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Atoms vs. Ions: Intermediates in Reversible Electrochemical Hydrogen Evolution Reaction

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Abstract: We present a critical analysis of the mechanism of reversible hydrogen evolution reaction based on thermodynamics of hydrogen processes considering atomic and ionic species as intermediates. Clear distinction between molecular hydrogen evolution/oxidation (H₂ER and H₂OR) and atomic hydrogen evolution/oxidation (HER and HOR) reactions is made. It is suggested that the main reaction describing reversible H₂ER and H₂OR in acidic and basic solutions is: 

\[ \text{H}_2\text{O}^+ + 2e^- \rightarrow \text{H}_2 + \text{OH}^- \]

and its standard potential is \( E^0 = -0.413 \text{ V} \) (vs. standard hydrogen electrode, SHE). We analyse experimentally reported data with models which provide a quantitative match (R.J.Kriek et al., Electrochem. Sci. Adv. e2100041 (2021)). Presented analysis implies that reversible H₂ evolution is a two-electron transfer process which proceeds via the stage of adsorbed hydrogen molecular ion \( \text{H}_2^+ \), as an intermediate, rather than \( \text{H}_2^+ \) as postulated in the Volmer-Heyrovsky-Tafel mechanism. We demonstrate that in theory, two slopes of potential vs. lg(\text{current}) plots are feasible in the discussed reversible region of H₂ evolution: 2.3RT/F ≈ 60 mV and 2.3RT/2F ≈ 30 mV, which is corroborated by the results of electrocatalytic hydrogen evolution studies reported in the literature. Upon transition to irreversible H₂ER, slowdown of \( \text{H}_2^+ \) formation in the first electron transfer stage manifests, and the slope increases to 2.3RT/0.5F ≈ 120 mV; \( R, F, T \) are the universal gas, Faraday constants and absolute temperature, respectively.

Keywords: H₂ER; H₂OR; HER; HOR; hydrogen; hydrogen molecular ion \( \text{H}_2^+ \); reversible process

1. Introduction

Hydrogen, the most abundant element in the universe, is expected to become carbon neutral fuel of the future. Water, H₂O, is essential to life on Earth and is a source of H₂, which can be generated by water splitting. Production of green hydrogen from water or sea water requires electrolysis using renewable power. This technological step was considered expensive a decade ago [1]. To make it practical, exact mechanisms and reactions with detailed steps and intermediates should be revealed and optimised for the highest efficiency. Electrochemical evolution of hydrogen can take place on the surface of various metals, semiconductor oxides, sulfides as well as other electrically conducting surfaces. Therefore, various issues related with hydrogen evolution reaction are thoroughly analysed in the scientific literature [2–6] with recent search for best performing composites [7,8]. Despite abundant studies in electrochemistry, electro- and photo-catalytic water splitting, there is no quantitatively satisfactory understanding of the hydrogen evolution and oxidation reactions as highlighted recently in [9].

Starting from the first works on this subject [10–12], it was assumed that reduction of H⁺ ions proceeds step-wise with formation of hydrogen atoms adsorbed on
the electrode surface, $H_{ad}$, as intermediates. It is generally accepted that electrochemical hydrogen evolution reaction occurring in acidic aqueous solutions is described by:

$$2H_2O^+ + 2e^- \xrightleftharpoons{H_{ad}} H_2 + 2H_2O,$$

whereas the one proceeding in neutral or alkaline medium is:

$$2H_2O + 2e^- \xrightleftharpoons{H_{ad}} H_2 + 2OH^-.$$

During the cathodic process, adsorbed $H_{ad}$ atoms are removed from the surface via chemical Tafel or electrochemical Heyrovski reactions. Various states such as $H_{top}$, $H_{bridge}$ and $H_{terminal}$ (according to H-atom position), which differ in their bond strength with the electrode surface are considered [3,13]. Such treatment of hydrogen evolution mechanism is commonly acknowledged and applied for interpretation of various electrocatalytic as well as photoelectrochemical processes taking place on different substrates [14].

The above described mechanism of $H_2$ evolution process is, however, contradictory, as elaborated further. Firstly, the standard potential of $H$ atom formation is $E^0_{H^+/H} = -2.106$ V [15]. Consequently, the energy of $H_{ad}$ interaction with surface, required to compensate depolarization of $H^+$ discharge from $-2.106$ V to 0 V, which is the case for Pt electrode, should be 203.2 kJ mol$^{-1}$. Such energy is typical to chemisorption, rather than adsorption. Thus, hydrogen atoms are considered to be adsorbed, whereas the indicated values of interaction energy are far too high for adsorptive interaction. If chemisorption took place, the formation of surface hydrides should occur on the electrode surface, but this is not the case for platinum group metals. In other words, the chemisorption as a prerequisite for the formation of hydrogen atom is replaced by adsorption. Another contradiction is related with the existence of a standard hydrogen electrode (SHE). Recently, in many publications the values of electrochemical potential are reported versus convenient reference hydrogen electrode (RHE) scale [16]. The very existence of such a reference electrode implies that a reversible two-electron transfer process ($2H^+ + 2e^- \equiv H_2$) with a Nernstian shift of

$$\frac{dE^0}{d(pH)} = \frac{2.3RT}{F} \approx 60 \text{ mV}$$

is feasible on Pt electrode surface under certain conditions ($R$ is the gas constant, 8.135 J K$^{-1}$mol$^{-1}$, $T$ is the absolute temperature, taken to be equal to 298 K in the expression above, $F$ is the Faraday’s constant, 96,845 C mol$^{-1}$, and 2.3 is a conversion factor from the natural log to log10). If so, then what is the real mechanism of hydrogen evolution reaction?

This work presents counter arguments for the commonly accepted treatment of hydrogen evolution reaction as well as arguments supporting the alternative concept of this process [17], which provides the quantitative explanation of the simultaneous charge and mass changes occurring on Pt electrode under the hydrogen evolution conditions. This revisiting view is mandated by recent experimental study, which can only explain Pt deposition on a carbon electrode via $H^+$ mediation [18]. Theoretical slopes of potential vs. lg(current) are derived and compared with the reported experimental results for electrocatalytic hydrogen evolution [19–21].

### 2. Mechanisms of H and H$_2$ Evolution/Oxidation Reactions

#### 2.1. Thermodynamics of H Atom Formation

The energy of chemical bond in $H_2$ molecule is $\Delta H = 453.6$ kJ.mol$^{-1}$, or $\frac{1}{2}D_{H_2} \approx 226.8$ kJ.mol$^{-1}$ if calculated per one atom [22]. In electrochemistry, usage of $\Delta G$ is more appropriate, since $\Delta G = -nFE^0$ and $\Delta G = \Delta H - T\Delta S$, where $G$, $H$ and $S$ are the thermodynamic functions (Gibbs free energy, Enthalpy and Entropy, respectively), $E^0$ is the standard potential, $T$ is the absolute temperature and $n$ is the number of electrons transferred in the reaction. From the electrochemical point of view, the standard potential of the so-called Volmer reaction involving the transfer of the first electron:

$$H^+ + e^- \equiv H,$$  \hspace{2cm} (1)
is \( E_{H^+/H}^0 = -2.106 \text{ V (SHE)} \) [15] (Figure 1). The transfer of the second electron as well as formation of \( H_2 \) molecule occurs in Heyrovsky step:

\[
H + H^+ + e^- \rightarrow H_2,
\]

the standard potential of which is \( E_{H,H^+/H_2}^0 = 2.106 \text{ V (SHE)} \) [15], i.e., exactly the same number with an opposite sign. Formal summing of the Equations (1) and (2) yields the well-known summary equation:

\[
2H^+ + 2e^- \rightleftharpoons H_2,
\]

with the value of standard potential \( E_{2H^+/H_2}^0 = 0 \text{ V (SHE)} \). In other words, formation of \( H_2 \) molecule fully compensates the electrochemical energy \( \Delta G = -nF \times E_{H^+/H}^0 = 406.4 \text{ kJ mol}^{-1} \), consumed for the formation of 2 moles of H atoms.

**Figure 1.** Thermodynamics of atomic (HER/HOR) and molecular hydrogen (H\(_2\)ER/H\(_2\)OR) processes in the potential range between Volmer and Heyrovsky reactions. The underpotential deposition regions UPD-I and UPD-II correspond to adsorption of \( H_{ad} \) and \( H_3O^+/H_2^+ \), respectively. The width of regions was evaluated on the basis of 50 kJ mol\(^{-1} \), which is the energy of hydrogen adsorption on Pt reported in the literature [3]. \( H_{hydr} \) stands for surface hydrides, formation of which can depolarize the discharge of \( H^+ \). The molecular hydrogen evolution and oxidation reactions (H\(_2\)ER/H\(_2\)OR) are reversible on a Pt electrode in the vicinity of 0 V denoted as Nernst region.

Under standard conditions the actual onset of hydrogen evolution on the surface of platinum group metals is observed at \( E = 0 \text{ V (SHE)} \). From the thermodynamic point of view, the transfer of the first electron at \( E = 0 \text{ V (SHE)} \) to form H atom should require an adequate energetic compensation. This is logical, since H atoms alone do not exist at normal conditions (room pressure and temperature) due to their highly reactive nature, which is based on an unpaired electron (can be considered a radical) with a short lifetime due to a strong reduction potential. In the context of current study, a hypothetical existence of H atoms could be contemplated if the huge 2.1 eV energy deficit is accounted for (see Figure 1). However, even then, the surface-trapped H-atoms should be immobile due to such chemisorption preventing \( H_2 \) formation. Indeed, it is well-known that in case there is a chemical interaction between the electrode surface and the discharging particle, the electrode process becomes depolarized. The effect is called underpotential deposition or UPD, and the extent of depolarization depends on the energy of interaction. In order to depolarize the first electron transfer process from \( E_{H^+/H}^0 = -2.106 \text{ V (SHE)} \) to \( E_{H^+/H}^0 = 0 \text{ V (SHE)} \), the energetic effect of such UPD should be as large as \( \Delta G = 203.2 \text{ kJ mol}^{-1} \) (see Figure 1). In the case of anodic hydrogen oxidation reaction on Pt, occurring at even more positive potentials, i.e., within 0–0.5 V (SHE), the energy of interaction between H atom and Pt surface can reach 260 kJ mol\(^{-1} \) according to the literature [2,23–26]. Interestingly, the energy of H adsorption on Pt surface evaluated experimentally as well as by recent DFT calculations is reported to range between 9 and 50 kJ mol\(^{-1} \) [3,27,28], which is significantly
less than 203.2 kJ mol\(^{-1}\) required to justify the existence of \(H_{\text{ad}}\) on Pt in the vicinity of 0 V (SHE) (see UPD-I region in Figure 1). Thus, there is a profound contradiction between chemisorptive interaction, which could justify the formation of \(H\) atom on Pt electrode surface within the discussed \(E\) range, and postulated adsorptive interaction deemed to stabilize \(H_{\text{ad}}\) on the electrode surface.

2.2. Energetics of Bond Breaking in \(H_2\) and \(H_2^+\)

The simplest molecular ion \(H_2^+\) attracts interest due to possibility to solve directly quantum mechanical model of its energy structure and to understand formation of covalent bonds [29]. It is useful to compare the above discussed H-atom thermodynamics from a \(H_2\) photo-ionisation point of view. The most efficient generation of \(H^+\) and \(H\) (atomic) from \(H_2\) at low pressure takes place via a rovibrational excitation of the \(H_2(E,F)\) state, which has one of the strongest known anisotropies of polarisability (5 \times 10^3 times larger than that of \(H_2\) ground state) [30]. There is a large difference of H-H internuclear distance in the ionic inner (E) and covalent outer F-states. By applying an additional strong external laser field of \(\sim (2-160)\) TW cm\(^{-2}\) intensity at 532 nm wavelength, photo-ionisation and photo-dissociation follows via \(H_2^+ \rightarrow H + H^+\) path as revealed by a velocity mapped imaging [30]. Theoretical predictions and experimental verification are closely following each other. An energy cost of this process is formidable considering that \(H_2(E,F)\) state is prepared by two-photon absorption at \(\lambda = 201.796\) nm wavelengths (photon energy \(h\omega = 1.24/\lambda[\mu m] = 6.144\) eV) and an additional two-photon process at \(\lambda = 532\) nm (2.33 eV) takes place for transition into the \(H_2^+\) ionised state before photo-dissociation. This is the least energy, hence, a high efficiency pathway of H and \(H^+\) production from \(H_2\). The portion of that energy required for \(H^+\) and \(H\) production from \(H_2\) is equal to the one photon absorption at green 2.33 eV (similar to \(E_\text{h}\) \(H^+/H = -2.1\) V or \(-2.31\) V [31]; see Figure 1). Equivalence of a potential applied electrically and optically by photon absorption manifests the energy conservation and thermodynamics underpinnings of energy transitions in molecular and ionic species of hydrogen.

The energy difference of molecular bond in \(H_2\) and \(H_2^+\) is \(4.48 - 2.69 = 1.79\) eV while the bond length increases from 74 pm (\(H_2\)) to 134 pm (\(H_2^+\)) [32]. Separation between H-atoms in \(H_3O^+\) is 154.5 pm considering an angle of 107° between hydrogens and the O–H bond length of 96.1 pm. The O–H length can increase by 10 pm during proton transport via the Grothuss mechanism, and it is 100.5 pm in anion \(OH^-\). It was demonstrated that in addition to a photo-induced dissociation of \(H_2^+\) from the excited vibrational states (stretched molecular ion), a Coulomb explosion also occurs, leading to generation of energetic (\(H^+ + H^+ + e\)) at laser intensities of \(5 \times 10^{13} - 10^{15}\) W cm\(^{-2}\) [33]. Bond breaking of \(H_2^+\) defined as a time required to localise an electron onto one of the atoms was directly measured by pump-probe method and found to be 15 fs [34], consistent with theoretical predictions [35].

2.3. Depolarization of \(H_2\) Evolution Due to Hydrogen Molecular Ion \(H_2^+\) Formation

First of all, it should be admitted that depolarization of the electrochemical process can be conditioned by any kind of interaction of the discharging particle with ions or atoms present in its close proximity. In aqueous solutions, there are two particles which can directly take part in \(H_2\) evolution process, i.e., \(H_2O\) molecule and \(H_3O^+\) ion. We hypothesize that the main particle irrespective of solution pH is hydronium ion \(H_3O^+.\) In neutral and alkaline solutions, a hydronium ion can be produced by dissociation of water molecules according to reaction:

\[
2H_2O \rightarrow H_3O^+ + OH^-
\]  
(4)

Reaction (4) is fast, because the energy of H–OH bond disruption is compensated by the energy of hydration of \(H^+\) ions, which is as high as 432 kJ mol\(^{-1}\) [36]. According to the literature [3], the activation energy of reaction (4) is about 75 kJ mol\(^{-1}\), which is not much; however, the necessity of step (4) to produce hydronium ion in solutions with
pH > 7 can explain why kinetics of hydrogen evolution reaction in alkaline medium is more sluggish [3].

As shown in our previous studies [17,37], the transfer of the first electron during electrochemical discharge of H$_3$O$^+$ ion should lead to formation of molecular hydrogen ion H$_2^+$, whereas the transfer of second electron should yield a H$_2$ molecule. An important property of H$_2^+$ ion is the energy of H–H$^+$ bond, which according to the literature [38] is $\Delta H_{298}^0 = 255.7$ kJ mol$^{-1}$. The energy for the formation of this bond is most likely derived from the energy of hydration of H$^+$ ion (432 kJ mol$^{-1}$ [36]), which is enough to depolarize the discharge of H$^+$ from $E^0 = -2.106$ V (SHE) to $E > 0$ V (SHE). The processes occurring at $E = 0$ V (SHE) can be described by the following sequence of electrochemical reactions:

$$H_3O^+ + e^- \rightleftharpoons (H_2^+)_{ad} + OH^- \quad (5)$$

$$\quad (H_2^+)_{ad} + e^- \rightleftharpoons H_2. \quad (6)$$

Overall reaction is:

$$H_3O^+ + 2e^- \rightleftharpoons H_2 + OH^- \quad (7)$$

In the vicinity of equilibrium potential both processes (5) and (6) are fast and reversible and proceed simultaneously; therefore, the overall two-electron process (7) describes redox processes occurring within certain rate limits on Pt surface in reversible hydrogen electrode (RHE) and determines the magnitude of exchange current, $i_0$, as well as $E$ of the process. At the equilibrium potential, the exchange current $i_0$ is equal to the anodic and cathodic components, which are compensating each other, and the total current through the electrode is zero (see Figure 2 and Section 2.4).

Figure 2. Analysis based on the Nernst equation for reaction (7). (a) The reversible polarization curves on Pt modelled for one- (dashed trace) and two-electron (solid trace) transfer processes according to Equation (20). (b) The log-line presentation of the same graph (a) to reveal the linear slope; $i_0$ is the exchange current. In experiments [19–21], the slope of 30 mV/dec was determined (solid lines). (c) Surface processes leading to H$_2$ER at 0 V. The proposed model is quantitatively matching the experiment of charge and mass changes on the electrode as shown by modelling based on the Nernst equation (adopted from [37]): adsorption and red/ox reactions of ions H$_3$O$^+$ and H$_2^+$ on Pt. The potential locations of the adsorbed (ads), desorbed (des), reduced (red) and oxidised (ox) species are shown by the corresponding markers.

Anodic oxidation of H$_2$ (H$_2$OR) proceeds according to reaction (6) and leads to formation of (H$_2^+\text{ad}$) rather than via the dissociation to H$_{\text{aq}}$ atoms. If reaction (4) is taken into
account, the sum of the Equations (4) and (7) yields the summary equation of reversible hydrogen evolution process:

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons (\text{H}_2^+)_\text{ad} \rightleftharpoons \text{H}_2 + 2\text{OH}^- \tag{8}
\]

Thus, molecular hydrogen ion \((\text{H}_2^+)_\text{ad}\) should be considered as intermediate in hydrogen evolution process instead of \(\text{H}_\text{ad}\) atom. As depicted in Figure 1, \(\text{H}_3\text{O}^+\) ion accommodates two \(\text{H}^+\) ions, which upon addition of two electrons can be used for the formation of \(\text{H}_2\) molecule. It is noteworthy that no additional chemical energy except for that resulting from the bond formation between \(\text{H}\) atoms, is required for Equations (5) and (6). On the contrary, the postulation of the bond between \(\text{H}_\text{ad}\) and the surface of platinum group metal acknowledges the need for additional interaction, which inevitably should have an adverse effect on the kinetics of \(\text{H}_2\) molecule formation and its detachment from the electrode surface.

Since the existence of reversible hydrogen electrode is an experimentally established fact, the \(E\) range above \(E^0_{2\text{H}^+/\text{H}_2} = 0\) V (SHE), known as hydrogen UPD region in the literature and denoted as UPD-II in Figure 1, should, in fact, be related with anodic oxidation of \(\text{H}_2\), rather than reduction of \(\text{H}^+\) ion to \(\text{H}_\text{ad}\) atom. In our previous study [37] on the basis of precise analysis of microgravimetric and coulombmetric data reported in [39], it was demonstrated that the current peaks observed in the voltammograms of Pt electrode in 0.5 M \(\text{H}_2\text{SO}_4\) within the \(E\) range between 0 V and 0.5 V (SHE) are related with reversible adsorption/desorption of the products of anodic oxidation of \(\text{H}_2\) molecule, i.e., \((\text{H}_3\text{O}^+)_{\text{ad}}\) and \((\text{H}_2^+)_{\text{ad}}\) (see Figure 2c for a detailed account of processes). The energy of adsorptive interaction of these surface compounds with electrode surface was evaluated to be 25.1 \(\text{kJ mol}^{-1}\) and 11.6 \(\text{kJ mol}^{-1}\), respectively. In fact, formation of \(\text{H}_\text{ad}\) as intermediate in the reduction of \(\text{H}^+\) could be hypothesized only in the cathodic range \(vs E^0_{2\text{H}^+/\text{H}_2} = 0\) V (SHE), i.e., at \(E < 0\) V. It is noteworthy that the formation of surface hydrides (denoted as \(\text{H}_{\text{hydr}}\) in Figure 1) can also depolarize the discharge of hydrogen ions (for details, see Appendix A in ref. [40]).

As one can see from the above discussion, in the case of reversible \(\text{H}_2\) evolution process (denoted as \(\text{H}_2\text{ER}\) and \(\text{H}_2\text{OR}\) in Figure 1), only those \(\text{H}_2\text{O}\) molecules which are contained in \(\text{H}_3\text{O}^+\) ion can participate in electrochemical reduction reaction. Other \(\text{H}_2\text{O}\) molecules participate in chemical processes of neutralization or dissociation (Equation (4)). This, however, does not imply that they cannot be electrochemically reduced on the surface under an adequate overvoltage via formation of hydrides, or be reduced chemically to \(\text{H}_2\) via the reactions with various electrochemically-produced metal oxide or sulfide surface species. These processes should be analysed, taking into consideration specific conditions of their occurrence, which are outside the scope of the present paper.

2.4. Kinetics and pH-Dependence of \(E\) in the Case of Reversible \(\text{H}_2\) Evolution/Oxidation Processes

In modern handbooks, one can find two hydrogen evolution equations for aqueous solutions:

\[
2\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{H}_2\text{O} \tag{9}
\]

with \(E^0 = 0\) V (SHE) for acidic medium and

\[
2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^- \tag{10}
\]

with \(E^0 = -0.826\) V (SHE) for alkaline medium. Both the above reactions are composite and can be subdivided into the steps as follows. For the acidic conditions:

\[
\text{H}_3\text{O}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 + \text{OH}^- ,
\]

\[
\text{OH}^- + \text{H}_3\text{O}^+ \rightleftharpoons 2\text{H}_2\text{O}
\]
and for the alkaline conditions:

\[
2\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+ ,
\]

\[
\text{H}_3\text{O}^+ + 2e^- \rightleftharpoons \text{H}_2 + \text{OH}^- .
\]

Thus, the Equation (7) is the same for all media, because the process is the same irrespective of solution pH. The processes of water dissociation (Equation (11)) either precede or follow the electrochemical act (Equation (7)), thus, in fact, there is one ion \(\text{H}_3\text{O}^+\) or \(\text{OH}^-\) participating in the two-electron transfer process.

The Nernst equation for reaction (7) is as follows:

\[
E = E^0 + \frac{RT}{2F} \times \ln \left( \frac{c_{\text{H}_3\text{O}^+}}{p_{\text{H}_2}c_{\text{OH}^-}} \right),
\]

(11)

where \(E^0\) is the standard potential, \(R\) is the gas constant, \(T\) is the absolute temperature, \(c_{\text{H}_3\text{O}^+}\) and \(c_{\text{OH}^-}\) are the concentrations of respective ions and \(p_{\text{H}_2}\) is the pressure of hydrogen gas. Under standard conditions (\(p_{\text{H}_2} = 1\) atm and \(T = 298\) K), \(E^0 = -0.413\) V (SHE) in neutral medium where \(c_{\text{H}_3\text{O}^+} = c_{\text{OH}^-} = 10^{-7}\) mol l\(^{-1}\), whereas in acidic or alkaline solutions, i.e., at \(c_{\text{H}_3\text{O}^+} = 1\) mol l\(^{-1}\) or \(c_{\text{OH}^-} = 1\) mol l\(^{-1}\), the standard potentials will be 0 V and \(-0.826\) V (SHE), respectively. If \(c_{\text{H}_3\text{O}^+} \times c_{\text{OH}^-} = K_w = 10^{-14}\) (where \(K_w\) is the ionic product of water), then Equation (11) can be written as:

\[
E - E^0 = \frac{RT}{F} \ln c_{\text{H}_3\text{O}^+} = -2.3 \frac{RT}{F} \times p\text{H}
\]

(12)

or

\[
c_{\text{H}_3\text{O}^+} = \exp \left( \frac{F(E - E^0)}{RT} \right)
\]

(13)

and the time derivative is

\[
\frac{dc_{\text{H}_3\text{O}^+}}{dt} = \exp \left( \frac{F(E - E^0)}{RT} \right) \times \frac{F}{RT} \frac{dE}{dt}
\]

(14)

because \((e^x)' = e^x\) and \(1/ \lg(e) \equiv \ln(10) = 2.303\). On the other hand, it is known that the relation between the rate of electrochemical reaction, i.e., the current \(i\), and the concentration of electroactive species, \(c\), is given by:

\[
i = nF \times \frac{dc}{dt},
\]

(15)

where \(n\) is the number of electrons transferred per one mole and

\[
\lg i = \lg(nF) + \lg \left( \frac{dc}{dt} \right)
\]

(16)

Combination of Equations (16) and (14) yields:

\[
\lg i = \lg(nF) + \frac{F(E - E^0)}{RT} \lg e + \ln \left( \frac{F}{RT} \right) + \lg \left( \frac{dE}{dt} \right) = \text{Const} + \frac{F(E - E^0)}{2.3RT},
\]

(17)

where the cumulative constant \(\text{Const} = \lg(nF) + \ln \left( \frac{F}{RT} \right) + \ln \left( \frac{dE}{dt} \right)\); the last term is the logarithm of potential sweep rate, which is a constant in electrochemical experiments. From Equation (17) it follows that under standard conditions:

\[
d \lg i = \frac{FdE}{2.3RT}, \quad \frac{dE}{d \lg i} = \frac{2.3RT}{F} \approx 60 \text{ mV/dec.}
\]

(18)
Combination of Equations (14) and (15) yields the expression for reversible polarization curves:

\[ i = nF \exp \left( \frac{F(E - E^0)}{RT} \right) \times \frac{F}{RT} \frac{dE}{dt} \text{, with } i_0 \big|_{E=E_0} = nF \times \frac{F}{RT} \frac{dE}{dt} \quad (19) \]

or

\[ i = i_0 \exp \left( \frac{F(E - E^0)}{RT} \right) \quad (20) \]

These polarization curves for the anodic and cathodic processes are shown in Figure 2a,b, whereas Figure 2c depicts polarization curves of surface electrochemical processes, taking place on the Pt electrode surface in the so-called hydrogen UPD region at \( E > 0 \) V (SHE). Thus, in the case of reversible hydrogen evolution process, the slope \( \frac{dE}{d\lg i} \) is equal to the slope \( \frac{dE}{dE} \); therefore, it is referred to as the Nernst slope in this study.

Equality \( \left[ c_{H_2O^+} \times c_{OH^-} \right] = K_w = 10^{-14} \) means that OH\(^-\) ion formed in reaction (11) will react with H\(_3\)O\(^+\), yielding 2 H\(_2\)O and vice versa in the anodic reaction. Consequently, in the case of reversible process, in accordance with Equation (9), where the formal ratio of H\(_3\)O\(^+\) to electron is 1:1, the Nernst slope of \( \frac{dE}{d\lg E_0} = \frac{2.3RT}{F} \approx 60 \) mV/dec and \( \frac{dE}{dpH} \approx 60 \) mV/pH should be observed. However, if due to some reason the concentration (or activity) of OH\(^-\) ions is not decreasing as a result of their interaction with H\(_3\)O\(^+\) (e.g., OH\(^-\) adsorption on the electrode surface, formation of (hydr)oxides (MeOH \( \rightleftharpoons \) Me\(^+\) + OH\(^-\)) or due to some hindrance of their transport at rough nanostructured surfaces), the rate of anodic half-reaction (7) as well as \( i_0 \) will increase and the path (7) will become dominant. The Nernst equation for reaction (11), when \( c_{OH^-} = \text{const} \) and \( p_{H_2} = 1 \) atm, can be written as:

\[ E = E^0 + \frac{RT}{2F} \ln \left( \frac{c_{H_2O^+}}{c_{OH^-}} \right) = \text{const} + \frac{2.3RT}{2F} \lg c_{H_2O^+} = \text{const} - \frac{2.3RT}{2F} pH \quad (21) \]

Consequently:

\[ \frac{dE}{dpH} = \frac{2.3RT}{2F} \approx 30 \text{ mV/pH unit} \quad (22) \]

It can also be shown that \( \frac{dE}{d\lg i} \approx \frac{2.3RT}{2F} \approx 30 \) mV/dec (detailed derivation of kinetic equations for the case when \( c_{OH^-} = \text{const} \) is presented in Appendix A).

The \( E \) limits, where hydrogen evolution and oxidation reactions proceed reversibly approximately are \( \pm \frac{2.3RT}{F} \), whereas \( i \) should not exceed 10 \( \times i_0 \) (Figure 2a,b). When cathodic current significantly exceeds the magnitude of exchange current of reaction (7), i.e., when \( i \gg i_0 \), transition to irreversible H\(_2\) evolution occurs. In such a case, the transfer of the first electron (Equation (5)) becomes hindered and turns out to be the rate determining step, whereas the transfer of the second electron proceeds instantaneously. The slope \( \frac{dE}{d\lg i} \) increases up to \( \frac{2.3RT}{F} = 120 \) mV, given that charge transfer coefficient \( \alpha = 0.5 \), and is referred to as the Tafel slope. Thus, it can be inferred that in the case of hydrogen evolution on Pt electrode, the decrease of slope \( \frac{dE}{d\lg i} \) to attain values \( \frac{2.3RT}{F} \approx 60 \) mV and \( \frac{2.3RT}{4F} \approx 30 \) mV as the potential approaches the equilibrium potential \( E = 0 \) V (SHE) demonstrates the transition towards conditions where the process proceeds reversibly.

2.5. Reversibility: Thermodynamics at Work for SHE Electrode

Reversibility is discussed next since the presented H\(_2\)ER/H\(_2\)OR processes are based on the reversible mechanism (Figure 3). Reversibility is key for thermodynamic analysis and is essential for existence of the SHE and RHE electrodes. In contrary to full reversibility, the Tafel rate equation defines kinetics of reaction dependent on overpotential, i.e., it is irreversible and non-equilibrium. The Tafel’s analysis of \( I-V \) characteristic’s slope from overpotential \( \alpha \lg i \) has become a corner stone for analysis of efficiency of electrochemical processes. The phenomenological Butler-[42] and Volmer-[43] model of electrode kinetics fits the Tafel’s current-voltage analysis and describes interface pro-
cesses in a microscopic per particle manner. Cases of non-equilibrium thermodynamics encountered at interfaces of fuel cells and batteries, e.g., intercalation, are actively investigated and their reversibility has paramount practical importance [44]. Kinetics of charge transfer on an electrode surface is inherently related to the hydrodynamics of reacting species. It is experimentally established that $H_3O^+$ diffuses twice faster than $OH^-$ in water, which was explained by ab initio calculations [45] as due to the Grotthuss mechanism dominating over hydrodynamics. Different 3D arrangement of possible proton docking sites is responsible to different probabilities of $O$–$H$ bond switching. The slower diffusion of $OH^-$ at nanostructured electrocatalytic surfaces is consistent with $\frac{dE}{d\log i} \approx 30 \text{ mV/dec}$ slope observed experimentally for hydrogen evolution reaction. Other processes such as oxidation/reduction of the electrode, adsorption, chemical reactions and hydrodynamics all can have a contribution to kinetics of $H_2$ER/$H_2$OR, especially in the non-reversible region of potentials (Figure 3).

Figure 3. Hydrogen evolution/oxidation reactions $H_2$ER/$H_2$OR in aqueous solutions; $\rightleftharpoons$ marks reversible processes while the colored arrows in electrochemical reactions occurring outside the reversibility range of $\pm 60 \text{ mV}$ mark irreversible processes. $E = 0 \text{ V vs. RHE}$ corresponds to equilibrium potential of $H_2$ER/$H_2$OR for a solution with any pH. The inset shows schematics of $H^+_2$ formation (Equation (5)) using pictorials of chemical structures of the participating species. Addition of expressions (1) and (2) in either the positive or negative side leads to the central equation, which defines the equilibrium condition of the SHE (RHE) electrode.

The existence of reversible $H_3O^+$/H$_2$, OH$^-$ electrode in the form of SHE or RHE implies the feasibility of a symmetric reversible two-electron transfer process, which proceeds at the same rate in both directions at its equilibrium potential. There is no distinction between those two electrons, as they are transferred simultaneously and the only possible intermediate is the $H^+_2$ ion. The reversibility of the commonly accepted two-electron process (Equation (3)), which proceeds in a step-wise manner and asymmetrically with $H^+ + e^- = H_{ad}$ as a forward reaction and $H_2 = 2H_{ad}$ as a backward first step, is questionable. Considering different energetics of the steps, it is highly improbable to have the very same rates as required for the known SHE and/or RHE performance. The hindrance of $H^+_2$ formation leads to the irreversible hydrogen evolution with Tafel slope of
120 mV/dec found for Pt electrodes [4]. In summary, the essential difference between the conventional HER/HOR and presented here H2ER/H2OR hydrogen evolution mechanisms is that \( \text{H}_{\text{ad}} \) is an intermediate stage in the two one-electron transfer steps, whereas \( \text{H}_2^+ \) is the intermediate in one two-electron transfer reaction. We propose in this thermodynamics-based study that H2 formation on Pt electrode surface is proceeding via a structural reorganisation inside the \( \text{H}_2\text{O}^+ \) ion, where two neighbouring H-atoms form a bond (they are already at the bond separation) as schematically illustrated in the top-inset in Figure 3. The energy costly and asymmetric process of hydrogen evolution/oxidation via H-atoms contradicts the reversibility of SHE and RHE electrodes, which apparently exists in reality and is used in practice.

3. Conclusions and Outlook

We propose that reversible electrochemical hydrogen evolution (H2ER) occurring in acidic, neutral and alkaline aqueous solutions can be described by one common reaction:

\[
\text{H}_3\text{O}^+ + 2e^- \xrightarrow{(\text{H}_2^+)_{\text{ad}}} \text{H}_2 + \text{OH}^- ,
\]

the potential of which is given by the Nernst equation:

\[
E = E^0 + \frac{2.3RT}{F} \ln \left( \frac{c_{\text{H}_3\text{O}^+}}{c_{\text{OH}^-}} \right),
\]

where \( E^0 = -0.413 \) V. The peculiar features of this reaction are as follows: (i) it involves transfer of two electrons per one \( \text{H}_3\text{O}^+ \) and one \( \text{OH}^- \) ion, (ii) the precursor of H2 molecule is molecular hydrogen ion (\( \text{H}_2^+ \))\(_{\text{ad}}\), which forms during the transfer of the first electron already, whereas the transfer of second electron yields H2, (iii) the energy of hydration which is conserved within \( \text{H}_3\text{O}^+ \) ion is consumed for the formation of bond in H2 molecule and accounts for depolarization of \( \text{H}^+ \) discharge from \( E^0_{\text{H}^+/\text{H}} = -2.106 \) V (SHE) to \( E > 0 \) V, known as hydrogen UPD phenomenon observed on Pt. Based on these considerations, formation of \( \text{H}_{\text{ad}} \) as intermediate in hydrogen evolution/oxidation reactions turns to be thermodynamically and kinetically unfavourable path. It is shown that in the vicinity of reversible potential of hydrogen evolution/oxidation reactions \( E \approx E^0 \pm \frac{2.3RT}{FT} \) two values of \( \frac{dE}{dz} \) slope are feasible: \( \frac{2.3RT}{FT} \approx 60 \) mV/dec, when \( c_{\text{H}_3\text{O}^+} \times c_{\text{OH}^-} \approx K_w \); and \( \frac{2.3RT}{FT} \approx 30 \) mV/dec, when \( c_{\text{OH}^-} \approx \text{const} \). The slope values of \( \approx 30 \) mV/dec found experimentally in the case of electrocatalytic hydrogen evolution process \( [4,19–21,46] \) serve as a proof of the alternative mechanism described herein. The twice faster diffusion of \( \text{H}_3\text{O}^+ \) compared to \( \text{OH}^- \) in water \( [45] \) is consistent with the presented model of H2ER/H2OR and the experimentally observed 30 mV/dec slope. Presented analysis is further supported by recent experimental results of Pt electrodeposition \( [18] \) which are explained by the mechanism involving formation of \( \text{H}_2^+ \) as intermediate in reversible hydrogen evolution on Pt.

Further insights into energetics and kinetics of H2ER via \( \text{H}_2^+ \) intermediate could be provided by the readily available toolbox of density functional theory (DFT) approaches equipped with bond formation modeling at the atomic scale \( [47] \), which currently models H atoms instead of \( \text{H}_2^+ \) \( [48,49] \). Numerical modelling is expected to reveal effects related to non-ideality and surface coverage of active hydrogen species (atoms, ions, molecules), which would expand on the presented ideal case of H2ER on Pt (also Pd). The theory and modelling should lead to development of practical water splitting applications. In addition to the surface reactions discussed in this study, the same \( \text{H}_2^+ \) deposition inside solid state of Pd explains the operation principle of optical hydrogen sensor based on metamaterials \( [50] \). Better understanding of the roles of hydrogen atoms, ions (protons) and molecular ions in water splitting and hydrogen sensing will expedite development of future technologies for green power, fuel cells and transportation.

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Appendix A

From Equation (21) it follows that \( \lg c_{\text{H}^{+}} = \frac{(E - \text{const})2F}{2.3RT} \) or \( \ln c_{\text{H}^{+}} = \frac{(E - \text{const})2F}{R} \).

Then, \( c_{\text{H}^{+}} = \exp \left( \frac{(E - \text{const})2F}{2.3RT} \right) \) and \( dc_{\text{H}^{+}} = \exp \left( \frac{(E - \text{const})2F}{2.3RT} \right) \times \frac{2F}{RT} \frac{dc}{dt} \). If \( i = nF \times dc/dt \), then \( \lg i = \lg(nF) + \lg(dc/dt) \), \( \lg(dc/dt) = \exp \left( \frac{(E - \text{const})2F}{2.3RT} \right) \) and \( \lg i = \text{const} + \exp \left( \frac{(E - \text{const})2F}{2.3RT} \right) \) or \( d[\lg i] = \frac{2F}{2.3RT} \exp \left( \frac{(E - \text{const})2F}{2.3RT} \right) \), which yields \( \frac{dE}{dt} = \frac{2F}{2.3RT} \approx 30 \text{ mV/dec} \) (derivation as for Equation (17) with cumulative constant term const).
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