

# Analysis of the Relationship between Dissolved Molecular Hydrogen Gas, pH and ORP using the Nernst Equation

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## Introduction

For decades, alkaline water ionizers have been marketed with claims about various health benefits. One tool used by marketers to demonstrate that their water is “different” from other types of water is the ORP meter. Many ionized water sales representatives are aware that, while most other waters have a positive ORP reading, ionizers produce water that has a negative ORP reading (-100 mV to -750 mV or more). Attempts to explain *why* the water has a negative ORP reading, as well as what the reading actually means, have spawned many theories, including that the water contains “free electrons” or some “special structure”. But, until recently, the fact that ionized water contained dissolved H<sub>2</sub> gas (produced during electrolysis) was not widely known, and, that the dissolved hydrogen, a reducing agent, was responsible for the negative ORP. In 2007, a landmark research study showed that drinking water which contained dissolved hydrogen gas (H<sub>2</sub>) could provide therapeutic benefits. In the ten years since, the number of research studies confirming the therapeutic benefits of H<sub>2</sub> has grown rapidly. As knowledge about the benefits of molecular hydrogen has spread over the past few years, some manufacturers have improved upon the design of their existing alkaline ionizers (originally designed as “pH” machines, not “hydrogen water” machines), in order to elevate the level of hydrogen gas in the water. Recently, new, innovative technologies have emerged, designed from the ground up to maximize the levels of dissolved hydrogen. These include neutral-pH hydrogen infusion machines, battery-operated portable hydrogen water bottles, special pre-packaged bottles and pouches, and tablets that produce H<sub>2</sub> gas. As the popularity of hydrogen water products has continued to grow, consumers have become more interested, not only in the therapeutic benefits of H<sub>2</sub>, but also in knowing how much hydrogen their water actually contains. The websites and marketing brochures of manufacturers and retailers make many claims about the performance level of their machines, declaring their ability to produce water having a “more negative ORP” than their competitors. The conventional view of the ORP reading is, “the more negative the reading, the higher the water’s therapeutic benefit”. Since we tend to think that “more is better”, on its face, the notion that *a more negative reading is superior to a less negative one* does seem plausible.

The growth in awareness about H<sub>2</sub> as a therapeutic agent, combined with the desire on the part of consumers to know precisely how much hydrogen their water contains, created the demand for a measuring device which eliminated the ambiguity and inconsistency associated with the ORP meter. In the last few years, relatively inexpensive portable “dissolved hydrogen meters” (approx. 500 dollars), claiming to accurately measure dissolved hydrogen gas, have appeared in the marketplace. Instead of measuring in units of millivolts like the ORP meter, these meters have a digital display showing dissolved hydrogen levels in units more appropriate for measuring dissolved compounds, parts-per-million/parts-per-billion (PPM/PPB). At first glance, it seems that they might be a good choice for measuring dissolved hydrogen. However, these meters are based on the ORP meter platform, and therefore only capable of measuring the water’s ORP, *not dissolved hydrogen gas*. Although the ORP measurement does represent *the tendency* of water to act as an oxidizing or reducing agent, other conclusions about the meaning of the negative ORP reading must be based on a precise understanding of the chemistry associated with ORP. Throughout this article, many questions surrounding H<sub>2</sub>, pH and negative ORP will be answered, but the focus will be on explaining what the negative ORP can and cannot tell us about the water, its therapeutic benefit, and the level of dissolved hydrogen gas it contains.

While this can be a complex and confusing subject, we will explain the pertinent concepts step-by-step, using well-defined terminology and easy to understand language, combined with many graphs and illustrations. In order to gain some valuable insight into the subject of ORP, we will use the Nernst equation to examine the relationship between the level of dissolved H<sub>2</sub> gas, pH, and the ORP measurement. In order to properly introduce the subject, it will be helpful to start by reviewing some terminology and fundamental concepts associated with the subject of ORP.

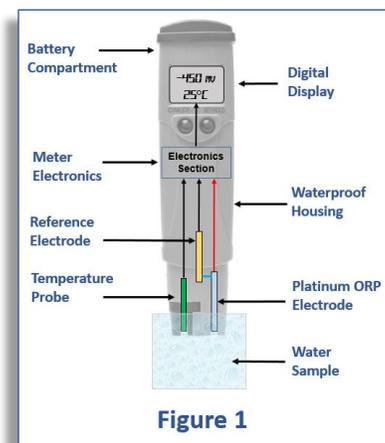
## Hydrogen water

When we talk about “hydrogen water”, we are referring to water containing dissolved molecular hydrogen gas ( $H_2$ ). It is similar to carbonated beverages, which contain dissolved carbon dioxide ( $CO_2$ ), the gas responsible for their “fizziness”. Water containing dissolved hydrogen can be produced in a variety of ways. Common methods include electrolysis (water ionizers), hydrogen-infusion machines (HIM’s), tablets which produce  $H_2$  gas when placed into water or swallowed, and  $H_2$  gas bubblers. It is important to note that, the  $H_2$  gas *dissolves* into the water, but *does not bind chemically* to the water molecules themselves, forming some new chemical substance (such as “ $H_4O$ ”). Although it is not unusual to see some gas bubbles, or even for the water to have a “foggy” appearance, the dissolved  $H_2$  gas is in the form of extremely small “nanobubbles”, which are invisible to the naked eye. Any visible bubbles are undissolved, and will quickly rise to the surface and escape into the air. Because  $H_2$  is a volatile gas, it has a relatively short shelf life, and, apart from the use of special packaging, will not remain dissolved in the water indefinitely. Just as after opening, a carbonated beverage will “go flat” as the  $CO_2$  gas escapes, the level of dissolved  $H_2$  gas will also gradually drop over time as the  $H_2$  gas escapes from the water. The approximate half-life for an open container is two hours. Dissolved hydrogen is usually measured in milligrams per liter (mg/L) or equivalent units, parts per million (ppm)<sup>1</sup>. Typical levels of dissolved  $H_2$  are in the range of 0.5 to 2mg/L. Although the saturation level of hydrogen is approximately 1.6 mg/L at sea level, super-saturated levels of 3mg/L or more are possible under the proper conditions of temperature and pressure. While our discussion will focus only on hydrogen drinking water, it should be noted that there are many other methods for administering hydrogen gas, including inhalation, intravenous injection of hydrogen-rich saline, and hydrogen baths.

Hydrogen water may also be referred to as  $H_2$  water, hydrogen-rich water, hydrogen-infused water or hydrogen-enriched water.

## The ORP meter

The ORP meter is a tool commonly used by operators and technicians in many commercial and industrial sectors, including environmental, wastewater treatment, food service, pool & spa, and horticulture. Combined with other measured parameters, such as temperature, pH and chlorine level, a high positive ORP measurement can indicate the effectiveness of sanitizing agents (oxidizers) used to kill various pathogens in water. **Figure 1** shows a pictorial diagram of a typical portable ORP meter. Although similar in some ways to a standard high-impedance digital voltmeter, there is one important difference, the meter’s ORP sensor electrode. The electrode (also called a “probe”), designed to be immersed into a sample of water, is constructed from an inert metal, usually platinum, which is resistant to oxidation. The meter also contains a second internal reference electrode (usually silver-silver chloride) mounted inside the housing. This electrode generates



a reference voltage to which the voltage from the platinum electrode is compared. While the ORP probes of smaller, portable units are integrated into the the meter’s housing, larger meters usually have probes which are externally located in a separate enclosure, and connected to the meter with a flexible cable. When placed into a sample of water, the platinum surface of the electrode will either give up or accept electrons, depending on the composition of the water. This transfer of electrons generates a very small voltage. The meter’s internal electronics process the voltage, compare it to the voltage generated by the internal reference, and display the resulting ORP value in millivolts (mV). Depending on the type of agents dissolved in the water, the polarity of the displayed voltage will either be positive (indicating the presence of oxidizing agents) or negative (indicating the presence of reducing agents). ORP meters are available in a wide range of prices, from inexpensive consumer-grade portable units, to more sophisticated industrial and laboratory models.

## Negative ORP and the source of the therapeutic benefit

As previously mentioned, water containing dissolved  $H_2$  gas will normally measure some level of negative ORP (-100 to -750mV or more). Marketers often say this is an indication that various “special qualities” have been imparted to the water by the electricity during electrolysis. These may include claims that the water has a “smaller molecular structure”, contains “free electrons”, or has a “negative charge”. While only a knowledge of basic chemistry is required to debunk such claims, nevertheless, they persist and even proliferate. This has led to confusion among marketers and consumers alike about the actual source of the water’s benefit, as well as uncertainty about the proper method for evaluating its therapeutic strength and efficacy. In fact, the negative ORP is produced by the presence of dissolved hydrogen gas. The process is simple: during electrolysis, electricity is responsible for the production of molecular hydrogen gas ( $H_2$ ) at the negative cathode, which then dissolves into the water as it flows across the cathode (a secondary result of electrolysis is the rise in pH). But, it is important to note that the electricity does not impart other “special therapeutic properties” to the water, and any hydrogen water, even if made *without the use of electricity* (e.g. using tablets or bubbling the gas into the water), will *also* have a negative ORP. The negative ORP is simply an *indicator of the presence* of the dissolved  $H_2$  gas, and is not related to whether or not electricity was used to produce the hydrogen water. Research clearly shows that the *dissolved  $H_2$  gas* is responsible for the therapeutic benefit, not some other property of the water. Also, as we will see later, the magnitude of the negative ORP measurement does not provide any useful information about the level of the dissolved hydrogen gas in the water.

A negative ORP does not always indicate therapeutic benefit. Some toxic substances can *also* produce a negative ORP in water. It is important to know what substance in the water is responsible for producing the negative ORP.

## ORP and Voltage Potential

We have mentioned “ORP” a few times now, but what is it? ORP is an acronym for “Oxidation-Reduction Potential”, a measurement which provides an indication of water’s tendency to act as either an oxidizing or reducing agent. Discussions about ORP usually focus on the “O” and the “R” (oxidation & reduction), but detailed descriptions about the “P” (potential) component are less often seen. While it is apparent that the ORP measurement, expressed in units of “millivolts” (mV, 1/1000 of a volt), describes some type of *electrical potential*, what is the nature of this potential, and what does the measured voltage potential really tell us about the water?

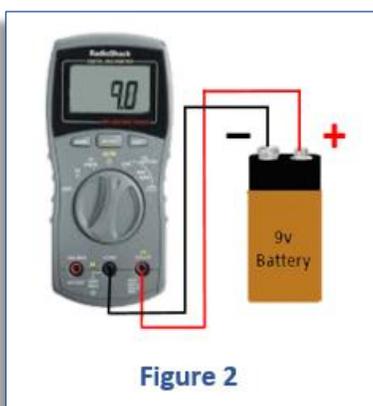


Figure 2

By definition, voltage is “the difference in electrical potential energy, per unit of charge, between two points”. The phrase “between two points” is important. A single object cannot have a “voltage”. For example, although the battery in **Figure 2** may be described as a “nine volt battery”, the battery itself does not “have a voltage of nine volts”. The nine volt potential exists *only between the two terminals of the battery*, the positive terminal, which is deficient in electrons, and the negative terminal, which has a surplus of electrons. In the same way that elevation is referenced to sea level, and temperature is referenced to the freezing point of water, voltage always represents the potential difference between two points, a *measured* point and a second, *reference* point. Referring back to **Figure 1**, both of these “points” can be seen, the platinum ORP sensor electrode, and the internal reference electrode.

Voltage potential represents the ability to do some amount of work using electricity (the flow of electrons). A battery has the *potential* to do work (even though it’s not doing work when sitting in a drawer). The work it can do covers a wide variety of everyday things, such as lighting a flashlight or powering a TV remote. Using a standard digital voltmeter (DVM), we can measure the stored potential in the battery, and, although the meter can tell us the electrical potential of the electrons stored in the battery, it cannot, by itself, tell us whether the battery is 100% charged, or 25% charged; it may

light our flashlight for an hour, or for only a few seconds. In either case, when placed into a device, the battery will deliver its “unknown quantity” of stored electrons, driven by a potential difference of nine volts, until they are depleted. When discussing voltage potential and electrons, we are referring only to the *tendency* of electrons to transfer between species, *not the quantity of electrons that will transfer*; the larger the measured potential, the greater the tendency. However, whether or not they actually do transfer, or *how many* transfer, when the battery is placed into a circuit, depends upon *the resistance of the circuit to the flow of electrons*. It is important to note that the potential for electron transfer (work) measured by the ORP meter does not necessarily mean that the transfer will ever occur. For example, if the wire connecting the flashlight’s bulb to the battery became corroded, then the resistance of the circuit could become large enough that, regardless of how good the battery was, nine volts might not be enough to overcome the resistance. Just like the electrons in the battery must overcome the resistance of the electrical circuit before they can flow, chemical reactions must be capable of overcoming a similar type of resistance, possibly requiring energy from an outside source (e.g. a catalyst) before they can occur.

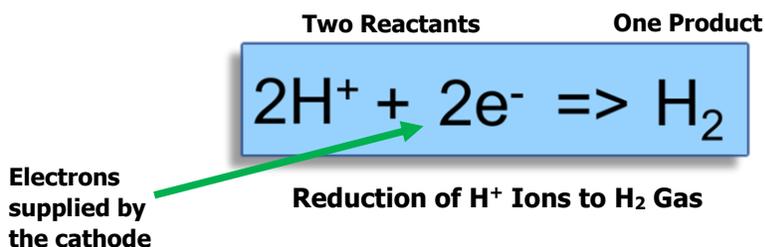
ORP measurements only measure “potential”, and do not guarantee that a particular reaction will occur. Other factors such as temperature, activation energy, and reaction rates must also be favorable.

Within the human body, some less-obvious forms of work are done, for example, the neutralization of a free radical by an antioxidant. Whether or not water having a negative ORP actually *does* act as an antioxidant inside the body depends, not only on what agent is responsible for producing the negative ORP, but the ability of the antioxidant reaction in question to overcome specific types of “chemical” resistance. Therefore, while in chemistry the term “potential” refers specifically to *voltage* potential, in this context, potential also conveys a second meaning, that of “possibility”. And, as we have seen, while the negative ORP demonstrates the *potential* for a reaction to occur, other factors must also be favorable before the reaction actually *can* occur.

## Oxidation and Reduction

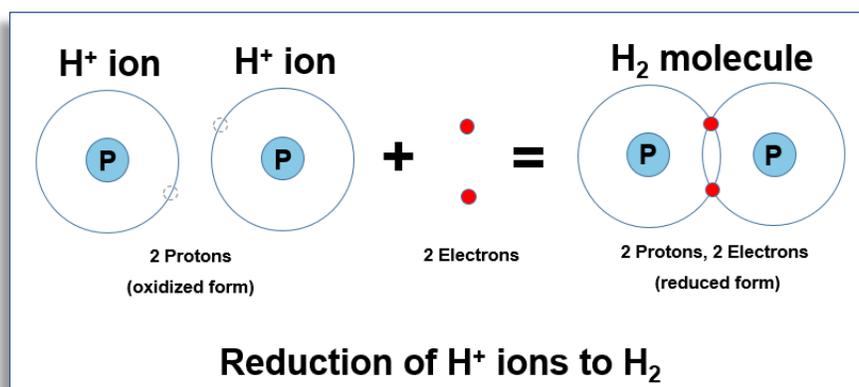
Now that we understand the “P” in “ORP”, we should also discuss the “O”, which refers to “oxidation”, and the “R”, which refers to “reduction”. Oxidation and reduction reactions are chemical reactions that involve the transfer of electrons between two different species (ions, atoms or molecules), one having a tendency to accept electrons (electron deficient), and another, having a tendency to donate electrons (a surplus of electrons). Chemists call these reactions “redox” reactions. Oxidation and reduction reactions always occur together; i.e., when one species loses electrons, another must gain those electrons. The species that loses electrons undergoes **oxidation**, and the species that gains electrons undergoes **reduction**. An easy way to remember oxidation and reduction is the mnemonic **OIL-RIG**: “**Oxidation is Loss, Reduction is Gain**”. Because electron configurations determine the chemical properties of a substance, the transfer of electrons, which changes the electron configurations of the reactants, results in products that have a different set of chemical characteristics. The reactions that produce H<sub>2</sub> and O<sub>2</sub> gas during the electrolysis of water are examples of oxidation and reduction reactions which occur simultaneously at the anode and cathode submerged in the water. During electrolysis, the cathode supplies the electrons that *reduce* hydrogen ions<sup>2</sup> to hydrogen molecules. **Equation 1** describes the production of H<sub>2</sub> gas at the negative cathode.

During electrolysis, the electrons added to the water at the cathode bond with hydrogen ions. They do not float in the water as “free electrons”.



**Equation 1**

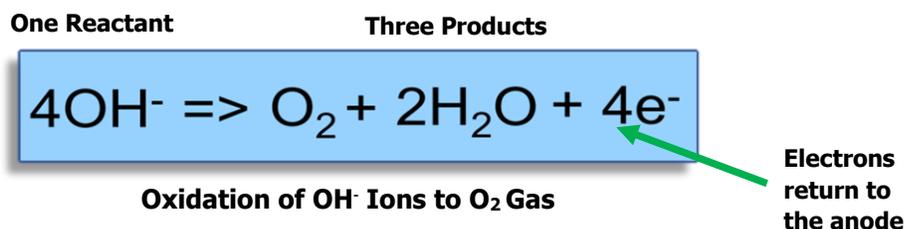
The reactants, hydrogen ions ( $H^+$ ) and electrons ( $e^-$ , supplied by the cathode), are on the left side of the equation. On the right side, there is only one product, molecular hydrogen gas ( $H_2$ ). Two hydrogen ions undergo reduction as they accept electrons from the cathode, form two hydrogen atoms, which then “pair-up” to form one hydrogen molecule. **Figure 3** shows a pictorial representation of the reduction reaction of Equation 1:



**Figure 3**

Notice that, prior to the reaction, the two  $H^+$  ions start with no electrons (only protons), and after the reaction is complete, the  $H_2$  molecule contains two shared electrons. Because electrons are charged particles, this disparity in electrons results in an *energy potential* between the two species. When dissolved in water, these two species represent the water’s *potential* to do work, and will, just like the battery in **Figure 2**, produce a corresponding voltage potential (ORP) at the surface of the meter’s platinum electrode. Any change in the *concentration*<sup>3</sup> of either one will result in a change in the voltage potential that they produce at the ORP electrode.

Before we leave the subject of oxidation and reduction, we mentioned earlier that each reduction reaction must be accompanied by a simultaneous oxidation reaction. **Equation 2** shows the accompanying oxidation reaction at the positive anode during electrolysis, where hydroxide ions ( $OH^-$ ) are oxidized to produce oxygen gas ( $O_2$ ), water ( $H_2O$ ), and electrons. These electrons are returned to the anode connected to the positive terminal of the power supply.



**Equation 2**

Because the waters produced at the anode and cathode are usually isolated from each other with a membrane so that they cannot mix, the water from the secondary hose (lower, acid hose) will measure a *positive* ORP. This is because, rather than the  $H^+/H_2$  redox couple, this water will contain a *different* redox couple (usually an oxygen species), which produces a positive reduction potential. Other types of devices, such as Brown’s gas generators, which do not use a membrane, will produce water containing *both* dissolved oxygen and hydrogen gas, and this water will therefore contain both oxidizing and reducing redox couples at a pH closer to neutral. Because our discussion about ORP focuses on the reaction at the cathode that produces hydrogen gas, we will not spend time examining the anode reaction in detail.

## Redox potential and the redox couple

Reduction Half-Reaction	$E^{\circ}$ (V)
$F_2(g) + 2 e^- \rightarrow 2 F^-(aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \rightarrow 2 H_2O(l)$	1.78
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
$Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.36
$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	1.23
$Br_2(aq) + 2 e^- \rightarrow 2 Br^-(aq)$	1.09
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2 H^+(aq) + 2 e^- \rightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2 e^- \rightarrow 2 I^-(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 4 OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2 e^- \rightarrow Sn^{2+}(aq)$	0.15
<b><math>2 H^+(aq) + 2 e^- \rightarrow H_2(g)</math></b>	<b>0</b>
$Pb^{2+}(aq) + 2 e^- \rightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2 e^- \rightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2 e^- \rightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$	-0.76
$2 H_2O(l) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3 e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

**Table 1**

Chemists have assigned voltage potentials to different chemical species according to their tendency to acquire electrons. These voltage potentials are called “standard reduction potentials”. **Table 1** is a table of standard reduction potentials. It lists reduction potentials for various species under **standard conditions** of concentration, pressure and temperature. Their values are calculated *relative* to the standard hydrogen electrode (SHE), which has been assigned an arbitrary potential of 0.00 mV (highlighted in blue). The strongest reducing agents will have the most negative potentials, and the strongest oxidizing agents will have the most positive potentials. Table 1 lists reduction potentials under **standard conditions**, but ORP meters are used to measure the potential of water under **non-standard conditions**. Thinking back to our earlier discussion about voltage potential, you will recall that we described it as *a difference in potential between two points*, the measured point (water sample), and a reference point (reference electrode). This potential, expressed in millivolts, is called “**redox potential**” (or ORP), and is a measurement of the electrical potential energy produced by a *pair* of species in the water, one in oxidized form and the other in reduced form, each at some concentration. The name given to this pair of oxidized and reduced species is **redox**

**couple**. A redox couple is comprised of either a strong reducer & weak oxidizer, or a strong oxidizer & weak reducer. As their dissolved concentrations change, the redox potential of the water itself also changes. The magnitude of the ORP reading, as well as whether it is positive or negative, depends on which redox couple we are discussing, as well as the relative concentrations of each species in the redox couple. A positive ORP indicates that the water will have the *tendency* to act as an oxidizing agent, while a negative ORP indicates that the water will have a *tendency* to act as a reducing agent.

Negative ORP does not indicate that the water has an *electrical charge*, but rather that it contains  $H_2$  gas, a reducing agent. Positive and negative ions must balance in water, insuring that the water itself remains electrically neutral.

## The hydrogen redox couple

While there are many redox couples in chemistry, when discussing hydrogen water and ORP, we are concerned with one particular redox couple, the  **$H^+/H_2$  redox couple**<sup>4</sup>. Earlier we showed the equation which describes the redox reaction in during which two hydrogen ions ( $H^+$ ) accept two electrons to form one molecule of  $H_2$  gas.



**Equation 3**

In **Equation 3**, you can see the two species which comprise the redox couple. “ $H^+$ ” is the oxidized form of hydrogen, containing no electrons, and “ $H_2$ ” is the reduced form, containing two electrons (see Figure 3). Because the  $H^+$  ion is a single proton that has no electrons to donate, it can act only as an oxidizing agent and accept electrons. Conversely, because the  $H_2$  molecule contains two electrons, it can (under the right conditions) donate them, and act as a reducing (or anti-oxidizing) agent. Later, we will see how the simultaneous presence in the water of both  $H_2$  gas and  $H^+$  ions produces a negative ORP.

## pH

As we will see later, the pH of the hydrogen water being tested has a strong influence on the ORP reading. Therefore, it is important to understand some basic concepts about pH.

Hydrogen ions are the acid component in water. Therefore, the higher the H<sup>+</sup> ion concentration, the more acidic the water is. pH, which stands for “potential of hydrogen”, is a measure of the concentration of hydrogen ions (H<sup>+</sup>) in water. When discussing the quantities of atoms, molecules ions, etc., the numbers can be extremely large or small. The pH scale was devised as a convenient way to express these types of numbers as powers of ten (exponents), instead of using equivalent (but more cumbersome) mathematical expressions such as 1 x 10<sup>-7</sup> or 0.0000001. The pH scale, which goes from 0 to 14, is a logarithmic scale in which the concentration of H<sup>+</sup> ions is expressed as a negative power of 10. **Equation 4** is the equation used to calculate pH.

The pH scale has a range of 0-14, but pH measurements can be less than zero (very strong acids) or greater than 14 (very strong bases).

$$\text{pH} = -\log_{10} [\text{H}^+]$$

**Equation 4**

Because pH is a logarithmic function, each **unitary** change in pH represents a **ten-fold** change in the hydrogen ion concentration. As a result, very large changes in the H<sup>+</sup> concentration are expressed as powers of ten. The presence of the minus sign before the “log” function allows the pH to be expressed, for simplicity, as only positive numbers, but also means that increases in the pH represent a *decrease* in the concentration (and vice-versa). Therefore, a pH of zero contains a very high concentration of H<sup>+</sup> ions, while a pH of 14 has a very low H<sup>+</sup> concentration.

The “potential of hydrogen” is often confused to mean “the potential of hydrogen gas”. However, pH is not associated with dissolved H<sub>2</sub> gas. Adding pure H<sub>2</sub> gas to water (e.g. by bubbling) *will not* change the water’s pH. However, certain methods used to produce hydrogen water may *indirectly* raise the water’s pH. For example, in an alkaline ionizer, during the electrolysis of water (which reduces H<sup>+</sup> ions to H<sub>2</sub> gas at the cathode), the water’s pH is raised, not because of the presence of H<sub>2</sub> gas, but because, as the H<sup>+</sup> ions (acid) are consumed, the level of OH<sup>-</sup> ions (base) increases. Recently, new hydrogen water technologies have emerged that focus on maximizing dissolved hydrogen levels while producing water at a pH closer to neutral.

The name “hydrogen” can refer to any one of four *different* species:

- 1) H<sup>+</sup>, positive hydrogen ion
- 2) H, hydrogen atom
- 3) H<sup>-</sup>, negative hydrogen ion
- 4) H<sub>2</sub>, hydrogen molecule

The term “pH” always refers to H<sup>+</sup>, the positive hydrogen ion.

Hydrogen Ion Concentration					
Decrease in H <sup>+</sup> Ion Concentration →	pH	Moles of H <sup>+</sup> Ions	Units	Number of H <sup>+</sup> Ions	
	0	1	1 x 10 <sup>0</sup>	1 mole	6.02 x 10 <sup>23</sup>
	1	0.1	1 x 10 <sup>-1</sup>	0.1 mole	6.02 x 10 <sup>22</sup>
	2	0.01	1 x 10 <sup>-2</sup>	0.01 mole	6.02 x 10 <sup>21</sup>
	3	0.001	1 x 10 <sup>-3</sup>	1 millimole	6.02 x 10 <sup>20</sup>
	4	0.0001	1 x 10 <sup>-4</sup>	0.1 millimole	6.02 x 10 <sup>19</sup>
	5	0.00001	1 x 10 <sup>-5</sup>	0.01 millimole	6.02 x 10 <sup>18</sup>
	6	0.000001	1 x 10 <sup>-6</sup>	1 micromole	6.02 x 10 <sup>17</sup>
	7	0.0000001	1 x 10 <sup>-7</sup>	0.1 micromole	6.02 x 10 <sup>16</sup>
	8	0.00000001	1 x 10 <sup>-8</sup>	0.01 micromole	6.02 x 10 <sup>15</sup>
	9	0.000000001	1 x 10 <sup>-9</sup>	1 nanomole	6.02 x 10 <sup>14</sup>
	10	0.0000000001	1 x 10 <sup>-10</sup>	0.1 nanomole	6.02 x 10 <sup>13</sup>
	11	0.00000000001	1 x 10 <sup>-11</sup>	0.01 nanomole	6.02 x 10 <sup>12</sup>
	12	0.000000000001	1 x 10 <sup>-12</sup>	1 picomole	6.02 x 10 <sup>11</sup>
	13	0.0000000000001	1 x 10 <sup>-13</sup>	0.1 picomole	6.02 x 10 <sup>10</sup>
14	0.00000000000001	1 x 10 <sup>-14</sup>	0.01 picomole	6.02 x 10 <sup>9</sup>	

**Table 2**

Technologies have emerged that focus on maximizing dissolved hydrogen levels while producing water at a pH closer to neutral.

**Table 2** shows the relationship between pH and the hydrogen ion concentration. The concentration of H<sup>+</sup> ions determines whether the water is acidic (below 7) or basic (above 7), with 7 representing a neutral pH. This table helps us to see the exponential (logarithmic) relationship between the pH and the actual number (concentration) of H<sup>+</sup> ions. It should come as no surprise that, because the H<sup>+</sup> ion is one of the two species in the redox couple, the water’s pH has a direct influence on the ORP reading. In the next section, we will introduce the Nernst equation, a mathematical tool which will help us evaluate this influence.

## The Nernst equation

The Nernst equation, named after the German chemist Walther Nernst who first formulated it, is an equation that relates the standard reduction potential of an electrochemical reaction to the concentration, pressure, and temperature of a chemical species undergoing reduction and oxidation under non-equilibrium conditions. It is the most important equation in the field of electrochemistry. **Equation 5** shows the general form of the Nernst equation:

$$E_{mv} = E^0 - \left( \frac{RT}{zF} \right) \ln \frac{[\text{red}]}{[\text{ox}]}$$

**Equation 5**

In this article, we will use the Nernst equation to analyze<sup>5</sup> the contributions of both dissolved hydrogen gas *and* pH to predict how much each one influences the ORP reading. In order to use the Nernst equation to predict ORP values for water containing dissolved hydrogen gas, we need to modify its general form slightly. Because  $E^0$ , the standard cell potential, is zero for hydrogen (see Table 1), we can eliminate that term. We will also substitute the terms “[red]” and “[ox]” with the reduced and oxidized forms of hydrogen,  $H_2$  and  $H^+$ , respectively.

The final form of the Nernst equation we will be using is shown in **Equation 6**:

$$E_{mv} = - \left( \frac{RT}{zF} \right) \ln \frac{[H_2]}{[H^+]^2}$$

**Equation 6**

Since the hydrogen water we measure does not exist under standard conditions, the Nernst equation allows us to substitute any values of concentration, pressure and temperature we choose, and predict the redox potential under non-standard conditions. Using the Nernst equation, we can experiment with different values for  $H_2$  and  $H^+$ , and analyze their predicted effect on the ORP. The following are definitions for the terms and values used in the Nernst equation:

- $E_{mv}$ , Nernst potential in millivolts (ORP);
- $E^0$ , standard cell potential, 0.00v;
- R, universal gas constant,  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- T, temperature, 298.15°K (25°C/77°F);
- z, # of electrons transferred in the reaction, 2;
- F, Faraday constant,  $96485.33 \text{ C mol}^{-1}$  (electron charge per mole)
- $[H_2]$ , hydrogen gas concentration (in partial pressure,  $p_{H_2}$ );
- $[H^+]$ , hydrogen ion concentration (derived from the pH).

ORP values predicted by the Nernst equation are calculated under ideal conditions. While actual field measurements of ORP will vary depending on a number of factors, the relationships between pH,  $H_2$  and ORP will remain the same.

In order to automate the calculation of the predicted ORP under a variety of temperature/ $H_2$ /pH scenarios, the math of the Nernst equation was programmed into a calculator (using MS-Excel/VBA). The calculated results for each scenario were then used to create the  $H_2$ , pH & ORP data table (x,y ordered pairs) required for plotting the various graphs used in this article. **Figure 4** shows the user interface for the Nernst calculator, which displays not only the predicted ORP, but most of the intermediate results:

Nernst ORP Calculator		
Temp (°C) =	25.0	H <sub>2</sub> mg/L = 1.60    pH = 7.0
User-Entered Temp (°C) : 25.0		
User-Entered H <sub>2</sub> Concentration in (mg/L) : 1.6		
User-Entered pH (H <sup>+</sup> ) : 7.00		
Calculation Summary		
Value of RT/zF (mv) : 12.85		
Convert H <sub>2</sub> conc. to pH <sub>2</sub> : 1.02E+00		
Convert pH to (H <sup>+</sup> ) <sup>2</sup> (mol/L) : 1.00E-14		
Divide pH <sub>2</sub> by (H <sup>+</sup> ) <sup>2</sup> (calculate Q) : 1.02E+14		
Calculate the natural log of Q : 3.23E+01		
Multiply by -RT/zF : -414.270		
Predicted ORP value (millivolts) : <b>-414.27</b>		

Figure 4

While it is not our purpose to discuss the Nernst equation in detail, a closer look at the last term in equation 6 will give us some important insight into how the ORP is calculated. Figure 5 shows the two species from the Nernst equation which form our “redox couple of interest”:

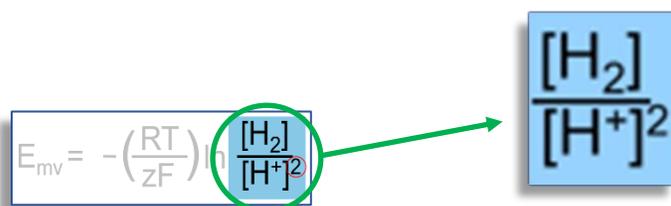


Figure 5

As we discussed earlier, these two forms of hydrogen (oxidized and reduced forms) represent the *two species* in the water whose concentrations contribute to the water’s redox potential. While water will normally contain multiple redox couples, whose redox potentials combine to produce the overall ORP, in our analysis, we will consider only the H<sup>+</sup>/H<sub>2</sub> redox couple.

The “[H<sub>2</sub>]” term represents the concentration of dissolved hydrogen gas (in terms of partial pressure, pH<sub>2</sub>), and the “[H<sup>+</sup>]” term represents the concentration of hydrogen ions (which we calculate from the water’s pH). Therefore, the ORP reading is not dependent on the concentration of the dissolved hydrogen gas alone, but on the concentrations of *both* the H<sub>2</sub> *and* H<sup>+</sup>. As we will see, each of these species contributes to the ORP reading. Since we have seen that the dissolved H<sub>2</sub> is *responsible* for the negative ORP, this implies *some* relationship between the two, and raises a few questions:

- How much dissolved H<sub>2</sub> is required to produce a negative ORP?
- How much does the ORP respond to changes in the H<sub>2</sub> concentration?
- Can we use the ORP reading to measure the level of dissolved H<sub>2</sub>?
- Can we use the ORP readings from two different samples to compare their relative dissolved H<sub>2</sub> concentrations?

The Nernst equation will help us answer these questions by permitting us to analyze how changes in H<sup>+</sup> & H<sub>2</sub> influence the ORP reading.

## How much dissolved H<sub>2</sub> is required to produce a negative ORP?

You might be wondering, “What level of dissolved H<sub>2</sub> is required to produce a negative ORP”? To determine the amount of H<sub>2</sub> required to produce even a “moderate” level of negative ORP, we can use the Nernst equation to predict the ORP at various H<sub>2</sub> concentrations, while maintaining the pH at seven (the answer may surprise you!)

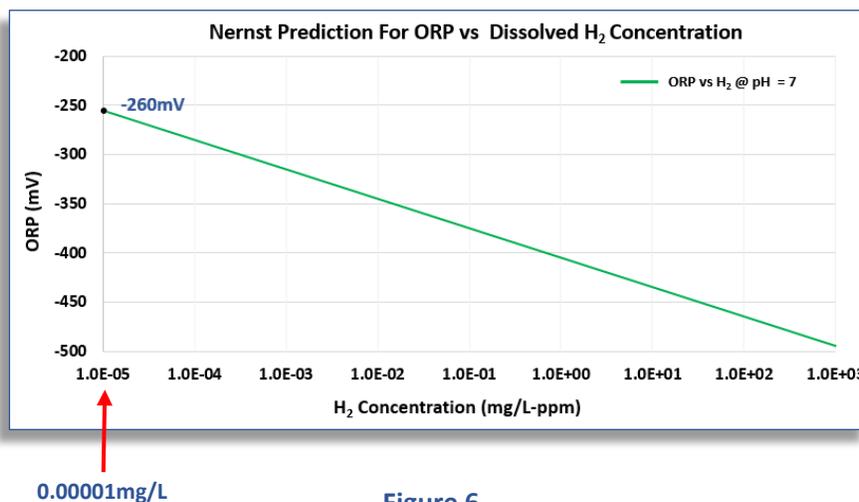


Figure 6

The graph in **Figure 6** shows that, at a pH of 7, an H<sub>2</sub> concentration of only  $1 \times 10^{-5}$  mg/L (0.00001mg/L), or *one hundred-thousandth of a milligram per liter* (orders of magnitude below the level considered to be therapeutic), is all that is necessary to produce a negative ORP of -260mV. Keep in mind that a dissolved H<sub>2</sub> level this small will only produce this value of negative ORP “on paper” using the Nernst equation, when no other redox couples in the water are being considered. In fact, if a water sample actually did contain such an extremely low level of dissolved H<sub>2</sub>, other *oxidizing* redox couples also present in the water (e.g. an oxygen species) would overpower the negative redox potential generated by the H<sup>+</sup>/H<sub>2</sub> redox couple, and the water would instead measure a positive ORP. However, this demonstrates the very low level of H<sub>2</sub> required to produce a negative ORP, and, as we shall see, shows us how little the negative ORP reading can actually tell us about how much dissolved H<sub>2</sub> the water contains.

To produce a slightly negative ORP, only an *infinitesimal* amount of dissolved hydrogen is required. At pH 7,  $1 \times 10^{-13}$  mg/L (0.1 trillionths of one mg/L) will produce an ORP of -24 millivolts.

## The relationship between dissolved H<sub>2</sub> concentration and ORP

When analyzing situations in which there are two or more variables, each of which have an impact on the final outcome being measured (here, the ORP), analysts will use the technique of changing only one variable at a time, while keeping the others at some constant value, in order to see how that variable alone influences the outcome. In this way, the individual effect that each variable has on the outcome can be observed. In our case, we have only two variables of interest, the concentrations of H<sub>2</sub> and H<sup>+</sup>, both of which have some influence on the ORP. Therefore, in order to examine the effects that changes in *only* the H<sub>2</sub> concentration have on the resultant ORP, we will experiment with different values for the H<sub>2</sub> concentration, while holding the pH constant at seven (later we will do the same thing to analyze the effects of H<sup>+</sup> on ORP). The graph in **Figure 7** below shows the predicted ORP readings for an H<sub>2</sub> concentration range typical for today’s hydrogen water machines, 0.5 to 2mg/L.

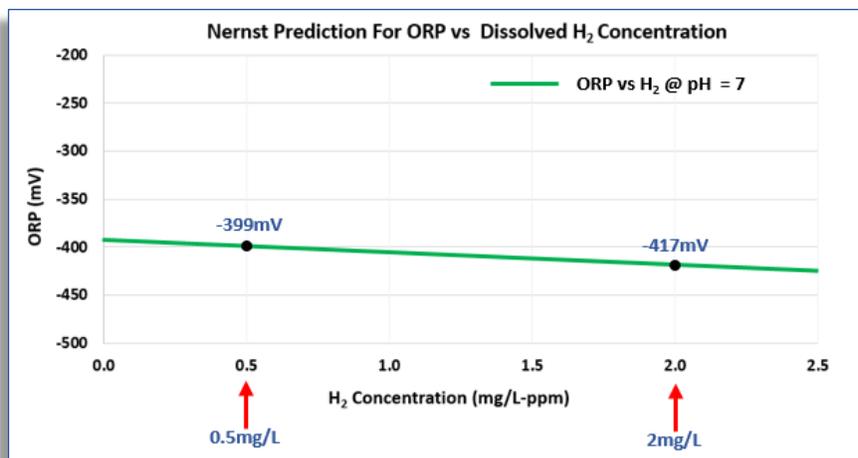


Figure 7

As the dissolved H<sub>2</sub> concentration increases from 0.5mg/L to 2mg/L, the ORP response is very “flat”, falling from -399mV to -417mV, only *18 millivolts more negative!* This means that each change in H<sub>2</sub> concentration of 1 mg/L (a large change in terms of possible therapeutic benefit) will change the ORP reading *by only 12 millivolts!* To emphasize just how small of an influence the dissolved H<sub>2</sub> has on ORP, we can expand the graph’s H<sub>2</sub> range by a massive amount. The graph in **Figure 8** shows the negative ORP readings for dissolved H<sub>2</sub> levels in the range of **0.5 to 50 mg/L!**

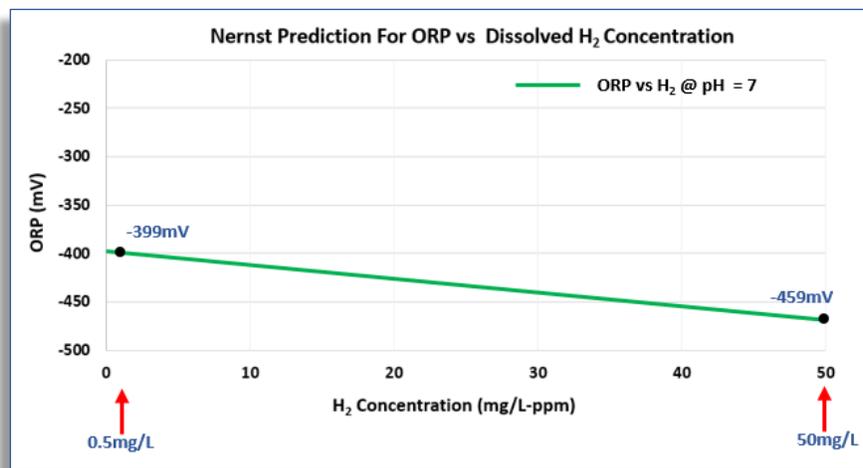


Figure 8

As you can see, even over the *extremely large* range of 0.5 to 50mg/L, the negative ORP increases from -399 mV to -459 mV, *only 60 millivolts more negative!* Although such a high dissolved H<sub>2</sub> level could likely only be achieved under extreme laboratory conditions, nevertheless, this shows us just *how little* the ORP responds to even extremely large changes in the H<sub>2</sub> concentration.

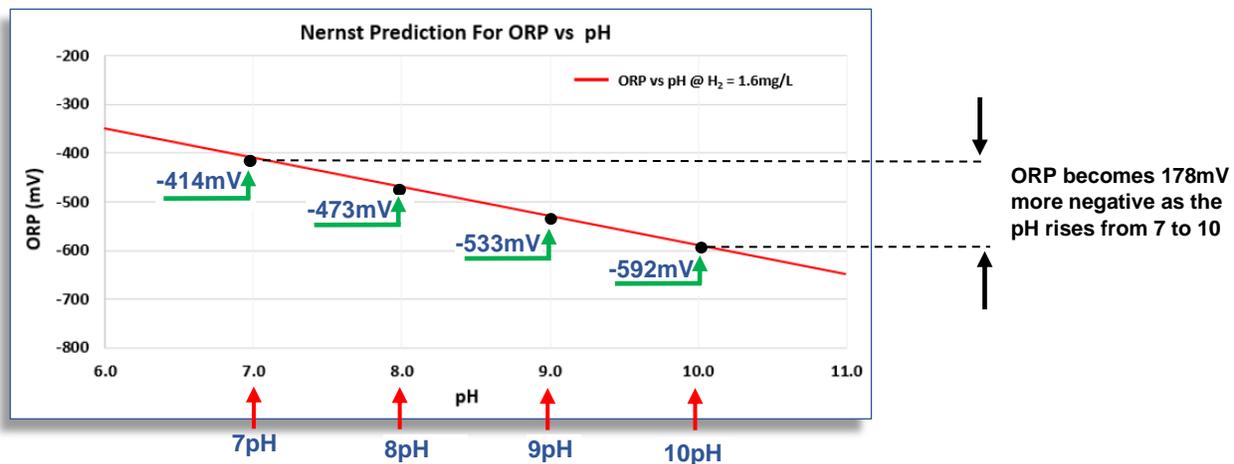
## The relationship between pH and ORP

In the last section, we examined the very small impact that changes in only the  $H_2$  concentration have on ORP, while maintaining the pH at *exactly seven*. In order to examine the impact that changes in *only the pH* have on the ORP, we will now make incremental changes only to the pH, while maintain the  $H_2$  concentration at 1.6mg/L. As you will see, in contrast to the influence of  $H_2$ , the degree to which pH influences the ORP will provide us with even more compelling evidence demonstrating why the ORP reading cannot be used to *measure*  $H_2$ .

Previously, we saw the small impact of changes to the  $H_2$  concentration when entering values into the Nernst calculator from a typical range of  $H_2$  concentrations (0.5 to 2mg/L). As we said, because the concentrations of *both* the  $H_2$  and  $H^+$  species contribute to the ORP, a change in *either one* will produce a change in the ORP reading. An important question to ask is, “do typical changes in each *contribute equally* to the ORP?” To answer this question, let’s now take a look at how changes in pH impact the ORP. In order to do a valid comparison, again we will use, as we did with  $H_2$ , a typical range of pH values.

Because the ORP becomes more positive as the pH decreases, at a pH of zero, a dissolved  $H_2$  concentration of 1.6mg/L will have an ORP of zero millivolts.

The graph in **Figure 9** shows the predicted ORP readings (in millivolts) for four different values of pH, all at the same dissolved  $H_2$  concentration of 1.6 mg/L.



**Figure 9**

The graph shows how a rise in only the pH (while maintaining a constant dissolved  $H_2$  level) influences the ORP reading. At a pH of seven, hydrogen water having a concentration of 1.6 mg/L measures an ORP reading of -414 mV. As the pH increases from seven to ten, notice the large increase in negative ORP, from -414 mV to -592 mV. Over this range of only three pH units, the predicted ORP becomes more negative by *178 millivolts!* Remember that the increase in the negative ORP is the result of *only* the rise in pH (decrease in  $H^+$ ), while the  $H_2$  concentration remains unchanged at 1.6 mg/L.

**Figure 10** below shows this change in ORP graphically:

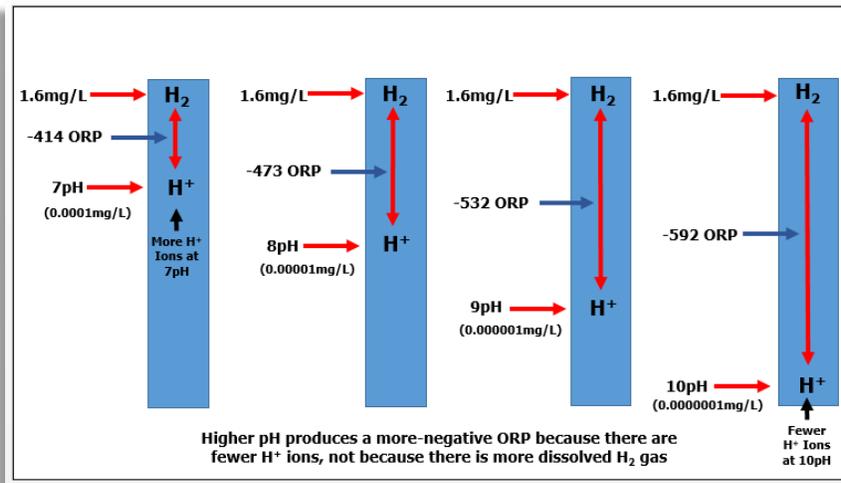


Figure 10

As the pH increases, the  $H^+$  concentration decreases, increasing the negative redox potential produced by the  $H^+/H_2$  redox couple. As a consequence, the ORP reading becomes more negative, not because the dissolved  $H_2$  concentration has *increased*, but because the  $H^+$  concentration has *decreased*; in other words, **not because something was added to the water, but because something was removed from the water!** This large increase in the negative ORP occurs with *no change* in the  $H_2$  concentration. Therefore, because ORP responds almost exclusively to changes in pH, the magnitude of the ORP reading does not provide any useful information about the actual level of dissolved  $H_2$  in the water.

### Comparing the influence of $H_2$ and pH on ORP

Now that we have looked at the *individual* effects that changes in  $H_2$  and pH have on ORP, it is also instructive to examine their effects together, using a specially-formatted graph. **Figure 11** shows an “overlay” graph, which plots the lines for both “ORP vs  $H_2$  concentration” and “ORP vs pH” on the same graph. As before, the graph of “ORP vs pH” (red line) holds the  $H_2$  concentration constant at 1.6mg/L, while the graph of “ORP vs  $H_2$  concentration” (blue line) holds the pH constant at seven. Notice that, for this graph, we have assigned to the horizontal axis two sets of labels, those for *both* the  $H_2$  concentration and pH values, each of which covers their typical ranges, 0.5 to 2mg/L for  $H_2$ , and 7 to 10 for pH. Using one graph to plot both relationships permits us to do a “side-by-side” comparison, and easily see just how differently the ORP responds to changes in each.

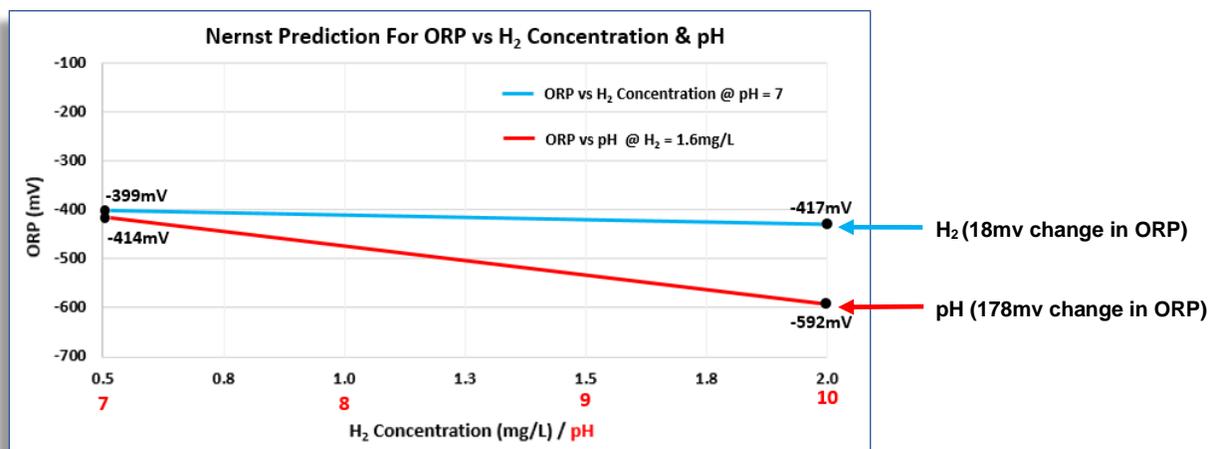
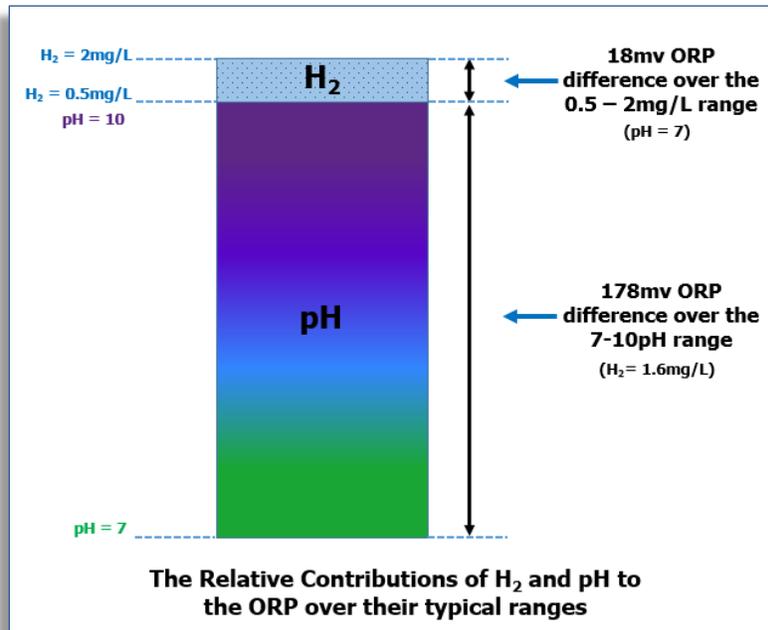


Figure 11

By comparing the slope of each line, we can clearly see the relatively “flat” response of the ORP to changes in H<sub>2</sub>, compared to the much “steeper” response of ORP to changes in pH.

The following graphic in **Figure 12** allows us to see how both H<sup>+</sup> and H<sub>2</sub> impact the ORP reading in terms of the percentage of their contributions:



**Figure 12**

Viewing their relative contributions this way, it can be seen that over a typical range of H<sub>2</sub> concentrations (0.5 to 2mg/L), the ORP will change by a total of only 18mV. In contrast, over a range of 3 pH units, the ORP will change 178mV. While the pH contributes about 90% of the ORP reading, the H<sub>2</sub> contributes only about 10%. Therefore, again we see how the ORP reading is dominated by the pH, while the contribution from the dissolved hydrogen is relatively insignificant.

### Larger negative ORP reading does not mean more dissolved H<sub>2</sub>

We have shown that the negative ORP reading cannot be directly correlated with any particular level of dissolved H<sub>2</sub>. But, is it possible to use the ORP measurements from two different water samples to compare the *relative* amounts of dissolved H<sub>2</sub> they contain? Let’s look at an example that shows why the ORP reading cannot be used *even to compare* dissolved H<sub>2</sub> levels. While the logical assumption might be that the water with the more negative ORP will also contain the highest level of dissolved H<sub>2</sub>, the following example shows why this assumption is *not necessarily* true.

**Table 3** shows the predicted ORP for two hydrogen waters, A and B, having different pH and dissolved H<sub>2</sub> levels:

WATER	ORP	pH	H <sub>2</sub> Level
H <sub>2</sub> Water A	-465mv	8.0	0.8mg/L
H <sub>2</sub> Water B	-414mv	7.0	1.6mg/L

**Table 3**

water A, with a pH of 8 and H<sub>2</sub> level of 0.8mg/L, measures an ORP of -465mV. But, water B, with a pH of 7.0 and an H<sub>2</sub> level of 1.6mg/L (twice as much H<sub>2</sub> as A), only measures an ORP of -414mv. Because A's pH is one pH unit higher than B's, its higher pH produces a *more negative* ORP, even though B has more dissolved H<sub>2</sub>. This scenario demonstrates why it is incorrect to assume that water having a more negative ORP reading has more dissolved H<sub>2</sub>. Some marketers will employ the technique of slowing down an ionizer's water flow to a "trickle" before measuring the ORP. This practice, in fact, usually *will* make the ORP more negative, but primarily *because it elevates the pH*. The more negative ORP *does not* necessarily indicate the presence of any more dissolved H<sub>2</sub>; in fact, the water with the more negative ORP could easily contain *less* H<sub>2</sub>.

## Why does pH have more influence on ORP than H<sub>2</sub>?

As we have seen, the concentrations of H<sub>2</sub> and H<sup>+</sup> both contribute to the ORP measurement, and, as the H<sup>+</sup> concentration changes, the ORP will also change, even with no change in H<sub>2</sub> concentration. In our analysis of the relationship between H<sub>2</sub>, H<sup>+</sup> and ORP, we have seen that the ORP reading responds *in a much greater way* to changes in pH than it does to changes in the levels of dissolved H<sub>2</sub>. However, "Why is this true?" Here is a summary of our findings:

### 1) The pH scale expresses H<sup>+</sup> concentrations as powers of 10.

In our previous discussion on pH, we showed the equation used to calculate it:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

Equation 7

The pH scale expresses changes in H<sup>+</sup> using powers of 10. When the pH increases by one unit, it represents a ten-fold *decrease* in the H<sup>+</sup> ion concentration ( $10^1 = 10$ ). This means that an increase in pH of two units represents a one hundred-fold decrease ( $10^2 = 100$ ), and a three-unit change, a one thousand-fold decrease in H<sup>+</sup> ( $10^3 = 1000$ ). Because changes in pH represent *exponential* changes in the H<sup>+</sup> concentration, even changes in pH that seem to be small can, in fact, represent *very substantial changes in the actual H<sup>+</sup> concentration*. And, since the pH of hydrogen water can easily span 3 units of pH (even more if you consider hydrogen water whose pH is below 7), the *H<sup>+</sup> concentration* of various H<sub>2</sub> waters can conceivably vary by a factor of 10,000 or more! Finally, keep in mind that pH is only a *mathematical representation* of the actual H<sup>+</sup> concentration (notice that pH is unitless), but the ORP electrode responds *to the actual H<sup>+</sup> concentration*, not the pH.

### 2) Concentrations of H<sub>2</sub> are expressed using a linear scale.

Unlike H<sup>+</sup> concentrations, which are expressed using a logarithmic scale (pH), H<sub>2</sub> concentrations are expressed using a *linear* scale, milligrams per liter (mg/L), and typically cover a much smaller concentration range than H<sup>+</sup>. Consequently, compared to the large changes possible in H<sup>+</sup>, changes in H<sub>2</sub> typically represent relatively small changes. For example, if we were to express H<sub>2</sub> concentrations as powers of ten like pH, then our concentration range 0.5 to 5mg/L would only represent a change in concentration of a factor of *a single power of ten* (a ten-fold change), not even close to the factor of 10,000 possible with pH. This inequality in the concentration ranges between H<sub>2</sub> and H<sup>+</sup> again helps to explain why H<sub>2</sub> has a much smaller impact on the ORP reading than pH. It is important to note here that, although a change in H<sub>2</sub> level of only 1 or 2 mg/L appears to be small, and does, in fact, have an imperceptible impact on the ORP reading, it is, nevertheless, from the standpoint of therapeutic benefit, *very significant*. Therefore, although we cannot use ORP to measure such small changes, we must have a method for measuring differences in H<sub>2</sub> concentration of only a few mg/L.

### 3) The Nernst equation performs an exponential math operation on the [H<sup>+</sup>] term.

If we look again at the hydrogen gas reaction equation along with the Nernst equation showing the hydrogen redox couple, we can see another reason for the large influence of pH on the ORP reading:

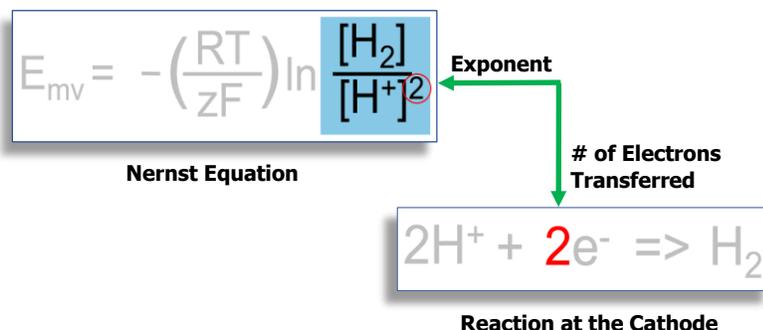


Figure 13

In the blue box of **Figure 13**, notice that the bottom term, “[H<sup>+</sup>]”, includes the exponent “2” outside of the brackets (circled in red), while the top term, [H<sub>2</sub>], does not. Look at the equation underneath to see where this exponent comes from. The Nernst equation requires that the number of electrons (measured in “moles”) required to convert the oxidized species of the redox couple (H<sup>+</sup>) to its reduced form (H<sub>2</sub>), must be expressed as an *exponent* for the [H<sup>+</sup>] term. The explanation for this is beyond the scope of our discussion; however, since by definition, reduction is a gain in electrons, it makes sense that the quantity of electrons required for the reduction reaction must be included when calculating the reduction potential. This exponent of “2” means that we must *square* the H<sup>+</sup> concentration (multiply the [H<sup>+</sup>] term by itself), whose value *is already an exponential representation of the H<sup>+</sup> concentration!* (because pH is an exponential scale). However, no similar exponential function is performed on the [H<sub>2</sub>] term. This exponential math operation required by the Nernst equation helps to explain how a seemingly small change in the water’s pH (of even just a few tenths) can result in such a large impact on the ORP reading, overpowering the relatively insignificant influence of the H<sub>2</sub> concentration on the ORP.

Considered together, points 1 through 3 clearly show why changes in pH, even those that appear to be small, represent *exponentially* larger changes in the actual H<sup>+</sup> concentration. Consequently, the large influence of pH on the ORP measurement overpowers the small influence of H<sub>2</sub>, and essentially “controls” the ORP reading.

## Dissolved hydrogen meters

Relatively inexpensive consumer-grade digital hydrogen meters are available on the market, costing approximately \$500. While widely used and accepted, these meters *do not specifically/selectively measure* dissolved hydrogen gas. Their design is, based on ORP technology, and, rather than using expensive hydrogen gas probes, instead use non-selective ORP electrodes to measure the water's reduction potential. But, these meters should not be confused with more sophisticated technologies which *are able* to measure hydrogen. For example, gas chromatography mass spectrometer (GC-MS) technology can be used to measure dissolved hydrogen, but can easily cost \$100,000 or more. Also, there are digital hydrogen meters which incorporate ultra-sensitive hydrogen gas probes (polarographic/voltammetric), but, meters like this can still cost \$10,000 or more. These technologies, designed primarily for scientific and industrial use, are very expensive, and beyond the reach of the average consumer. In this section, we will assess, based on our previous discussions about the relationship between H<sub>2</sub>, pH and ORP, the ability of the ORP-based dissolved hydrogen meter to accurately measure dissolved H<sub>2</sub>. ORP-based dissolved hydrogen meters attempt to determine the dissolved H<sub>2</sub> level by measuring the water's redox potential which, as we have seen, results mostly from the contribution of the H<sup>+</sup> species of the H<sup>+</sup>/H<sub>2</sub> redox couple, (represented by pH), and also, to a relatively insignificant degree, from the H<sub>2</sub> species of the redox couple.



The meter attempts to determine the H<sub>2</sub> concentration from the ORP measurement using the following process:

- 1) The Nernst predictions for the ORP of 7pH H<sub>2</sub> water are factory-programmed into the meter's computer firmware;
- 2) The redox potential of the sample water (in mV) is determined by the meter's ORP and reference electrodes and processed by the electronics section;
- 3) The dissolved H<sub>2</sub> level of the sample is calculated by comparing the redox potential of the sample (whose pH is assumed to be *exactly* 7) to the Nernst predictions for the ORP of 7pH hydrogen-infused water stored in the computer's firmware.
- 4) The H<sub>2</sub> level in PPB/PPM is displayed on the meter's LCD screen.

For example, we can see from the graph in **Figure 14** that, at a pH of exactly seven, waters containing two different dissolved H<sub>2</sub> levels, 0.1mg/L and 2mg/L, are predicted by the Nernst equation to have ORP values of -379mV and -417mV respectively

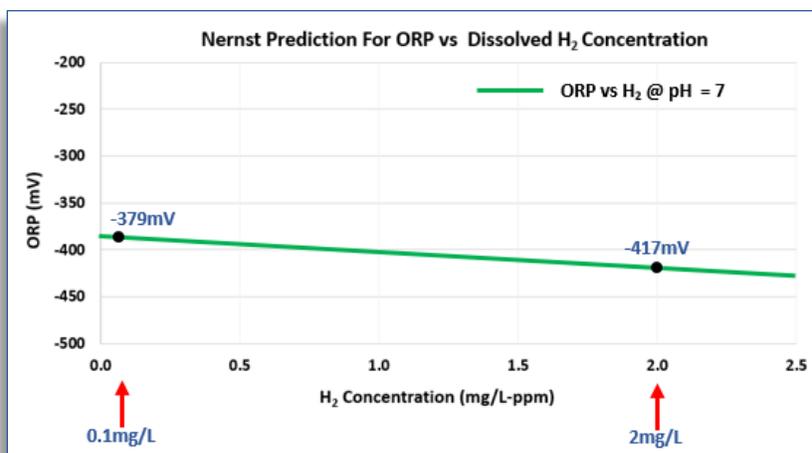


Figure 14

(2ppm is the typical upper limit for this type of meter). Therefore, it seems logical that, if our water sample has a pH of exactly 7, and if its ORP measures -379mV, it should, in fact, have a dissolved H<sub>2</sub> level of 0.1mg/L; likewise, if its ORP measures -417mV, it should have a dissolved H<sub>2</sub> level of 2mg/L. And, if the measured ORP falls somewhere in between these two, it is a simple matter for a computer to interpolate the reading and display the corresponding H<sub>2</sub> level.

However, consider the following points:

1) Water will rarely have a pH of *exactly* 7, and any deviation, even as small as ½ of a pH unit, will change the ORP reading *by almost as much as the entire contribution made by the dissolved H<sub>2</sub>* over the range of 0.1 to 2mg/L (30mV vs 38mV). Because the meter does not measure the pH, (there would be no practical procedure for correcting the water's pH to exactly 7 if it *was* measured), this inevitable variance in the water's pH will prevent the use of the redox potential to accurately measure H<sub>2</sub>.

2) In our discussion about the Nernst predictions for ORP, we said that we would not be considering *other redox couples in the water*, which *also* contribute to the measured ORP (another form of the Nernst equation can predict the redox potential for multiple redox couples). But, water does normally contain other redox couples, which will contribute a *positive* redox potential, and work in opposition to the negative ORP produced by the dissolved hydrogen. However, even though we are aware of their presence, there is no simple way to measure and “subtract out” their contributions to the overall ORP. Therefore, they will influence the ORP measurement in an unpredictable way and skew the H<sub>2</sub> measurement.

## Observations about the shortcomings of ORP technology

Our analysis of the relationship between H<sub>2</sub> concentration, pH and ORP used the results predicted by the Nernst equation when entering selected values for both pH and H<sub>2</sub> concentrations. When comparing real-world ORP measurements with the predicted results, actual ORP readings will deviate, possibly significantly, for a variety of reasons. The reasons are associated, not only with the water being tested, but with the ORP meter itself. Keep in mind that, while ORP meters cannot be used to measure H<sub>2</sub>, they also have a number of inherent shortcomings, limiting their usefulness for even their designed purpose, *measuring ORP*.

While we did not discuss pH meters, their design is very similar to the ORP meter, and therefore they suffer from most of the same limitations

- ORP meter probes will accumulate organic matter/minerals and produce inaccurate readings if not kept clean.
- Depending on the presence of ions or other chemical species in the water, which contribute to the overall redox potential, actual ORP readings will deviate from the predicted results.
- Temperature will influence ORP, but most consumer-grade ORP meters do not compensate for temperature.
- ORP measurements are time-sensitive, but there is no standard amount of time to wait before taking a reading.
- Stirring may be required to stabilize the reading, but there is no standard for how much to stir the sample.
- ORP probes may last for years, but they do have a lifespan and will eventually fail to give accurate readings.
- As the pH rises, the concentration of H<sup>+</sup> ions may become so low that the ORP electrode has difficulty detecting them, resulting in spurious ORP readings.

Therefore, in addition to their inability to directly measure dissolved H<sub>2</sub>, any “hydrogen meter” built on the ORP platform will also have these additional inherent weaknesses.

## Applying these results to other hydrogen-water devices & technologies

In recent years, many new types of hydrogen water technologies have emerged. Regardless of the method used to create the hydrogen water, the relationships we have seen between  $H_2$ , pH and the predicted ORP remain the same. Unfortunately, it is likely that, for the foreseeable future, marketers will continue to use the ORP meter as a tool for promoting the therapeutic benefits of their particular water. Because of the disproportionate influence of pH on ORP, neutral-pH devices will, on average, tend to produce water with less-negative ORP readings than alkaline water, even if the neutral-pH water has *the same or even greater concentration of  $H_2$* . For example, the Nernst ORP prediction for  $H_2$  water at a pH of 7 and a concentration of 1.6mg/L is -414 mV. The same 1.6mg/L water at 9.5pH will measure -562mV. Marketers of alkaline water devices might seek to exploit the ORP difference (due solely to a difference in pH), and use it to convince sales prospects that, based on its more negative ORP, the alkaline water has a higher level of dissolved  $H_2$  and/or more therapeutic benefit than the neutral-pH water of their competitors. Armed with an understanding of the concepts presented here, sales representatives who sell neutral-pH hydrogen water products will be able, not only to address the disparity in the ORP readings, but, more importantly, to explain why the magnitude of the negative ORP reading is not an indication of the concentration of dissolved  $H_2$ .

Although hydrogen-infusion machines (HIM's) are often referred to as "neutral-pH" devices, the pH of the water they produce is typically about the same as the pH of their source water, which may or may not be "neutral".

## Measuring dissolved hydrogen using a redox titration reagent

Until now, the methods we have discussed for measuring dissolved hydrogen have only focused on measurements using various types of electric devices. However, we should investigate another simple and proven method for measuring dissolved hydrogen gas using a redox titration reagent.

### What is titration?

When presented with a solution containing an unknown quantity of a dissolved compound or gas (solute), chemists often use titration to determine the level of the unknown concentration. Titration is commonly used to measure such properties as pH, chlorine or dissolved oxygen in water. In a titration, small, precise amounts (drops) of a solution of known concentration (the titrant) are slowly added to a precise amount of a test sample (approx. 6mL) containing an unknown concentration of solute, until there is some indication (such as a color change) that the titration has been completed. This is called the "titration endpoint", and, based on the amount of titrant that was added to reach the endpoint, the unknown concentration of solute in the solution can be determined.

### The redox reagent commonly used for detecting dissolved hydrogen

In order for a redox reagent to function as an indicator for a particular dissolved compound, the reagent must be carefully selected to insure that it will react with the dissolved solute in question. Because, in our case, we want to measure dissolved hydrogen gas, we must choose a compound which we know will, under the expected conditions of temperature, pH, etc., react to give visible indications, both of the presence of  $H_2$ , as well as when we have reached the titration endpoint. A good choice for measuring dissolved hydrogen is methylene blue, a dark green powder which turns deep blue when dissolved in a solvent such as ethanol. MB is used in medicine as a biological tissue dye and an agent to treat a variety of medical conditions. As an oxidizing agent, MB, when dissolved in a carrier solvent, is known to react with molecular hydrogen (in the presence of a platinum catalyst) to produce the clear form of MB, leucomethylene blue (leucoMB), as follows:



Oxidized Form

Reduced Form



Equation 8

As **Equation 8** shows, methylene blue (MB), which starts out as blue liquid, will, after reacting with  $\text{H}_2$ , become leucomethylene blue (leucoMB), the reduced form of MB. Because this form of MB is “clear” when dissolved in water, it satisfies the requirement that the titrant provide some “visible indication” of the presence of our dissolved substance,  $\text{H}_2$ . The two structure diagrams in **Figure 15** show both the oxidized and reduced forms of the MB molecule:

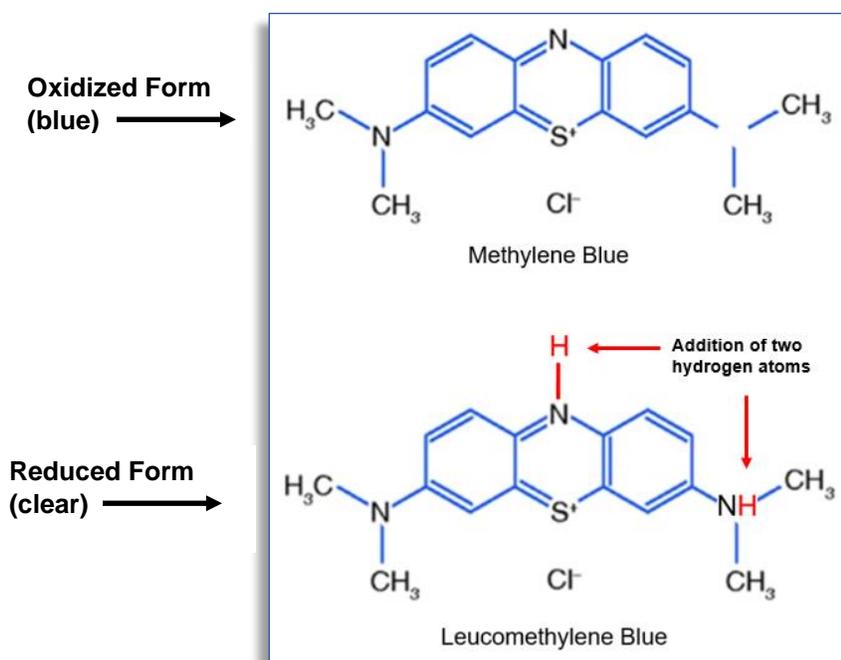


Figure 15

As you can see, the only difference between the two molecules is the addition of the two hydrogen atoms (in red) in the bottom diagram, which bind to the MB molecule during the reaction. These atoms come from the hydrogen molecule, which starts out as two hydrogen atoms bound together ( $\text{H}_2$ ). During the reaction,  $\text{H}_2$  (aided by the platinum catalyst) splits into two hydrogen atoms (H), which then bind to the MB molecule at two different locations.

Therefore, as the methylene blue reagent is added to the sample containing dissolved  $\text{H}_2$ , the  $\text{H}_2$  molecules are “consumed” as they react with MB. As more drops are added, all of the  $\text{H}_2$  in the sample will eventually be depleted. At this point, any titrant added will remain blue, indicating that the titration endpoint has been reached. It is also worth noting that there is a one-to-one correspondence in the reaction between the  $\text{H}_2$  and MB molecules, and each MB molecule consumes one  $\text{H}_2$  molecule (two hydrogen atoms). Therefore, knowing the molecular weights of each, it becomes a straightforward matter to design a reagent which consumes a known amount of dissolved  $\text{H}_2$  per drop (1 drop

typically represents 0.1mg/L of dissolved H<sub>2</sub>). This allows us to add up the total number of drops required to consume all of the H<sub>2</sub> in the test sample (titration endpoint), and thereby determine the concentration of dissolved H<sub>2</sub> in the sample.

Like many other redox reactions, the reaction between H<sub>2</sub> and MB does have a small degree of pH sensitivity at the extremes of the pH scale (recommended test sample range is 4 to 10pH). But, because this method does not rely upon the measurement of redox potential like an ORP-based device, the reagent's response is "flat" well beyond the likely pH range of most, if not all, hydrogen drinking waters. A popular methylene blue redox titration reagent, **H<sub>2</sub>Blue**<sup>®</sup>, provides consumers with a simple, reliable, and inexpensive method for accurately measuring dissolved hydrogen gas.

## Is molecular hydrogen a “conventional antioxidant”?

This article has focused primarily on the relationship between dissolved hydrogen gas and the negative ORP reading, rather than on its therapeutic properties. However, because the negative ORP of H<sub>2</sub> water is so often associated with the water's therapeutic or “antioxidant” properties, some discussion about H<sub>2</sub> as an antioxidant is warranted.

When comparing the ORP readings from various waters, an assumption is usually made that a more negative reading is indicative of a higher antioxidant capacity and/or therapeutic benefit. Also, because alkaline ionized water contains higher levels of hydroxide (a negatively-charged ion, OH<sup>-</sup>), some, perhaps unaware of the presence of H<sub>2</sub>, contend that the hydroxide is responsible for the negative ORP reading, and even go so far as to identify it as the “antioxidant agent” in the water (although hydroxide *is not* a biological antioxidant). Hopefully, the information contained in this and other articles will help to dispel these and other myths about the negative ORP and the source of the therapeutic benefit. We now know that the magnitude of the negative ORP reading cannot be used to measure either the level of dissolved H<sub>2</sub> in the water or its therapeutic benefit. Over 750 research studies now show that the benefits derived from water containing dissolved H<sub>2</sub> are due to the dissolved H<sub>2</sub>, not the pH, and, when the H<sub>2</sub> is removed from the water, so is the benefit. In light of the many myths surrounding water containing H<sub>2</sub>, we should ask, “is there any evidence to support the claim that water containing dissolved H<sub>2</sub> can actually function as an antioxidant *inside the body*, or is this just another myth?

What we know is that there are now hundreds of research studies (in vitro, animal and human) which confirm the ability of H<sub>2</sub> to reduce the levels of some free radicals (particularly the very dangerous hydroxyl radical, •OH), leading to a corresponding reduction in the level of oxidative stress. Therefore, based on the research, it would seem legitimate to call H<sub>2</sub> an “antioxidant”. However, because the thermodynamics of the scavenging reaction between H<sub>2</sub> and the •OH radical are extremely unfavorable, some scientists have been skeptical about the possibility that the reductions in free radicals seen in the research were the result of *direct free-radical scavenging* of •OH by H<sub>2</sub>. It now appears more likely that, rather than acting as a free-radical scavenger (conventional antioxidant), H<sub>2</sub> is, instead, somehow acting *to reduce the formation* of •OH radicals (the precise mechanism is still being investigated). Therefore, while the end result is still an overall reduction in free radicals/oxidative stress, the role of H<sub>2</sub> appears an *indirect* one, acting as a signal modulator to activate *second messenger molecules* (proteins/enzymes), which then act to reduce the formation of free radicals. It is, therefore, more *technically correct* to refer to this therapeutic property of H<sub>2</sub> as “antioxidant-like”.

## Summary

Based on our detailed analysis of the influence that both dissolved H<sub>2</sub> and pH have on the ORP, it should be clear that measuring the reduction potential of hydrogen water using an ORP meter is not an accurate method for determining the level of dissolved hydrogen gas. While the dissolved H<sub>2</sub> is responsible for the negative ORP reading, we can only conclude,

based on the negative reading, that *some level* of dissolved  $H_2$  is present in the water. Inherent fluctuations in the ORP meter, combined with the large impact that even small changes in pH have on the ORP, will always dominate the ORP reading, preventing us from using the *magnitude* of the reading to determine *how much*  $H_2$  there is. In order to know the actual level of dissolved  $H_2$ , we must use a method that *directly measures the  $H_2$  gas itself*, rather than one that relies on the measurement of the redox potential, with its inherent dependence on pH. While there are laboratory-grade devices available that do measure dissolved  $H_2$ , they can cost between 10,000 and 100,000 dollars or more. In contrast, the inexpensive portable “dissolved hydrogen” meters are based on ORP technology, and measure only redox potential, not the dissolved  $H_2$ . While consumers have become conditioned to trust measurements produced by digital electronic devices, they are not always the best choice. For hundreds of years, chemists have used titration to measure the levels of a wide variety dissolved compounds. A redox reagent such as **H<sub>2</sub>Blue**<sup>®</sup> offers a simple, accurate and inexpensive method for determining dissolved hydrogen levels over a broad range of pH.

## About H2 Sciences Inc.

H2 Sciences Inc., a US corporation located in Henderson, NV, manufactures and distributes the **H<sub>2</sub>Blue**<sup>®</sup> hydrogen test reagent, a simple and reliable method for measuring the dissolved hydrogen concentration in hydrogen-infused water. H2 Sciences Inc. also offers engineering and marketing consulting services to hydrogen water companies worldwide. These services include: performance evaluation and certification of hydrogen water devices; training for sales and service representatives; writing and proofing technical content for websites, marketing brochures, and product technical manuals.

For more information:

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## About the Author



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Notes: 1. Dilute concentrations measured in “ppm” are equivalent to mg/L 2. The hydrogen ion is referred to as  $H^+$ , instead of its aqueous form,  $H_3O^+$  (hydronium ion) 3. The term “concentration” is used when referring to ion/solute density instead of “activity” 4.  $2H^+/H_2$  redox couple referred to as  $H^+/H_2$  for simplicity. 5. Nernst calculations and graphing performed using MS Excel 2013/VBA

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