_3\) and desorbing. This shows that although the formation of O\(_3\) occurs via the same reaction step, the chemistry of each catalyst is not necessarily the same, and thus this could have an overall effect of the CE of O\(_3\) as a result. For β-PbO\(_2\) the \(E_{\text{ads}}\) (O\(_3\)) was -0.50 eV and for Ni/Sb-SnO\(_2\) it was -0.15 eV with entropy considerations. Although the adsorption is stronger on the β-PbO\(_2\) surface the
CE values are much higher for Ni/Sb-SnO$_2$; this is because the adsorption energy is too strong hence the active sites become blocked easier resulting in a lower CE.

![Figure 5 Energy profile for step 4 of the mechanism, the transformation from O$_2$ and O to O$_3$. The atoms highlighted in green are the interacting atoms in the mechanism. The initial state shows the O$_2$ (ads) and O (ads), the transition state shows both these atoms in a closer proximity to one another, and the final state shows both atoms bonded to form surface O$_3$.](image)

**Catalyst Regeneration**

When choosing a catalyst, it is not only activity and selectivity that are important, but also the lifetime. For a catalyst with a long lifetime, it must be able to regenerate itself. This is an area that needs improvement upon with regards to the EOP mechanism and the Ni/Sb-SnO$_2$ anodes are said to have a moderate lifetime. Examining equation 12, which shows the $E_{\text{ads}}(\text{O}_3)$, it can be seen that the calculated value of adsorption for O$_3$ was -0.15 eV. In order to make a catalyst regenerable this O$_3$ must be easily displaced in order to increase the lifetime, thus making the anode regenerable, freeing up the active sites for EOP. When trying to desorb the O$_3$ using DFT it was found the O$_3$ preferred to re-adsorb onto the surface, hence enhancing its stability. This DFT study does not account for some experimental factors such as potential and flow rate. It is also the case that this study involves the gas phase reaction, whereas experimentally an aqueous acidic electrolyte is employed. One final thing to consider is that this study shows the successful formation of a single O$_3$ molecule on the Ni/Sb-SnO$_2$, whereas when run experimentally there may be multiple O$_2$ and O$_3$ molecules along with other OH and O intermediates on the surface at the one time. As a result there will be electrostatic repulsion between the competing adsorbates thus weakening the adsorption leading to the successful desorption of O$_3$. Taking all of this into account and the literature with regards to high CE values quoted, the catalyst can clearly represent one that is regenerable and future work needs to be done both experimentally and theoretically to discover new methods of increasing the overall lifetime.

**Conclusions**

The H$_2$O splitting mechanism is one well studied experimentally on Ni/Sb-SnO$_2$ for O$_3$ formation. The study of the mechanism using DFT is a first attempt from a theoretical perspective. Using DFT calculations, possible pathways including $E_{\text{act}}$ and $E_{\text{ads}}$ were determined and a suitable reaction mechanism with the formation of O$_3$ occurring via a Langmuir Hinselwood surface reaction was identified. By calculating SnO$_2$ (110) as the most stable facet, further studies into the doping of the top layer (surface) with Sb and Ni were performed with a model catalyst generated. The concept of surface vacancies (oxygen vacancies) was introduced into the model catalyst and the electrochemical ozone production (EOP) mechanism run. Future studies on this system need to be carried out to first model the EOP mechanism with O$_3$H as the intermediate, offering a comparison to the direct O$_3$ formation discussed within this paper. The effect of the oxygen vacancy on the $E_{\text{act}}$ and $E_{\text{ads}}$ needs to be further investigated with comparisons between the reaction energy of a system with an oxygen vacancy and opposed to one without an oxygen vacancy.

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**Notes and references**