Mechanisms and energetics of surface reactions at the copper-water interface

A critical literature review with implications for the debate on corrosion of copper in anoxic water

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Abstract

In order to make a critical analysis of the discussion of corrosion of copper in pure anoxic water it is necessary to understand the chemical reactivity at the copper-water interface. Even though the most fundamental issue, i.e. the nature and existence of a hypothetical product that is thermodynamically stable, is still under debate, it is clear that if anoxic corrosion really exists, it must be initiated through oxidative surface reactions at the copper-water interface.

This report presents a survey of the peer reviewed literature on the reactivity of copper surfaces in water. Reactions discussed involve molecular adsorption of water, dissociation of the OH-bonds in adsorbed water molecules and hydroxyl groups, the disproportionation/synproportionation equilibrium between hydroxyl groups/hydroxide ions, water molecules and atomic oxygen, the surface diffusion of adsorbed species, and the formation of hydrogen gas (molecular hydrogen). Experimental, as well as theoretical (quantum chemical) studies are reviewed. It is concluded that a limited amount of hydrogen gas (H_2) should be formed as the result of dissociative water adsorption at certain copper surfaces.

Quantitative estimates of the amounts of H_2 that could form at the copper-water interface are made. Assuming that the water-cleavage/hydrogen-formation reaction proceeds on an ideal [110] or [100] surface until a hydroxyl monolayer (ML) is reached, the amount of H_2 formed is ~ 2.4 ng cm^{-2} copper surface. Based on the literature cited, this is most likely possible, thermodynamically as well as kinetically. Although not proven, it is not unlikely that the reaction can proceed until an oxide ML is formed, which would give 4.8 ng cm^{-2}. If the formation of an oxide ML is thermodynamically feasible the surface will probably react further, since $Cu_2O(s)$ is known to activate and cleave the water molecule when it adsorbs at the $Cu_2O(s)$ surface. Assuming the formation of a hydroxide ML on top of an oxide ML would give 7.2 ng cm^{-2} copper surface.

Another factor that determines the amount of H_2 that could be formed is the roughness of the copper surface. Mechanically polished copper surfaces has roughly twice the surface area of an ideally planar surface (on which the estimates above are based) and could thus form up to about 14 ng H_2 per cm^2 macroscopic copper surface. This amount is less than six times lower than the largest amount of hydrogen gas detected per surface area in any published experimental study. Possibly, the water-cleavage/hydrogen-formation reaction could proceed even further via diffusion of the adsorbed species into the bulk metal, or through extensive surface reconstruction.

Sammanfattning

För att kritiskt kunna analysera diskussionen om korrosion av koppar i rent syrefritt vatten är det nödvändigt att förstå reaktiviteten i gränsskiktet mellan koppar och vatten. Även om den mest grundläggande frågan, det vill säga förekomsten av en hypotetisk korrosionsprodukt som är termodynamiskt stabil relativt elementärt koppar och vatten, fortfarande debatteras, råder ingen tvekan om att om anoxisk korrosion verkligen existerar, måste den initieras via oxidativa reaktioner i gränsskiktet koppar-vatten.

Denna rapport sammanfattar vetenskaplig litteratur som berör reaktiviteten av kopparytor i vatten. Reaktioner som diskuteras är adsorption av molekylärt vatten, dissociation av adsorberade vattenmolekyler och hydroxylgrupper/hydroxidjoner, jämvikten mellan adsorberade hydroxylgrupper, vattenmolekyler och atomärt syre (disproportionering/synproportionering), diffusion av adsorberade koppar-, syre- och väteatomer, samt bildandet av vätgas (molekylärt väte). Såväl experimentella som teoretiska (kvantmekaniska) studier sammanfattas. En viktig slutsats är att en begränsad mängd av vätgas (H_2) bör kunna bildas i systemet koppar-vatten som ett resultat av dissociativ adsorption av vatten på vissa kopparytor.

Kvantitativa uppskattningar av mängden H_2 som kan bildas vid koppar-vattengränsytan görs. Förutsatt att den vattenklyvande och vätgasbildande reaktionen på en idealisk [110] eller [100] yta fortskrider till dess att ett monolager (ML) av hydroxylgrupper har bildats, blir mängden vätgas ca 2,4 ng cm^{-2} kopparyta. Den citerade litteraturen antyder att detta är sannolikt möjligt, såväl termodynamiskt som kinetiskt. Det är inte osannolikt att reaktionen kan fortskrida tills ett monolager oxid bildas på kopparytan, vilket skulle ge ca 4,8 ng cm^{-2} koppar. Om bildandet av ett oxidskikt är termodynamiskt möjligt är det sannolikt att ytan reagerar ytterligare, eftersom det är känt att $Cu_2O(s)$ adsorberar vatten dissociativt. Antar man att den vattenklyvande och vätgasbildande reaktionen fortgår på en initialt ideal och kemiskt reducerad yta till dess att ett monolager hydroxid bildats ovanpå ett monolager oxid ger detta 7,2 ng cm^{-2} kopparyta.

En annan faktor som avgör hur mycket vätgas som kan bildas enligt resonemanget ovan är kopparytans mikroskopiska area, dvs dess skrovlighet. Den mikroskopiska arean av en mekaniskt polerad kopparyta är ungefär dubbelt så stor som arean för en idealiskt plan yta (för vilken uppskattningarna ovan är baserade). Det betyder alltså att omkring 14 ng H_2 per cm^2 skulle kunna bildas genom att en ren kopparyta reagerar med vatten. Denna mängd vätgas mer än en sjättedel av den största mängden vätgas som detekterats experimentellt och rapporterats. Det är möjligt att reaktionen kan fortgå något längre genom rekonstruktion av ytan, t ex genom att hydroxyl/oxid-skiktet diffunderar genom de yttersta lagren av kopparatomer.

Contents

1   Introduction

The discussion of the long-term stability of the copper canisters used in the KBS-3 method for the deposition of spent nuclear fuel, has raised the question of which chemical mechanisms that operates at copper surfaces in anoxic water (Kärnavfallsrådet 2009). In order to get a better understanding of the reactivity of copper with water, the kinetics and thermodynamics of these reactions must be considered. Although copper is conventionally assumed to be immune towards corrosion by water itself, long-term experiments have been performed that might indicate anoxic corrosion of copper in pure water (Gråsjö et al. 1995, Hultquist et al. 2008, 2009, 2011, Seo et al. 1987, Szakálos et al. 2007, 2008). In order to understand the difficulty with this interpretation of the experiments, it is useful to briefly review the thermodynamics of copper oxidation. Both forms of solid crystalline copper oxides, cuprous oxide (Cu_2O) and cupric oxide (CuO), are thermodynamically stable with respect to elemental/metallic copper under atmospheric oxygen pressure. Using the terminology of thermodynamics *the transformation of copper and oxygen to any of the copper oxides is exergonic, $\Delta G° < 0$ (as well as exothermic, $\Delta H° < 0$)* (CRC 2003).

$$Cu(s) + ¼O_2(g) \rightarrow ½Cu_2O(s) \qquad (\Delta H° = -0.88 \text{ eV}, \Delta G° = -0.76 \text{ eV}) \qquad (1)$$

$$Cu(s) + ½O_2(g) \rightarrow CuO(s) \qquad (\Delta H° = -1.63 \text{ eV}, \Delta G° = -1.35 \text{ eV}) \qquad (2)$$

These thermodynamic data explain the well-known fact that metallic copper corrodes under atmospheric oxygen pressure (i.e. the copper is oxidized until the surface is kinetically passivated by the presence of an oxide layer).

On the contrary all known phases of oxidized copper, containing only oxygen and/or hydrogen, are thermodynamically unstable with respect to metallic copper and water. In other words *the bulk conversion of copper and water to any of the known copper oxides or hydroxides and hydrogen gas is endergonic, $\Delta G° > 0$ (as well as endothermic, $\Delta H° > 0$)* (CRC 2003, Landolt 2007).

$$Cu(s) + ½H_2O(l) \rightarrow ½Cu_2O(s) + ½H_2(g) \qquad (\Delta H° = 0.61 \text{ eV}, \Delta G° = 0.47 \text{ eV}) \qquad (3)$$

$$Cu(s) + H_2O(l) \rightarrow CuO(s) + H_2(g) \qquad (\Delta H° = 1.34 \text{ eV}, \Delta G° = 1.11 \text{ eV}) \qquad (4)$$

$$Cu(s) + 2H_2O(l) \rightarrow Cu(OH)_2(s) + H_2(g) \qquad (\Delta H° = 1.27 \text{ eV}, \Delta G° = 1.05 \text{ eV}) \qquad (5)$$

It should be noted that even for the least endergonic process (**3**), the value of the Gibbs free energy, $\Delta G° = 0.47$ eV, corresponds to an equilibrium constant of 10^{-8}, meaning that essentially no cuprous oxide is formed under standard conditions (atmospheric pressure and room temperature).

As a consequence of the release of hydrogen molecules to the gas-phase the entropy effect ($-T\Delta S°$) is negative on the Gibbs free energy (**3**, **4**, **5**). Since the entropy effect depends linearly on the temperature, $\Delta G°$ will eventually become negative when the temperature is increased. The entropy effect for the formation of cuprous oxide (**3**) is $-T\Delta S° = -0.14$ eV, meaning that $\Delta G = 0$ when T = 1,300 K. Since such high temperatures are irrelevant for the spent nuclear fuel repository it can safely be concluded that the initially elevated temperature will not alter the thermodynamic stability of the copper canisters with respect to water (King et al. 2001).

Despite the thermodynamics of **3**, **4**, and **5**, it is possible that an initial sub-equilibrium concentration of hydrogen gas could drive a corrosive process (Le Chatelier's principle). The significance of this mechanism has been discussed by Hultquist and Szakálos, who claims that sub-equilibrium partial hydrogen pressures could appear and become critical for the long-term stability of the copper canisters used in the KBS-3 method for nuclear waste storage (Hultquist et al. 2008, 2009, Szakálos et al. 2007, 2008).

The equilibrium hydrogen pressure per mol $Cu_2O(s)$ (~ 10^{-16} bar) is far below the partial hydrogen pressure of the earth's atmosphere ($5.5 \cdot 10^{-7}$ bar), which efficiently suppresses reaction **3**. Since these are well established thermodynamic data, Hultquist and Szakálos draws the conclusion that the corrosion product of their long-term experiment is an hitherto unknown phase of oxidized copper for which the equilibrium hydrogen pressure is 2,000 times the partial pressure of hydrogen in the atmosphere (~ 10^{-3} bar), which makes the unknown corrosion product stable with respect to water and metallic copper (Szakálos et al. 2007).

In a closed system, equilibrium levels of hydrogen would eventually be reached, even if the initial hydrogen pressure would be below equilibrium with respect to the copper/water oxidation reaction (**3**). The reasons for sub-equilibrium pressure to be sustained could be either: 1) a fast transport of hydrogen gas from the reacting site (i.e. an open system) or 2) a chemical process that consumes hydrogen.

Due to the strong endergonicity ($\Delta G° \gg 0$) of the anoxic oxidations **3**, **4**, and **5**, and the very low corresponding equilibrium hydrogen pressures, none of these transformations are expected to be of importance under atmospheric hydrogen pressure.

Because of the unusual anoxic conditions and long time-scale needed to study hydrogen evolution in a system of copper and water, there are few scientific reports except those of Hultquist and Szakálos (Eriksen et al. 1988, 1989, Simpson and Schenk 1987). As far as the authors are aware there are no peer-reviewed reports at all dealing with the mechanisms of such process. Some insight can, however, be gained from studies of other aspects of the reactivity of copper surfaces, such as the copper catalyzed water-gas shift reaction, wetting of copper, oxygenation-, and hydrogenation of copper surfaces (Ammon et al. 2003, Andersson et al. 2005, 2008, Campbell and Daube 1987, Carrasco et al. 2009, Chen et al. 2010, Díaz et al. 2009, Fajín et al. 2009, Gokhale et al. 2008, Jiang et al. 2004, Kojima et al. 1980, Liem et al. 1998, Liu and Rodriguez 2007, Nakamura et al. 1990, Nakashima et al. 1988, Ren and Meng 2006, 2008, Siegbahn et al. 1989, Tang and Chen 2007a and b, Wang et al. 2003, 2006, Wang and Nakamura 2010). It is rather obvious that any corroding process must be initiated by surface reactions. The importance of surface reactivity in order to better understand the reactivity of copper with water has been emphasized by Chuah (Kärnavfallsrådet 2009, p 23).

Before reviewing the literature on these topics, it is appropriate to briefly discuss the mechanisms that, hypothetically, would initiate corrosion of copper in anoxic water (Figure 1-1). It is reasonable to start the discussion from S1 (State 1), in which the copper surface is covered with adsorbed water molecules and some amount of pre-adsorbed oxygen. Atomic oxygen will be present even on a polished/reduced copper surface, since a significant amount of molecular oxygen/air will be buried with the copper canisters, and since the oxidation of metallic copper by molecular oxygen is both rapid and spontaneous (reactions 1 and 2) (CRC 2003).

In Figure 1-1, a significant part of the adsorbed water molecules and oxygen atoms have been omitted in order to make the illustration more clear. In the real situation the copper surface should be covered with water molecules and pre-adsorbed oxygen atoms. The relative amount of these species varies between different crystallographic planes, but surface experiments have shown that at normal temperatures and oxygen pressure it is difficult to achieve coverage above 2/3 of an oxygen atom monolayer (ML) on Cu[110] (Gruzalski et al. 1984a, b, Liem et al. 1998). Similarly, it has been shown that a Cu[100] surface becomes unstable and reconstructs when the oxygen coverage is higher than 1/3 ML (Fujita et al. 1996). It is thus reasonable to assume that even on an oxidized copper surface there is a significant surface area on which copper atoms are exposed and able to adsorb water molecules. A more thorough discussion of oxidized copper surfaces can be found in Korzhavyi and Johansson (2011).

Even if the initial oxygen coverage would be very low (as can be achieved experimentally by mechanical polishing and chemical reduction (Clendening and Campbell 1989)), the oxide layer could grow also in anoxic water due to the cleavage of water molecules. By cleaving the water molecules in **S1**, initially into hydroxyl groups and hydrogen atoms (**S2**), subsequently into adsorbed oxygen and hydrogen atoms (**S4**), the oxygen coverage would increase and hydrogen gas could evolve by the recombination of adsorbed hydrogen atoms on the copper surface. The mechanism and kinetics of water cleavage and hydrogen gas formation will be thoroughly discussed herein. Increased oxygen coverage could also be reached by initial symproportionation of adsorbed oxygen atoms and water molecules into hydroxyl groups (**S9**), which could be further cleaved into adsorbed oxygen and hydrogen atoms.

Another mechanism that could be involved in the equilibration of adsorbed surface species is the reaction of molecular hydrogen with atomically adsorbed oxygen and hydroxyl groups, increasing the levels of hydroxyl groups and water, respectively. This mechanism has been pointed out by Hultquist and Szakálos as a possible explanation of the initial 150 h delay in the detection of hydrogen gas in a long-term study of copper in anoxic water (Szakálos et al. 2007).

Via these mechanisms the surface would eventually reach an equilibrium state of adsorbed oxygen atoms, hydrogen atoms, hydroxyl groups and intact water molecules. The existance and importance of such surface oxidized state(s) has been pointed out by Shoesmith (Kärnavfallsrådet 2009, p 43), as well as in peer-reviewed papers (Bojinov et al. 2010, Forster et al. 2011, Härtinger et al. 1995, Maurice et al. 2000, Protopopoff and Marcus 2005).

In Figure 1-1, **S6** shows a spot on the surface at which the oxygen coverage is high. Where the surface density of atomic oxygen is high, it is likely that the surface will be less reactive with respect to water splitting and further oxidation. Activation of the oxygen-saturated surface would then require the exposure of copper atoms on the surface again. This could be the result of the diffusion of oxygen atoms into the copper metal (**S7** and **S8**), or, essentially with the same result, diffusion of copper atoms from the bulk through the oxide layer on the surface.

Another mechanism that could lead to the exposure of copper atoms on an oxidized surface is the dissolution of either copper hydroxide (**S11**) or copper oxide clusters or nano-particles from the surface. In Figure 1-1, **S11** shows the hydroxylated copper surface after the dissolution of $Cu(I)OH(aq)$ from the surface. Although the dissolution of both $Cu(I)OH(aq)$ and $Cu(II)(OH)_2(aq)$ from metallic copper in water are strongly endergonic (Beverskog and Puigdomenech 1997), there is a possibility that semi-stable clusters/nano-particles of unknown stoichiometry ($Cu_XO_YH_Z$) could be formed through the intermediate formation of $Cu(I)OH(aq)$ or $Cu(II)(OH)_2(aq)$. Something similar have been suggested by Shoesmith (Kärnavfallsrådet 2009, p 47).
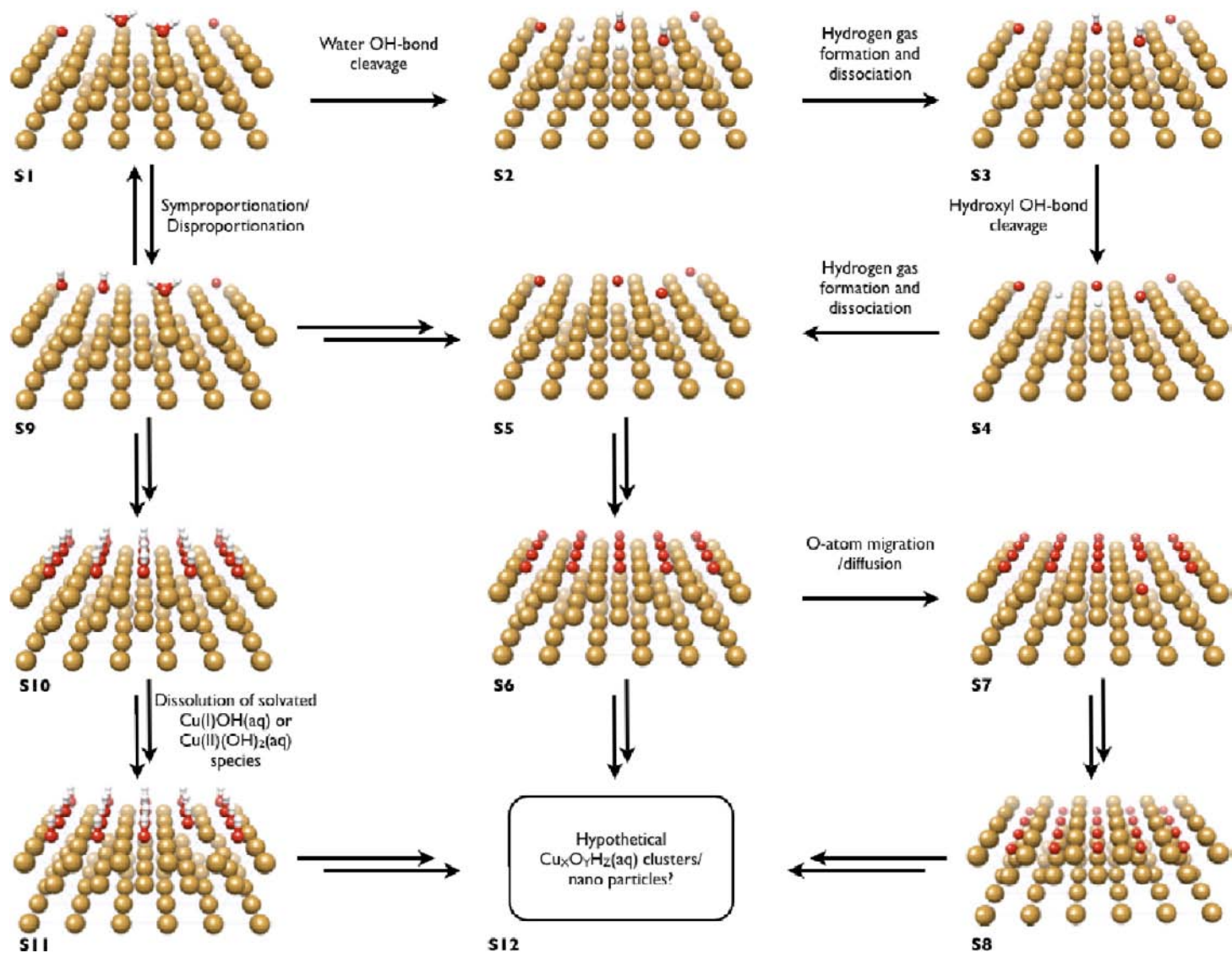
Figure 1-1. *Hypothetical reaction landscape at the copper-water interface.*

2 Water adsorption and the structure of water on copper surfaces

A number of studies have been published dealing with the thermodynamics of water adsorption and the structure of wetted copper surfaces. Although it has been generally accepted that water forms cyclic hexamers when adsorbed at metal surfaces (Bange et al. 1984, Lackey et al. 1989, Mariani and Horn 1983, Tang and Chen 2007a, Yamada et al. 2006), recent research reveals that the arrangement of water molecules depends on the metal surface structure (Henderson 2002, Menzel 2002).

On the close-packed [111] surfaces of copper (and silver), the formation of cyclic water hexamers has been confirmed using low-temperature scanning tunneling microscopy (LT-STM) and density functional theory (DFT) calculations (Michaelides and Morgenstern 2007). On the sparsely packed [110] surface the situation is somehow more complex. Scanning tunneling microscopy (STM) and DFT calculations predict the formation of cyclic hexamers (Kumagai et al. 2011). However, another study combining STM with reflection adsorption infrared spectroscopy (RAIRS) and DFT calculations have shown that the water molecules are arranged in cyclic pentagons when adsorbed on the [110] surface of copper (Carrasco et al. 2009). Nevertheless, a conflicting study using STM and low energy electron diffraction (LEED), has revealed a structure of alternating water molecules and hydroxyl-groups forming a distorted hexagonal network (Forster et al. 2011). It should be noted that the cited studies all concern the adsorption of water at ideal- or mono-crystalline copper surfaces. Most likely, the structure of adsorbed water is less regular on a rough poly-crystalline surface, especially at the grain boundaries.

Experimental methods and DFT calculations show in agreement that the adsorption energy of mono-meric molecular water on copper depends on the crystallographic plane and increases in the order Cu[111] < Cu[100] < Cu[110] (Andersson et al. 2005, Carrasco et al. 2009, Mariani and Horn 1983, Michaelides and Morgenstern 2007, Tang and Chen 2007a, Zapol et al. 2001). The major difference between these three crystallographic planes is the surface atom-density, which is highest for [111] and lowest for [110]. In other words, in surfaces with lower atom-density, the copper atoms have higher affinity for water molecules. In agreement with this correlation, DFT calculations have shown that certain edges of the stepped copper surfaces [210] and [211] adsorb water even stronger than the sparse [110] surface (Tang and Chen 2007a). Thus, there seems to be a clear correlation between the copper surface atom density and the adsorption energy of water; a lower surface atom density in the copper surface (or a longer average Cu-Cu bond distance) makes the adsorption of water stronger (i.e. more exothermic) (Tang and Chen 2007a).

It has also been found that water adsorption on some metal surfaces is dissociative, i.e. that a dominant fraction of the adsorbed water molecules are cleaved and form adsorbed hydroxyl groups and atomic hydrogen on the surface (Feibelman 2002, Menzel 2002). This is known experimentally to be the case for Cu[110], although the temperature at which dissociation occurs has been debated (Ammon et al. 2003, Andersson et al. 2005, 2008), and conflicting results have been reported (Forster et al. 2011, Uy et al. 1983). Furthermore, there are computational predictions that the same applies for Cu[100] at high water coverage (condensed phase) (Wang and Nakamura 2010), which will be discussed further in the next section.

3   Water-gas shift reaction

Some insight into the reactivity at the copper-water interface can be gained from studies of the copper-catalyzed water-gas shift (WGS) reaction,

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

which is used industrially to enhance the yield of hydrogen from the steam-reforming of natural gas/methane.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{7}$$

A significant amount of the hydrogen produced by reactions **6** and **7** is used for the production of ammonia in the Haber-Bosch process. The industrial significance of the WGS reaction (**6**) and the costs associated with it has motivated a large number of studies of the process. Together with the Haber-Bosch process, the WGS reaction is one of the most intensively studied heterogeneous processes. Historically, a wide variety of transition metal based heterogeneous catalysts, including pure transition metals, metal oxides, Cu/Zn/Al-alloys, and magnetite (Fe_3O_4), have been used. Metallic copper was recognized at an early stage of development of the WGS reaction (Grenoble and Estadt 1981, Ladebeck and Wagner 2003) and consequently several reports have been published on the mechanism and kinetics of the copper-catalyzed water-cleavage and WGS reaction (Ammon et al. 2003, Andersson et al. 2005, 2008, Belonoshko and Rosengren 2010, Campbell and Daube 1987, Chen et al. 2010, Fajín et al. 2009, Gokhale et al. 2008, Jiang et al. 2004, Liu and Rodriguez 2007, Nakamura et al. 1990, Nakashima et al. 1988, Ren and Meng 2006, 2008, Rodriguez et al. 2009, Spitzer and Lüth 1982, Spitzer et al. 1985, Tang and Chen 2007a and b, Tang et al. 2009, Wang et al. 2003, 2006, Wang and Nakamura 2010).

In the late eighties, Campbell and Nakamura investigated the mechanism and kinetics of the copper-catalyzed WGS reaction using ultra-high vacuum technology and atomically clean polished single-crystal copper surfaces at high temperatures (600 K) (Campbell and Daube 1987, Nakamura et al. 1990). *Atomically clean surface*, here means that the surfaces were polished under vacuum (base pressure $< 1.3 \cdot 10^{-13}$ bar) and that subsequent analysis of the heteroatom coverage using Auger electron spectroscopy (AES) showed that there were less than two sulfur atoms per 100 copper atoms ($\Theta_S < 0.02$) (Clendening and Campbell 1989, Nakamura et al. 1990). The amount of carbon and oxygen on the surface was even lower and could not be distinguished from the background levels/noise. The purity of the surfaces used in these experiments made it possible to isolate the catalytic effect of the copper surface from effects of adsorbed heteroatoms.

An important observation made by Campbell and Nakamura was that the WGS reaction is highly sensitive to the surface structure of the catalyst. The (overall) WGS reaction is ten times faster when it is catalyzed by the sparsely packed Cu[110] surface ($1.09 \cdot 10^{15}$ atoms cm^{-2}), than on the more densely packed Cu[111] surface ($1.77 \cdot 10^{15}$ atoms cm^{-2}). Thus, on a rough poly-crystalline copper surface the most active site should not be the Cu[111] plane but rather the Cu[110] plane or some even more sparsely packed-, stepped-, or non-ideal surface structure. The higher activity of the Cu[110] plane is most likely an effect of the longer Cu-Cu bonds in the low-density Cu[110] surface, which makes the copper valence electrons more available for substrate activation and copper-hetero-atom bond-formation.

Another very important result obtained by Campbell and Nakamura was an experimentally determined potential energy surface (PES) for the Cu[110]-catalyzed WGS reaction (Figure 3-1) (Nakamura et al. 1990). The PES was determined from kinetic data of each reaction step to an accuracy of ± 0.13 eV. The proposed reaction mechanism for the WGS reaction involves some of the transformations

pictured in Figure 1-1, which are likely to occur at the copper-water interface, e.g. water splitting, disproportionation reactions, and hydrogen formation. These steps will in the following discussion be referred to as numbered below:

$$H_2O_{ad} \rightarrow OH_{ad} + H_{ad} \tag{8}$$

$$OH_{ad} \rightarrow O_{ad} + H_{ad} \tag{9}$$

$$2OH_{ad} \rightarrow O_{ad} + H_2O_{ad} \tag{10}$$

$$2H_{ad} \rightarrow H_2(g) \tag{11}$$

The molecular adsorption of water on the [110] surface of copper is exothermic with $\Delta H° = -0.43$ eV, meaning that water is weakly bound to the copper surface even at the high temperature (600 K) employed in the experiment (Figure 3-1). The activation energy of the forward reaction ($E_{a,f}$), i.e. the dissociation of the OH bond in the adsorbed water molecule (**8**) is 0.91 eV, which corresponds to a rate constant $k > 10^5$ s^{-1} at 600 K, i.e. a rapid process. At room temperature (298 K), the reaction becomes much slower, $k \sim 10^{-3}$ s^{-1}, but it is still highly significant on longer time-scales. Reaction **8** is slightly exothermic with $\Delta H° = -0.05$ eV, which regarding the standard deviation of ± 0.13 eV, means that a surface hydride-hydroxide state is in a thermo-neutral equilibrium with the initial state of molecularly adsorbed water.

The kinetics of the dissociation of the adsorbed hydroxyl group into adsorbed oxygen- and hydrogen atoms (**9**), is somehow unclear in the work by Campbell and Nakamura (not shown in Figure 3-1) (Nakamura et al. 1990). However, there are other experiments suggesting that the activation energy for this step must be lower than the activation energy for the formation of molecular hydrogen (**11**) (Nakashima et al. 1988). Although the kinetics of step **9** is unknown, it is clear that **9** is endothermic with $\Delta H° = +0.39$ eV on the [110] surface of copper. As pointed out by Nakamura, it is possible that the intermediate region of the PES is more complex than reaction **9**, due to the disproportionation of adsorbed hydroxyl-groups into water and adsorbed oxygen atoms (**10**). The PES in Figure 3-1 reveals that the disproportionation **10** is endothermic with $\Delta H° = +0.45$ eV, and has an activation energy ($E_{a,f}$) of 0.56 eV on Cu[110]. The formation and desorption of hydrogen gas (**11**) on the [110] surface has an activation energy ($E_{a,f}$) of only 0.56 eV but is endothermic with $\Delta H° = +0.15$ eV. The thermodynamics (and kinetics) of hydrogen formation and its implications is further discussed in Section 7.

Deeper insight into the mechanisms and structure-sensitivity at the copper-water interface, can be obtained from computational/theoretical studies of the WGS reaction using various types of density functional theory (DFT) and transition state theory (TST) (Belonoshko and Rosengren 2010, Chen et al. 2010, Fajín et al. 2009, Gokhale et al. 2008, Jiang et al. 2004, Liu and Rodriguez 2007, Ren and Meng 2006, 2008, Rodriguez et al. 2009, Tang and Chen 2007, Tang et al. 2009, Wang et al. 2003, 2006, Wang and Nakamura 2010). Although there are quantitative differences between the experimental (Figure 3-1) and theoretical (Figure 3-2) potential energy surfaces (PES) for the WGS reaction on the [110] surface of copper, the qualitative agreement of the two allows several conclusions to be drawn also from theoretical investigations of the reactivity at the copper-water interface on crystallographic planes for which none or limited experimental data exist. The most striking agreement between theory and experiment is the higher activity of Cu[110] compared to Cu[111]. The activation energy for the water cleaving reaction (**8**) on the [110] surface ($E_{a,f} = 1.05$ eV) is 0.23 eV lower than on the [111] surface ($E_{a,f} = 1.28$ eV). These results are in good agreement with experimental data for both the absolute and relative activation energies for water cleavage on the two crystallographic planes (see Section 4).
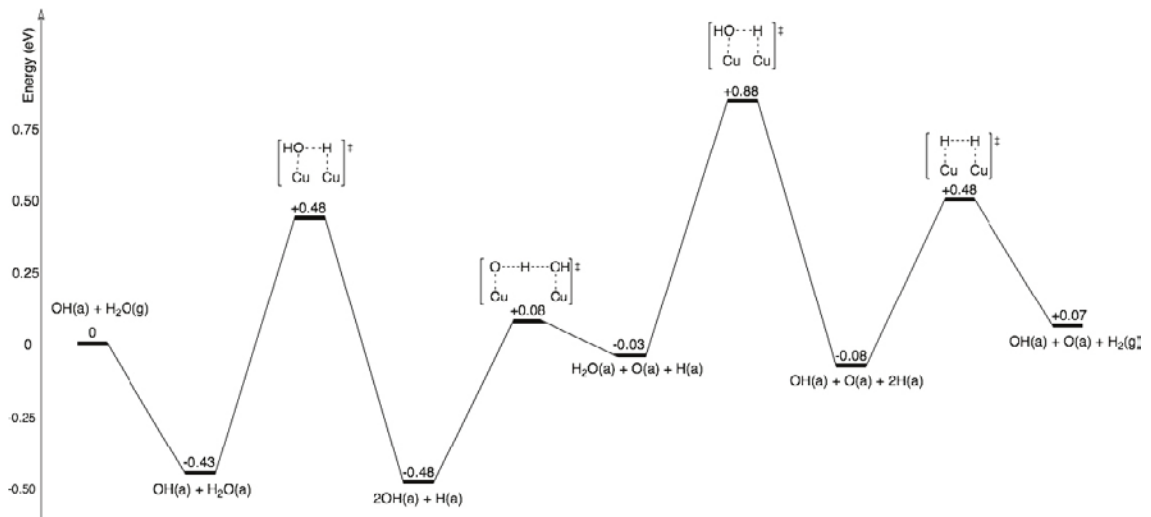
Figure 3-1. *PES for the water-splitting steps and hydrogen formation in the WGS reaction on Cu[110] (eV). The PES was compiled from kinetic data in Nakamura et al. (1990). The CO oxidation of the WGS reaction has been omitted since it is irrelevant for the topic of this report. The notation (a) indicates a surface adsorbed species, while (g) denotes a gaseous species.*
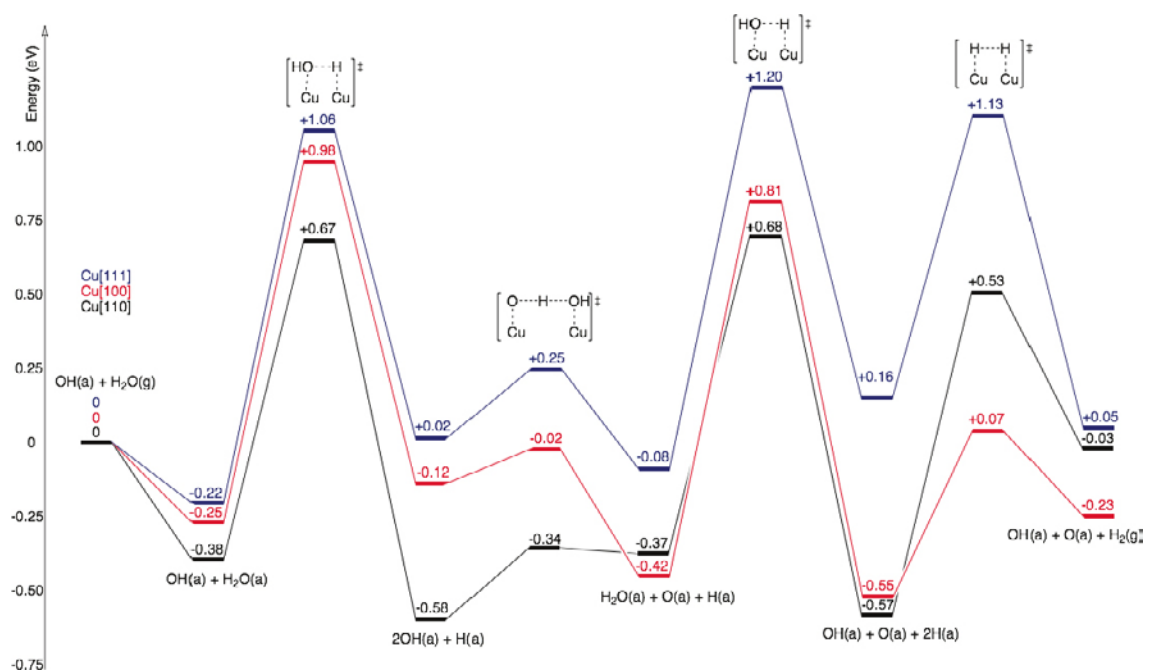

Figure 3-2. *PES for the water-splitting steps and hydrogen formation in the WGS reaction on Cu[111], Cu[110] and Cu[100] (eV). The PES was compiled from computational (DFT) data in Wang and Nakamura (2010). The CO oxidation of the WGS reaction has been omitted since it is irrelevant for the topic of this report.*

4 Water fission

Table 4-1 summarizes experimental and computational data for the water-cleavage reaction on copper at low water coverage or in the gas-phase. We have chosen to include all papers found in the peer-reviewed literature (Ammon et al. 2003, Andersson et al. 2005, 2008, Belonoshko and Rosengren 2010, Campbell and Daube 1987, Chen et al. 2010, Fajín et al. 2009, Gel'man et al. 1986, Gokhale et al. 2008, Jiang et al. 2004, Liu and Rodriguez 2007, Nakamura et al. 1990, Nakashima et al. 1988, Ren and Meng 2006, 2008, Rodriguez et al. 2009, Spitzer and Lüth 1982, Spitzer et al. 1985, Tang and Chen 2007a and b, Tang et al. 2009, Taylor et al. 2008, Wang et al. 2003, 2006, Wang and Nakamura 2010), although it is obvious that some values suffer from limitations of either the models or methods applied (Jiang et al. 2004, Wang et al. 2003).

The experimental activation energy for water cleavage (**8**) catalyzed by the densely packed mono-crystalline [111] surface of copper is approximately 1.20 eV, while DFT calculations have given values between 0.92 eV and 1.28 eV. At the sparsely packed [110] copper surface, the experimental activation energy is 0.91 eV, while DFT values ranges from 0.62 eV to 1.05 eV. For the [100] crystallo-graphic plane no experimental value has been found, but DFT results ranges from 1.03 eV to 1.23 eV.

Concerning the thermodynamics of water cleavage (**8**) the results of all studies listed in Table 4-1 are in qualitative agreement with Wang's computationally determined PES (Figure 3-2). The dissociation of water (**8**) is exothermic at the [110] surface, while it seems to be endothermic at Cu[100] and Cu[111]. DFT calculations on Cu[111] have given quite different results indicating that the results depends on either the methods applied (e.g. density functional) or on how the reactions are modeled (there could be more than one mode of adsorption of the reacting species, as well as in the transition state).

All the values summarized in Table 4-1 are gas-phase enthalpies, while DFT calculations conducted by ourselves show that dielectric effects of the solvent (water) and entropy effects ($-T\Delta S$) both favor dissociation of the water molecule and makes the reaction energy of **8** slightly more negative at the [110] surface ($\Delta G° = -0.09$ eV, $\Delta H° = -0.04$ eV). These values have not been published elsewhere but the methodology used is described in Johansson et al. (2011).

Chen et al. investigated the water cleaving reaction (**8**) on Cu_7- and Cu_{10}-clusters, since it has been shown experimentally that nanoparticles form on the copper catalyst surface under WGS reaction conditions (Chen et al. 2010). These clusters might be regarded as representatives for a non-ideal surface structure. The activation energy for the forward reaction ($E_{a,f}$) was 1.09 eV when a Cu_7-cluster was used, and 0.95 eV for a Cu_{10}-cluster. This is similar to what has been found for the sparsely packed [110] surface. An interesting result is that the water cleaving reaction is more exothermic on the copper clusters than what DFT calculations predict for the mono-crystalline surfaces (Table 4-1). This indicates that the thermodynamic driving force for water fission is larger on a non-ideal surface than on an ideal mono-crystalline surface. Similar conclusions have been postulated in Taylor et al. (2008) and Belonoshko and Rosengren (2010).

A few experimental studies have been made on the copper-water reactivity under solution-like conditions (high water coverage) at low temperatures in order to better understand the reactivity in condensed phase (Ammon et al. 2003, Andersson et al. 2005, 2008). Ammon and coworkers used high resolution X-ray photo electron spectroscopy (HRXPS) and low energy electron diffraction (LEED) to study a [110] copper surface covered by 2.9 ML of water and observed water dissociation already at 95 K. Similar observations were made by Andersson et al. who report that dissociation starts at 150 K. These observations of water dissociation at low temperatures makes it possible to conclude that water cleavage (**8**) in condensed phase is a spontaneous (exergonic, $\Delta G° < 0$) reaction at room temperature (298 K). The fact that water dissociation is spontaneous on Cu[110] in the gas-phase was shown by Spitzer already in 1982 (Spitzer and Lüth 1982).

Andersson et al. measured the rate-constant for **8** on Cu[110] in solution, which according to the Eyring equation (see Appendix A) correspond to an activation energy of only 0.53 eV (Table 4-2). This should be compared to the significantly higher activation energy of 0.91 eV, at the [110] surface in gas-phase, which was determined by Nakamura (Figure 3-1, Table 4-1). It can thus be said that water dissociation on the [110] copper surface is autocatalytic and significantly more rapid than in the gas-phase. Andersson and coworkers proposed an explanation for this autocatalysis of water dissociation based on the Brønsted-Evans-Polanyi relation. Their idea was that the hydroxyl group and hydrogen atom in the reaction product are stabilized by the water solvent through hydrogen bonding and that the stabilization is present already in the transition state of **8**. This explanation was later elegantly confirmed by Ren et al. who used periodic DFT calculations to model a [110] copper surface covered by a water monolayer (Ren and Meng 2008). Ren's DFT study did not only reproduce both the gas-phase and condensed phase activation energies, but also provided detailed insight into the structure and mechanism of the autocatalysis of water dissociation. A value for the reaction energy of **8** in solution, $\Delta H° = -0.34$ eV (Table 4-2) was also reported by Ren (Ren and Meng 2008). This is slightly more exothermic than predicted by DFT calculations in gas-phase (Table 4-1) (Tang and Chen 2007b, Wang and Nakamura 2010).

In the study by Chen and coworkers referred to above, comparison was made with a Cu_7-cluster saturated with water molecules (Chen et al. 2010). Similar to Ren they found that the adsorbed water layer had a dramatic effect on the reaction, reducing the activation energy to 0.47 eV (1.09 eV in gas-phase) and enhancing the exothermicity from –0.5 eV at the bare cluster (gas-phase) to –1.0 eV for the water-covered cluster (Table 4-2).

So far, only partial fission of the water molecule into an adsorbed hydroxyl group and a hydrogen atom has been discussed, but in principle also the OH-bond in the hydroxyl group could be cleaved at the copper surface (**9**). Experimental surface studies of the WGS reaction at copper [110] (Nakamura et al. 1990), as well as DFT calculations at the mono-crystalline copper surfaces [111], [100], and [110] (Gokhale et al. 2008, Tang et al. 2009, Wang and Nakamura 2010) have shown that the complete fission of the water molecule, i.e. by dissociation of the hydroxyl group resulting from reaction **8**, is moderately to strongly endergonic (0.43–0.86 eV).

Nevertheless, a recent experimental study of water adsorption on copper nano-particles of ~ 3 nm in diameter, reports on the partial conversion of the copper nano-particles to Cu_2O-particles, suggesting that also hydroxyl groups are cleaved at the particle surface (Chen et al. 2011). These findings suggest that although not thermodynamically possible at perfect crystalline surfaces, the cleavage of hydroxyl groups could be feasible at rough (non-ideal) copper surfaces.

Table 4-1. Experimental- and computational energetics (eV) for the water-splitting reaction (8) in gas-phase or at low surface coverage.

Surface	$E_{a,f}$[a]	$E_{a,r}$[a]	$\Delta H°$	Method[b]	Reference
Cu[111]	1.17	–	–	Exp.	Campbell and Daube 1987
Cu[111]	0.92–1.25	0.68–0.75	0.24–0.50	DFT PBC	Fajín et al. 2009
Cu[111]	1.15	0.98	0.17	DFT PBC	Gokhale et al. 2008
Cu[111]	1.16	1.16	0.00	DFT PBC	Tang et al. 2009
Cu[111]	1.28	1.04	0.24	DFT PBC	Wang and Nakamura 2010
Cu[111]	–	–	–0.07	DFT PBC	Taylor et al. 2008
Cu[111]	1.18	–	–	DFT	Wang et al. 2003
Cu[110]	0.91	0.96	–0.05	Exp.	Nakamura et al. 1990
Cu[110]	0.62	0.74	–0.12	DFT PBC	Tang and Chen 2007b
Cu[110]	1.05	1.25	–0.20	DFT PBC	Wang and Nakamura 2010
Cu[110]	0.95	–	–	DFT	Wang et al. 2003
Cu[100]	1.13	0.74	0.39	DFT PBC	Liu and Rodriguez 2007
Cu[100]	1.23	1.10	0.13	DFT PBC	Wang and Naklamura 2010
Cu[100]	1.03	–	–	DFT	Wang et al. 2003
Cu_7-cluster	1.09	1.59	–0.50	DFT	Chen et al. 2010
Cu_{10}-cluster	0.95	1.45	–0.50	DFT	Chen et al. 2010
Cu_{29}-cluster	0.93	1.14	–0.21	DFT	Liu and Rodriguez 2007
Cu_{38}-cluster	–	–	–0.30	DFT	Taylor et al. 2008

[a] $E_{a,f}$ denotes the activation energy of the forward reaction, while $E_{a,r}$ is the activation energy of the reversed reaction.
[b] Exp. means experimental data. The acronyms DFT and PBC denote density functional theory and periodic boundary conditions, respectively.

Table 4-2. Experimental- and computational condensed phase data (eV) for the water-splitting reaction.

Surface	$E_{a,f}$[a]	$E_{a,r}$[a]	ΔE	Method[b]	Reference
Cu[110]	–	–	$\Delta G° < 0$	Exp.	Ammon et al. 2003
Cu[110]	0.53	–	$\Delta G° < 0$	Exp.	Andersson et al. 2005
Cu[110]	0.57	0.91	$\Delta H° = –0.34$	DFT PBC	Ren and Meng 2008
Cu_7-cluster	0.47	1.47	–1.0	DFT	Chen et al. 2010

[a] $E_{a,f}$ denotes the activation energy of the forward reaction, while $E_{a,r}$ is the activation energy of the reversed reaction.
[b] Exp. means experimental data. The acronyms DFT and PBC denote density functional theory and periodic boundary conditions, respectively.

5 Disproportionation of adsorbed hydroxyl-groups and reaction of water with pre-adsorbed oxygen atoms

The PES in Figure 3-2 reveals that the thermodynamics of disproportionation of hydroxyl groups into adsorbed atomic oxygen and water (**10**), differs qualitatively between the crystallographic planes considered. While reaction **10** is moderately exothermic on the [100] surface (–0.30 eV), it is only weakly exothermic (–0.10 eV) on Cu[111], and endothermic (0.21 eV) on Cu[110] (Wang and Nakamura 2010). There is thus no obvious correlation between the surface atom-density and the energetics of disproportionation (**10**), as was the case for water splitting (**8**).

The computed energetics for reaction **10** on the [110] surface agrees qualitatively with experimental data (compare PES in Figure 3-1 and 3-2) (Nakamura et al. 1990, Spitzer and Lüth 1982), which makes it reasonable to believe in the relative reaction/activation energies predicted by DFT calculations for the other crystallographic planes, for which no experimental data exists. This means that although water fission (**8**) itself is an endothermic process on Cu[100], cleavage of water is possible also on the [100] surface, but with the thermodynamic product being atomic oxygen and water, as the result of subsequent disproportionation (**10**) of adsorbed hydroxyl groups (Figure 3-2). DFT calculations have further shown that disproportionation of hydroxyl groups on copper-clusters/nano-particles is moderately endothermic (0.45 eV) (Chen et al. 2010).

The reversal of **10** can be regarded as the fission of water by interaction with pre-adsorbed atomic oxygen through hydrogen abstraction. The PES in Figure 3-2 suggests that just as for the clean mono-crystalline copper surfaces [111], [100], and [110], only at the [110] surface can pre-adsorbed oxygen activate and cleave the water molecule directly. However, for the [111] surface the reaction energy (0.10 eV) is close to thermo-neutral and conflicting results have been reported suggesting that pre-adsorbed oxygen atoms on Cu[111] actually can assist in cleaving water (Wang et al. 2006).

In any case, the synproportionation/disproportionation equilibration is rapid. Experimentally the activation energy for the disproportionation (**10**) on Cu[110] is 0.56 eV (Figure 3-1), while DFT calculations on mono-crystalline copper surfaces predict the barrier to be lower than 0.24 eV for the [111], [100], and [110] surfaces (Figure 3-2). DFT calculations have further shown that pre-adsorbed oxygen atoms in the proximity of adsorbed water molecules have indirect effects on water cleavage by lowering the activation energy and stabilizing the product (Tang and Chen 2007b).

When the coverage of atomic oxygen on the copper surface is high it is likely that the chemical properties of the surface starts to resemble those of the copper oxides Cu_2O (cr) and CuO (cr). This issue will be discussed further in Section 8.

6 Surface diffusion of adsorbed atoms

Due to the many possible configurations of adsorbed species on the copper surface, it is important to understand the kinetics of configuration rearrangements and whether these could be rate limiting. A variety of experimental methods have been used to measure the diffusion rate of copper ad-atoms on the copper [100] surface (Breeman and Boerma 1992, Ernst et al. 1992, Miguel et al. 1987). Although the measured diffusion rate seems to depend on the experimental method used, the activation energies fall within the range of 0.28 eV to 0.40 eV (Table 6-1), meaning that copper ad-atoms diffuse quite rapidly on the [100] surface. DFT calculations tend to overestimate this barrier slightly (0.49 eV), but also predict rapid diffusion of copper ad-atoms (Boisvert and Lewis 1997).

The calculated (DFT) activation energy for diffusion of copper ad-atoms on the Cu[110] surface ranges between 0.25 eV and 0.38 eV, depending on the direction of diffusion (Liem et al. 1998). Diffusion is found to be faster along the [110] channel than across it.

Scanning tunneling microscopy (STM) have shown that adsorbed oxygen atoms move fast in the direction of the [110] channel at the copper [110] surface, even at low temperatures (70 K) (Buisset et al. 1996). This observation is in good agreement with DFT calculations, which predicted an activation energy of only 0.15 eV for the diffusion of oxygen atoms in the [110] direction and slightly higher barriers for the diffusion in other directions (Table 6-1) (Liem et al. 1998).

The diffusion of atomic hydrogen adsorbed on the copper [110] surface has been investigated thoroughly with periodic DFT calculations (Ren and Meng 2008). The activation enthalpy ($\Delta H^{\ddagger} \approx E_a$) for the diffusion of atomic hydrogen along the [110] channel was only 0.15 eV (Table 6-1). Since the hydrogen atom is a very light particle it is likely that quantum mechanical tunneling effects enhances the diffusion rate even further, which means that atomic hydrogen is extremely mobile on copper. Another very interesting result from Ren's study is that the activation energy for the diffusion of hydrogen atoms is almost independent of an adsorbed water layer ($\Delta\Delta H^{\ddagger} = 0.02$ eV) (Ren and Meng 2008). This result indicates that diffusion of atomic hydrogen is very rapid in solution, as well as in the gas-phase.

It can thus be concluded that adsorbed atomic- and formally radical species diffuse rapidly on ideal copper surfaces. An important consequence is that changes of adsorption configurations are kinetically possible and should not be rate limiting. Nevertheless, it is possible that diffusion of adsorbed species on non-ideal/rough copper surfaces is significantly slower, but as far as the authors are aware this has not been investigated.

Table 6-1. Activation energies (eV) for the diffusion of adsorbed species on mono-crystalline copper surfaces.

Surface	Species	E_a	Method[a]	Reference
Cu[110]	O_{ad}	0.15–0.30	DFT PBC	Liem et al. 1998
Cu[110]	Cu_{ad}	0.25–0.38	DFT PBC	Liem et al. 1998
Cu[110]	H_{ad}	0.15	DFT PBC	Ren and Meng 2008
Cu[100]	Cu_{ad}	0.28	Exp.	Ernst et al. 1992
Cu[100]	Cu_{ad}	0.39	Exp.	Breeman and Boerma 1992
Cu[100]	Cu_{ad}	0.40	Exp.	Miguel et al. 1987
Cu[100]	Cu_{ad}	0.49	DFT PBC	Boisvert and Lewis 1997

[a] Exp. means experimental data. The acronyms DFT and PBC denote density functional theory and periodic boundary conditions, respectively.

7 Formation of molecular hydrogen

In the Sections 3-5 above, it has been shown that atomic hydrogen can be produced at the copper-water interface, either directly through the dissociation of water molecules, but also, when water dissociation in itself is endothermic, disproportionation of hydroxyl groups can serve as a thermodynamic driving force. It is thus reasonable to ask whether the formation of molecular hydrogen is thermodynamically and kinetically feasible. Table 7-1 summarizes experimental and computational data for the adsorption/desorption of hydrogen on copper. In the following discussion, desorption of molecular hydrogen (**11**) is defined as the forward reaction, since it seems most natural in the context of processes subsequent to water splitting. However, some experimental data are taken from studies of hydrogenation of copper in the gas-phase (Campbell and Campbell 1991, Anger et al. 1989, Johansson et al. 2008, Tabatabaei et al. 1999).

Experimentally determined rate constants gives activation energies of around 0.7 eV for desorption of hydrogen from a hydrogenated poly-crystalline copper surface, while the activation energy for adsorption is only around 0.4 eV (Kiyomiya et al. 1974, Kojima et al. 1980, Tabatabaei et al. 1999). This means that the hydrogen adsorption/desorption equilibrium ($\pm$ **11**) on poly-crystalline copper is a rapid process at room temperature (an activation energy of 0.7 eV corresponds to a rate constant of $\sim 10 \text{ s}^{-1}$ at 298 K). Mono-crystalline surface experiments have shown that the desorption is slightly faster on the low-density surface [110] ($E_{a,f} = 0.56$ eV), while the adsorption has a kinetics which is very similar to the adsorption on poly-crystalline copper (Nakamura et al. 1990).

For the high-density surface [111], the activation energy of **11** has been calculated in several DFT studies, giving values between 0.70 eV and 1.07 eV (Kratzer et al. 1996, Gokhale et al. 2008, Sheng and Zhang 1993, Tang et al. 2009, Wang and Nakamura 2010). Experimentally, the activation energy of the hydrogen adsorption reaction (–**11**) has been determined to 0.65 eV (Díaz et al. 2009), while computational studies have predicted the activation energy for the adsorption ($E_{a,r}$) to be between 0.51 eV and 1.08 eV.

For the intermediate-density [100] surface no experimental kinetic data have been found in the literature. However, various types of density functional theory (DFT) calculations have been applied with similar results (Johansson et al. 2011, Wang and Nakamura 2010). The computed gas-phase activation energy for hydrogen formation at the [100] surface seems to be slightly lower than the experimental values for poly-crystalline copper surfaces (Table 7-1).

For further discussion of the kinetic and thermodynamic reactivity data available in the literature, it is necessary to make a note of theoretical character. As a chemical reaction, desorption of hydrogen (**11**) differs fundamentally from the water splitting (**8**) and most of the other reactions discussed here, since the molecularity (i.e. the number of particles) of the system changes during the reaction. Molecular hydrogen does not stick to copper surfaces (Clarke 1937, Balooch et al. 1974, Siegbahn et al. 1989), meaning that the hydrogen molecule (H_2) formed in **11** immediately desorbs from the surface and enters the solution or gas-phase. Due to this change in molecularity, desorption of hydrogen from copper (**11**) is associated with a large increase in the systems entropy.

A closer look at the references behind the experimental activation energies summarized in Table 7-1 (Kiyomiya et al. 1974, Kojima et al. 1980, Tabatabaei et al. 1999, Nakamura et al. 1990), reveals that these numbers are activation enthalpies ($E_a = \Delta H^{\ddagger}$), defined as the slope of the Eyring plot (Atkins and de Paula 2006, Laidler 1996). Although these might be reasonable approximations of the activation free energies ($\Delta G^{\ddagger}$) for the forward reaction (desorption), they give a poor description of the adsorption kinetics and consequently also the adsorption/desorption equilibrium.

In Table 7-1, the reaction enthalpy is calculated as the difference $\Delta H^{\circ} = E_{a,f} - E_{a,r}$. Experimental data shows that the desorption reaction (**11**) is endothermic ($\Delta H^{\circ} > 0$) at poly-crystalline copper as well as at the [110] surface. Although no experimental data exists, all DFT studies in the literature predicts that **11** is endothermic also at the [110], and [100] surfaces.

By combining the experimental reaction enthalpies ($\Delta H°$) listed in Table 7-1 with the theoretically derived entropy effect ($-T\Delta S° = -0.47$ eV) (Johansson et al. 2011), it is possible to estimate the Gibbs free energy ($\Delta G°$) for reaction **11**. It is then found that the formation of molecular hydrogen (**11**) is exergonic ($\Delta G° < 0$) at poly-crystalline copper and for the mono-crystalline [100] surface (Table 7-1). Despite the fact that a two DFT studies predict conflicting results for Cu[111] and Cu[110], i.e. a weakly endergonic process, the combination of all experimental enthalpies with the calculated entropy effect ($-T\Delta S° = -0.47$ eV, T = 298 K) predict that the desorption of hydrogen is exergonic (and thus spontaneous) also at these surfaces. These predictions are in qualitative agreement with experimental hydrogenation studies of both poly-crystalline copper and mono-crystalline copper [110] surfaces, which reports virtually no adsorption of hydrogen at room temperature and a hydrogen pressure of 1 bar (Anger et al. 1989, Johansson et al. 2008, Tabatabaei et al. 1999). It should be noted that the hydrogen pressure used in these experiments (1 bar) is $1.8 \cdot 10^6$ times higher than the partial hydrogen pressure in the atmosphere, meaning that there should be no adsorption of hydrogen on copper under atmospheric conditions.

The formation of molecular hydrogen at Cu[100] in water solution has recently been investigated by the present authors using DFT calculations (Johansson et al. 2011). The solvent water was represented using a dielectric continuum model and by including explicit water molecules in the quantum model. Thermodynamic potentials ($\Delta G°$, $\Delta H°$, $\Delta S°$) were evaluated using the partition functions of a non-interacting gas. Three reaction mechanisms were considered in this study: 1) direct formation of molecular hydrogen through the addition of atomic hydrogen (black pathway in Figure 7-1); 2) a sequential mechanisms in which water and atomic hydrogen forms molecular hydrogen and an adsorbed hydroxyl group, which reacts further with another hydrogen atom at the surface in order to regenerate the water molecule (blue pathway in Figure 7-1); and 3) a concerted variant of the previous reaction with water (red pathway in Figure 7-1). The activation free energies of the three condensed phase mechanisms investigated are relatively similar in magnitude, ranging from 0.70 to 0.92 eV (Figure 7-2). The mechanism with the lowest activation free energy in solution is the formation of hydrogen through direct collision of adsorbed hydrogen atoms (TS1 in Figure 7-3). It can thus be concluded that the solvent has a purely electrostatic effect on the kinetics of desorption, i.e. the water molecules are not explicitly involved in the reaction.

Table 7-1. Experimental and theoretical energetics (eV) for the formation of molecular hydrogen (11) on copper. Unless otherwise noted the values are gas-phase data.

Surface	$E_{a,f}$[a]	$E_{a,r}$[a]	$\Delta H°$	$\Delta G°$[b]	Method[c]	Reference
Cu[111]	–	0.65	–	–	Exp.	Díaz et al. 2009
Cu[111]	0.70	0.51	0.19	–0.28	DFT PBC	Kratzer et al. 1996
Cu[111]	1.07	0.54	0.53	0.06	DFT PBC	Gokhale et al. 2008
Cu[111]	0.85	0.54	0.31	–0.16	DFT PBC	Tang et al. 2009
Cu[111]	0.97	1.08	–0.11	–0.58	DFT PBC	Wang and Nakamura 2010
Cu[110]	0.56	0.41	0.15	–0.32	Exp.	Nakamura et al. 1990
Cu[110]	1.10	0.56	0.54	0.07	DFT PBC	Wang and Nakamura 2010
Cu[110]	–	0.62	–	–	Exp.	Campbell and Campbell 1991
Cu[100]	0.70	0.60	0.10	–0.37	DFT PBC	Kratzer et al. 1996
Cu[100]	0.62	0.30	0.32	–0.15	DFT PBC	Wang and Nakamura 2010
Cu[100] (gas)	0.56	0.39	0.17	–0.30	DFT	Johansson et al. 2011
Cu[100] (solv)	0.70	0.34	0.36	–0.12	DFT	Johansson et al. 2011
Poly-cryst.	0.74	0.39	0.35	–0.12	Exp.	Kiyomiya et al. 1974
Poly-cryst.	0.74	0.39	0.35	–0.12	Exp.	Kojima et al. 1980
Poly-cryst.	0.71	0.44	0.27	–0.20	Exp.	Tabatabaei et al. 1999

[a] $E_{a,f}$ denotes the activation energy of the forward reaction, while $E_{a,r}$ is the activation energy of the reversed reaction.
[b] The entropy effect ($-T\Delta S = -0.47$ eV, T = 298 K) was calculated using the DFT functional PWPW91 and the partition functions of an ideal-gas. Details of the calculations are given in the reference Johansson et al. (2011).
[c] The abbreviation Exp. means experimental data, while the acronyms DFT and PBC denote density functional theory and periodic boundary conditions, respectively.
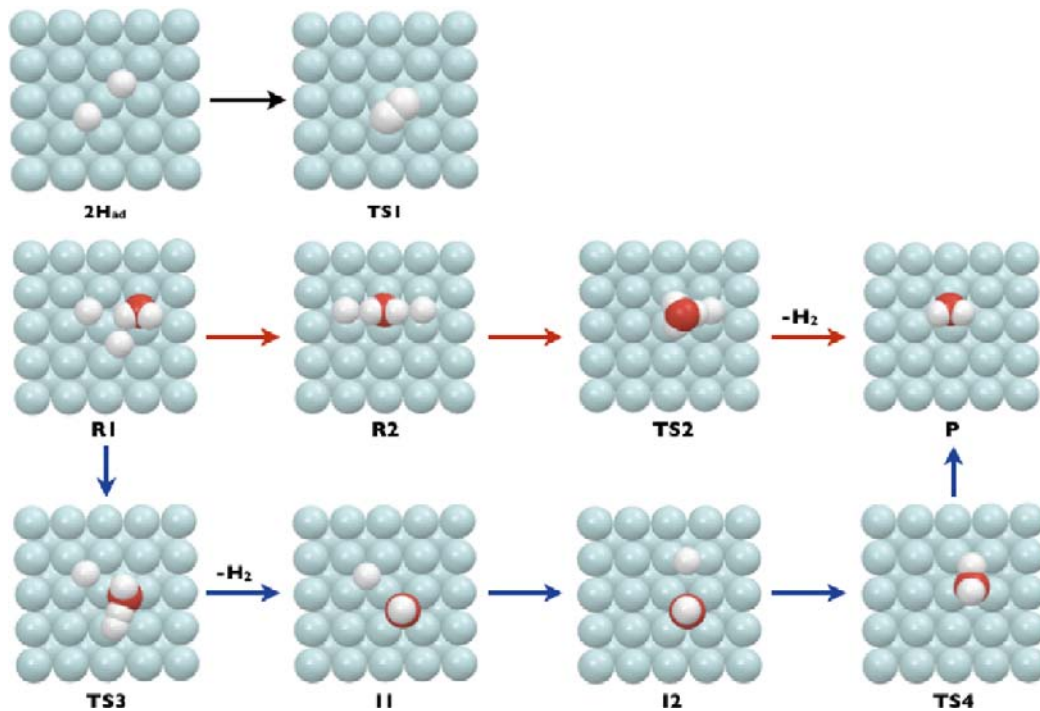
Figure 7-1. Hydrogen desorption mechanisms in condensed phase (Johansson et al. 2011).
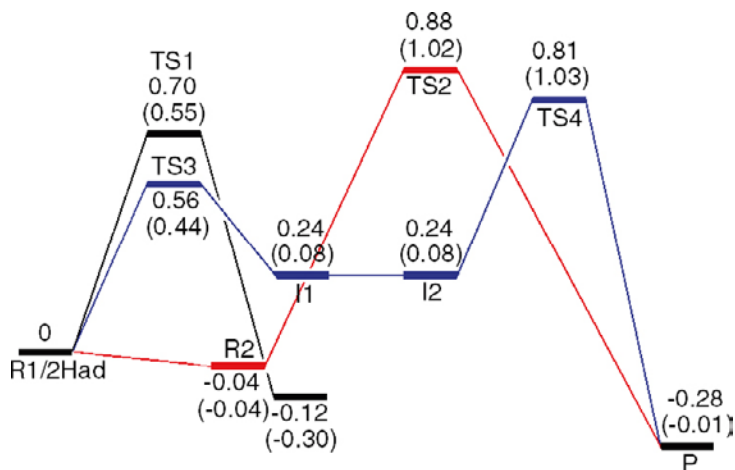

Figure 7-2. Condensed phase Gibbs free energy profile for the desorption mechanisms illustrated in Figure 7-1. Gas-phase energies are given in parenthesis (eV) (Johansson et al. 2011).
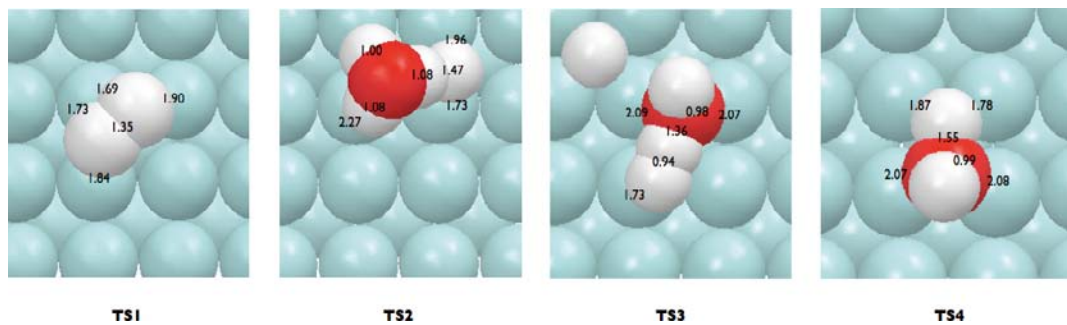

Figure 7-3. Transition states of the condensed phase desorption mechanisms. Numbers denote inter-atomic distances (Å) (Johansson et al. 2011).
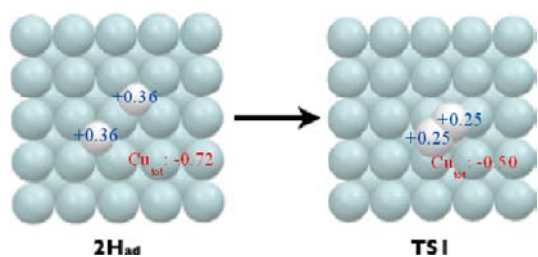
Figure 7-4. *Charge distribution in the reactant ($2H_{ad}$) and transition state (TS1) for the direct desorption mechanism (Johansson et al. 2011).*

The Gibbs free energy of desorption in gas-phase was –0.30 eV, which in agreement with the experimental hydrogenation studies discussed above means that atomic hydrogen, formed by water fission, desorbs spontaneously from the copper surface. The electrostatic character of the solvent raises the barrier from 0.55 eV in gas-phase to 0.70 eV in solution. It also reduces the exergonicity from –0.30 eV to –0.12 eV. The solvent-effect can be understood in terms of electrostatic considerations. In the reactant state ($2H_{ad}$ in Figure 7-4) the partial atomic charge on each hydrogen atom is +0.36. There is thus an electrostatic repulsion between the adsorbed hydrogen atoms/protons at the surface. In the transition state (TS1 in Figure 7-4) this partial charge has decreased to +0.25, and the reaction product is electrostatically neutral. Since the dielectric nature of water ($\varepsilon = 80.0$) stabilizes the charge separation (the dielectric constant, ε, enters the denominator of the Coulomb potential) in the adsorbed reactant state with respect to the less polarized transition state and the neutral product state, the activation energy becomes higher in solution and the reaction becomes less exergonic (compare the gas- and condensed phase values for the direct desorption in Figure 7-2, black curve).

The interaction of molecular hydrogen with small copper clusters in the gas-phase has been modeled with DFT calculations and transition state theory (TST) (Forrey et al. 2006, Guvelioglu et al. 2006). The thermodynamics of dissociative chemisorption of hydrogen on copper was calculated for copper clusters consisting of up to 15 copper atoms. It was found that the adsorption enthalpy varies significantly with cluster size and the mode of adsorption (Guvelioglu et al. 2006). In many of the cases investigated, the adsorption bond enthalpy exceeds the associated entropy penalty referred to above ($-T\Delta S° = -0.47$ eV, T = 298 K) (Johansson et al. 2011), meaning that adsorption of hydrogen on these clusters is spontaneous at room temperature. Since the chemical properties of copper clusters could be representative also for rough/nano-structured/non-ideal copper surfaces, it is likely that these surfaces differ from the ideal surfaces discussed above, in that there are modes of adsorption of hydrogen that are thermodynamically stable. The kinetics of dissociative adsorption of hydrogen was modeled for copper clusters containing up to nine copper atoms (Forrey et al. 2006). The activation energies (and consequently the rate constants) varies with the cluster size, however, in most cases the adsorption is found to be a rapid process ($\Delta H^{\ddagger} \sim 0.6$ eV).

8 Effects of the presence of a surface oxide-layer

Under atmospheric exposure a copper surface is always, to some extent, covered with an oxide layer due to dissociative adsorption of molecular oxygen. At the copper-water interface, even under anoxic conditions, an oxide layer could also form if the water cleaving reaction discussed above proceeds beyond the state of a hydroxyl monolayer. It is thus of interest to discuss the reactivity at the Cu_2O- and CuO-water interfaces, under anoxic conditions.

In the early 1990s Cox and Schulz made a series of investigations on the reactivity of the [111] and [100] surfaces of solid Cu_2O (Cox and Schultz 1991, Schultz and Cox 1991, 1992). The adsorption of several chemical species, e.g. water, hydrogen, oxygen, and small organic molecules, was monitored using thermal desorption spectroscopy (TDS) and ultraviolet photoelectron spectroscopy (UPS). At low temperature (110 K) 90 percent of the adsorbed water molecules were intact (molecular adsorption), while the remaining 10 percent had been cleaved and adsorbed at the Cu_2O-surface as hydroxyl groups. Increasing the temperature had dramatic effects on the dissociation equilibrium and at room temperature (300 K) dissociation of the water layer was complete (Cox and Schultz 1991). Although not stated explicitly by Cox and Schultz, the strong temperature dependence on the equilibrium indicate that there is a large entropy effect on the Gibbs free energy of dissociative adsorption, which most likely is the result of subsequent formation and dissociation of hydrogen gas. This is further discussed below.

The dissociation of water on Cu_2O has been further investigated theoretically using quantum mechanical methods (e.g. periodic DFT calculations) (Nygren and Pettersson 1996, Li et al. 2011). These studies show that the hydrogen atom resulting from water dissociation forms a hydroxyl group with oxygen atoms at the Cu_2O surface, and that this reaction is rapid ($\Delta H^{\ddagger} = 0.42$ eV) and exothermic ($\Delta H^{\circ} = -1.77$ eV). Just as for metallic copper surfaces, the dissociation of the hydroxyl group is endothermic ($\Delta H^{\circ} = 0.6$ eV), meaning that the hydroxyl layer is most likely stable with respect to further oxidation of hydroxyl groups.

As mentioned above, there are experimental results indicating that hydrogen-gas forms subsequent to water cleavage on solid Cu_2O (Cox and Schultz 1991). Zhang and co-workers have investigated the interaction of hydrogen gas with a solid Cu_2O surface using periodic DFT (Zhang et al. 2010). The calculated reaction enthalpy for dissociative adsorption of hydrogen on a perfect Cu_2O[111] surface was only -0.03 eV. Since the entropy loss associated with surface adsorption should be similar in magnitude to the adsorption on metallic copper ($-T\Delta S^{\circ} = 0.47$ eV of which the major part is the translational contribute $-T\Delta S^{\circ}_{trans} = 0.36$ eV, which is independent of the surface structure) (Johansson et al. 2011)), it seems like hydrogen does not adsorb at a perfect Cu_2O[111] surface. However, the adsorption enthalpy calculated for hydrogen at an oxygen deficient Cu_2O[111] surface was -0.42 eV, suggesting that the hydrogen adsorption/desorption is a reversible process at oxygen-deficient surfaces of solid Cu_2O.

9 Summary of the literature on mechanisms and kinetics

A few conclusions can be drawn on basis of the peer-reviewed literature concerning the reactivity at the copper-water interface:

- Water adsorption on an ideal Cu[110] surface is dissociative in condensed phase, as well as in the gas-phase (Ammon et al. 2003, Andersson et al. 2005, 2008, Campbell and Daube 1987, Nakamura et al. 1990, Ren and Meng 2006, 2008, Spitzer and Lüth 1982, Spitzer et al. 1985, Wang and Nakamura 2010). In condensed phase, the dissociation of water is a rapid process ($T = 298$ K, $k = 10^4$ s^{-1}) (Andersson et al. 2005, 2008), while it is moderately fast in gas-phase ($T = 298$ K, $k \sim 10^{-3}$ s^{-1}) (Nakamura et al. 1990). It is likely that water adsorption is dissociative also on Cu[100] in condensed phase, since even if the dissociation step in itself is endothermic (Spitzer et al. 1985, Wang and Nakamura 2010), the subsequent disproportionation of hydroxyl groups into atomic oxygen and water is exothermic and probably exergonic as well (Wang and Nakamura 2010). It is highly probable that stepped surfaces and copper ad-atoms enhance the reactivity of the copper surface with water, meaning that a rough poly-crystalline copper surface could be more active in cleaving water than any of the mono-crystalline surfaces.

- Atomic hydrogen adsorbed on poly-crystalline copper (as well as on the ideal mono-crystalline surfaces Cu[111], Cu[110] and Cu[100]) through high pressure exposure forms molecular hydrogen, since the desorption is exergonic and thus spontaneous (Anger et al. 1989, Johansson et al. 2008, Tabatabaei et al. 1999). Desorption is a rapid process in gas-phase ($k \sim 0.5 \cdot 10^4$ s^{-1}) (Johansson et al. 2011, Kiyomiya et al. 1974, Kojima et al. 1980, Nakamura et al. 1990, Tabatabaei et al. 1999, Wang and Nakamura 2010), as well as in condensed phase ($k \sim 10$ s^{-1}) (Johansson et al. 2011).

- Even though dissociation of adsorbed hydroxyl-groups is endothermic on mono-crystalline copper surfaces, experiments have shown that copper nano-particles in water are covered with an oxide layer, which might indicate that non-ideal copper surfaces can cleave hydroxyl-groups (Chen et al. 2011).

- Water adsorption on the mono-crystalline [111], and [100] surfaces of solid Cu_2O is experimentally known to be dissociative in the gas-phase (Cox and Schultz 1991, Schultz and Cox 1991, 1992). Cox and coworkers reported that dissociation of the water layer is complete at 300 K. If the water cleavage reaction can proceed even further at the Cu_2O surface is unclear.

- There are experimental and theoretical indications of that atomic hydrogen formed through water fission at the [111] and [100] surfaces of Cu_2O, forms molecular hydrogen (Chen et al. 2011, Zhang et al. 2010).

10 Comparison with experimental detection of hydrogen gas

Based on the peer-reviewed literature reviewed above, it seems clear that water cleavage and hydrogen formation occurs at the copper-water interface. Since the hydrogen gas detected by Hultquist and coworkers is claimed to be a byproduct of anoxic corrosion, i.e. an oxidative process that does not decline until either the water or the copper metal is consumed and completely converted into cuprous oxide, it is of interest to compare the measured amounts of hydrogen with the amounts that could be formed from the surface reactions discussed above.

Let us start by making an estimate of the amounts of hydrogen gas that would be formed when an ideally planar copper surface reacts with water to yield hydrogen gas and a hydroxide- or oxide monolayer. The surface density of metallic copper is ~ $1.4 \cdot 10^{15}$ atoms cm^{-2} ($1.09 \cdot 10^{15}$ atoms cm^{-2} for Cu[110] and $1.77 \cdot 10^{15}$ atoms cm^{-2} for Cu[111]). If water is cleaved to the extent that there is one adsorbed hydroxyl group per surface copper atom (1 ML OH$_{ad}$), then $0.7 \cdot 10^{15}$ hydrogen molecules ($1.2 \cdot 10^{-9}$ moles) or 2.4 ng of hydrogen gas would be formed per square centimeter copper surface. If the reaction proceeds beyond this state and the adsorbed hydroxyl layer dissociates until the extent that there is an oxide layer with one oxygen atom per surface copper atom (1 ML O$_{ad}$), then the amount of hydrogen gas would be 4.8 ng cm^{-2} copper. As discussed above the surface of cuprous oxide also adsorbs water dissociatively, which means that another 2.4 ng hydrogen could form if the oxidized surface reacts until 1 ML of OH$_{ad}$ is formed on top of the O$_{ad}$ ML. Starting from an ideal and reduced copper surface the total amount of hydrogen formed would be 7.2 ng cm^{-2}.

So far, we have not accounted for the fact that a rough (non-ideal) copper surface, has a larger (microscopic) surface area than an ideal surface (for which the microscopic surface area is equal to the macroscopic surface area). Experimentally, the roughness of copper electrode surfaces has been evaluated on the basis of differential capacitance and specific charge of adsorbed species (Valette 1982). For mechanically polished copper surfaces the roughness factor is typically in the order of two. This means that about 14 ng cm^{-2} (macroscopic area) would form if a rough reduced copper surface reacts with water until a hydroxyl monolayer is formed on top of an oxygen covered surface. If the surface is rougher, as would be the case for an unpolished copper surface, even larger amounts of hydrogen gas could evolve through reactions with the copper surface.

Let us now turn to the amounts of hydrogen gas detected by Hultquist and coworkers. In one experiment the detection chamber had the volume 60 cm^3 and three evacuations were made (Hultquist et al. 2009). The first evacuation was made when the pressure had reached 0.55 mbar, the second evacuation at 0.75 mbar, and the final evacuation was made when the pressure was 1 mbar. The experimental temperature was 318 K. Taking into account that there was a gas volume of 60 cm^3 below the collection chamber in the experimental setup (see Figure 2 in Hultquist et al. 2009) a total amount of 10 μmol of hydrogen gas was produced during the experiment. This amount corresponds to $2.0 \cdot 10^4$ ng of hydrogen (2.02 g mol^{-1}) being produced. The surface of the copper rods immersed in the anoxic water was 140 cm^2, which gives that the amount of hydrogen gas formed in the experiment was approximately 140 ng cm^{-2} macroscopic copper surface, which corresponds to 70 ng cm^{-2} microscopic surface area. Similarly, other experiments by Hultquists group have given 60 ng cm^{-2} macroscopic area (Szakálos et al. 2007), and 160 ng cm^{-2} macroscopic area (Hultquist et al. 2011), thus corresponding to 30 ng cm^{-2} microscopic area and 80 ng cm^{-2} microscopic area respectively.

It is emphasized that the largest amount reported by Hultquist, 80 ng cm^{-2} microscopic surface area, is less than six times more than the theoretical estimate made in this report on the basis of surface reactions with the outermost layer of copper atoms only. The formation of larger quantities of hydrogen by surface reactions would probably require that the copper surface reconstructs to create a rougher surface with a larger surface area, or that surface adsorbed atomic oxygen (or hydroxyl groups) diffuses into the bulk copper metal, which would make the copper atoms at the surface available for reacting further. Another possible mechanism could be that some type of oxide/hydroxide is

dissolved, so that more copper surface can be displayed for water cleavage. Similar mechanisms have been suggested elsewhere (Belonoshko and Rosengren 2010, Johansson et al. 2011). Even if the suggested mechanisms are unknown at the present stage, it is not unlikely that they could exist and be thermodynamically available.

Recently, the Swedish Radiation Safety Authority published a report based on a study carried out by Studsvik Nuclear AB (Becker and Hermansson, 2011). The amount of hydrogen gas formed in that experiment was only 4 ng cm^{-2} macroscopic copper surface, which is equal to the amount that would be formed if a mechanically polished copper surface cleaves water and generates hydrogen until the extent of an OH_{ad} ML is formed (as shown above). However, since the pressure was rising at the time when the experiment was stopped, it is likely that larger amounts could have been produced if the experiment would be allowed to proceed for a longer time.

It can thus be concluded that *the small difference between the amounts of hydrogen detected experimentally, and the amounts, which, as it seems could be formed by reactions with the outermost layers of copper atoms only*, makes it impossible to determine whether the hydrogen measured is actually a product of anoxic corrosion or just the result of a passivating surface reaction.

Since none of the copper oxides/hydroxides familiar to science are thermodynamically stable with respect to elemental copper and water it seems more likely that the hydrogen gas detected by Hultquist originates from surface oxidizing and passivating reactions, in which water is cleaved and hydrogen formed until the surface reaches a passivated state of oxidation.

11 Areas for further research

In this report it is shown that based on peer-reviewed literature it seems clear that copper (metallic as well as solid Cu_2O) activates and cleaves water at the copper-water interface, intermediately resulting in the formation of atomically adsorbed hydrogen, which forms molecular hydrogen that desorbs. In order to better understand these reactions the following issues needs to be resolved.

- The stability of surface oxidized states needs to be better understood in order to understand how far the water-cleaving/hydrogen-forming reactions could proceed. More precisely, the surface-states of metallic copper with adsorbed mono-layers of OH_{ad} or O_{ad}, needs to be investigated. Similarly, the OH_{ad} and O_{ad} states at the solid Cu_2O surface should be considered. The relative energies of such surface states could be estimated using Density Functional Theory (DFT).

- Natural (non-reduced) copper surfaces are to some extent covered by an oxide layer. Therefore the reactivity of the Cu_2O surface needs to be better understood. It is known that the [100] surface of Cu_2O cleaves the adsorbed water layer completely at room temperature in gas-phase. However, it is not known that the dissociation of water is complete in condensed phase or if it could proceed even further. Also, it is not known whether the hydrogen atoms produced by water cleavage form hydrogen gas or if they adsorb at the surface (or diffuse into the bulk). The interaction of Cu_2O with water could be investigated experimentally, using setups similar to those used by Hultquist and others for metallic copper. The reactivity of the Cu_2O surface could also be probed using DFT calculations and transition state theory (TST).

- As discussed above in Section 10, a rough copper surface would produce more hydrogen for the simple reason that its effective microscopic surface area is larger than the macroscopic surface area. The surface roughness of the copper rods used in the experiments, could be determined experimentally, using for example Atomic Force Microscopy (AFM) and Confocal Profilometry.

- The amount of hydrogen dissolved in the water solution and in the copper metal needs to be investigated in order to quantify the total hydrogen content due to water splitting in the work by Hultquist.

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It might be useful for the reader of this report to have a short review of the different kinetic terms used in the text. For detailed explanations of chemical kinetics see further Atkins and de Paula (2006) or Laidler (1996).

The rate of a typical chemical reaction

$$aA+bB \rightarrow cC+dD \tag{A-1}$$
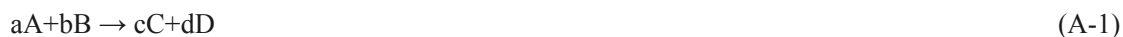
is formally defined as

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \tag{A-2}$$

where the square brackets denote molar concentrations of the reacting chemical species.

Very often the reaction rate is found to be proportional to the reactant concentrations

$$r = k\,[A]^a[B]^b \tag{A-3}$$

Here, k is a temperature dependent rate constant.

Transition state theory (TST) assumes that the transition state is in thermal equilibrium with the reactant state, and that the rate constant (k) is related to the Gibbs free energy of activation ($\Delta G^{\ddagger}$) by the Eyring equation

$$k = \frac{K_B T}{h}\,\exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \tag{A-4}$$

Here, K_B is the Boltzmann constant, T is temperature, h is Planck's constant, R is the gas constant, and $\Delta G^{\ddagger}$ is the difference in Gibbs free energy between the reactant and transition state. Since $\Delta G°$ can be partitioned in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) through the relation $\Delta G° = \Delta H°-T\Delta S°$, the Eyring equation can be expressed

$$\frac{k}{T} = \frac{K_B}{h}\,\exp\left(\frac{-\Delta H^{\ddagger}}{RT}\right)\exp\left(\frac{-\Delta S^{\ddagger}}{R}\right) \tag{A-5}$$

By equivalence

$$\ln\left(\frac{k}{T}\right) = \left(\frac{-\Delta H^{\ddagger}}{R}\right)\frac{1}{T} + \left(\frac{\Delta S^{\ddagger}}{R}\right) + \ln\left(\frac{K_B}{T}\right) \tag{A-6}$$

Plotting $\ln(k/T)$ versus $1/T$ makes it possible to interpret expression A6 as a straight line ($y = kx+m$), with the slope $-\Delta H^{\ddagger}/R$ and the intercept $(\Delta S^{\ddagger}/R)+\ln(K_B/h)$. This analysis allows the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ to be determined from measurements of k as a function of T.