# Analyzing the Influence of Dissolved Hydrogen Gas, pH, and Temperature on the ORP of Water 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 oxidation-reduction potential meter, commonly referred to as an ORP meter. This type of meter measures the tendency of water to act as either an oxidizing or reducing agent, and the measurement is technically referred to as "redox potential". Many alkaline water sales representatives are aware that, while most other waters have a positive ORP reading, water ionizers produce water that has a negative ORP reading (-200 mV to -750 mV or more). Attempts to explain why this water has a negative ORP reading, as well as what it might mean to those who consume it, have spawned many theories, including that the water contains free electrons or has been altered to have some special structure. But, until recently, the fact that ionized water contained dissolved molecular hydrogen gas ($H_2$) produced during electrolysis, and that it was the hydrogen gas in the water that was responsible for producing the negative ORP, was not widely known.

In 2007, a landmark research study showed that drinking water that contained dissolved hydrogen gas could provide therapeutic benefits. In the fifteen years since, the number of research studies confirming the therapeutic benefits of $H_2$ has grown steadily. As knowledge about the benefits of molecular hydrogen has spread, some alkaline water machine manufacturers have attempted to improve upon the design of their existing water ionizers (originally designed as "pH machines", not hydrogen water machines) to optimize the level of hydrogen gas in their 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, pre-packaged cans, bottles, pouches, and tablets that produce $H_2$ gas. As the popularity of hydrogen water products has continued to grow, consumers have become more interested, not only in the therapeutic benefits of $H_2$, but also in knowing how much hydrogen their water contains. While in recent years many manufacturers, distributors, and retailers have changed their marketing messages to promote the benefits of hydrogen, many companies still make performance claims about their products based on the ability of their machines to produce water that has a "more negative ORP" than their competitors. For some, the conventional view of the ORP measurement is still, "the more negative the reading, the higher the water's therapeutic benefit". Since we do tend to think that "more is better", the notion that a more negative reading is superior to a less negative one does seem plausible but, as we will see, does not stand up under technical scrutiny. The growth in awareness about $H_2$ as a therapeutic agent combined with the desire on the part of consumers to know precisely how much hydrogen their water contains, has created the demand for a measuring method that eliminates the ambiguity and inconsistency associated with the ORP meter. In the last few years, relatively inexpensive portable dissolved hydrogen meters (≈ 500 dollars) claiming to accurately measure dissolved hydrogen gas have appeared in the marketplace. Instead of measuring in units of millivolts (mV) like the ORP meter, these meters have a digital display showing dissolved hydrogen levels in units such as parts-per-million (ppm) or mg/L more appropriate for measuring the concentration of dissolved compounds. At first glance, it seems that they might be a good choice for measuring dissolved hydrogen. However, these meters do not use expensive hydrogen-specific probes, but instead use ORP sensors that are not specific to hydrogen and therefore are only capable of measuring the water's ORP, not the dissolved hydrogen gas. Although the negative ORP is a direct result of the presence of dissolved $H_2$ gas, and the ORP does represent the tendency of water to act as an oxidizing or reducing agent, in this article we will explain why the ORP cannot be used to measure dissolved $H_2$, and why interpretations about the meaning of the negative ORP must be based on a precise understanding of ORP chemistry. Throughout this article, we will answer many questions about how dissolved $H_2$, pH, and temperature, influence the water's ORP, but our focus will be on explaining what the negative ORP can and cannot tell us about the water, the level of dissolved hydrogen gas it contains, and the therapeutic benefit it may or may not provide. 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. To help us gain some valuable insight into the subject of ORP, we will use the Nernst equation to examine how the level of dissolved hydrogen gas, pH, and water temperature influence the ORP measurement. To properly introduce the subject, we will start by reviewing some terminology and fundamental concepts associated with the subject of ORP.

Note: This is a simplified version of our recently published peer-reviewed article, *ORP should not be used to estimate or compare concentrations of aqueous $H_2$: An in silico analysis and narrative synopsis*, published in Frontiers in Food Science and Technology. For a more detailed technical analysis of ORP and hydrogen water, please see the following journal article: https://doi.org/10.3389/frfst.2022.1007001.

## ORP

We have mentioned "ORP" a few times now, but what is it? ORP is an acronym for oxidation-reduction potential, a measurement that indicates water's *tendency* to act as either an oxidizing or reducing agent based on the composition of the dissolved substances it contains. Some dissolved substances which tend to act as oxidizers (e.g. oxygen or chlorine) will produce a positive ORP value, while other substances which tend to act as reducing agents (e.g. hydrogen gas) will produce a negative ORP. You may have noticed that we used the phrase "tendency to act" when describing the ORP measurement. As we will see later, without having more information about the substance responsible for producing the positive or negative ORP, the measurement itself does not guarantee that the water will act as either an oxidizer or reducer.

## 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 be a good indicator of the effectiveness of sanitizing agents (oxidizers) used to kill various pathogens in water. **Figure 1** shows a typical portable ORP meter as well as some design variations. The meter always has some type of digital display with a typical measurement range of -1000 to +1000 millivolts (mV). Although an ORP meter is similar in some ways to a standard high-impedance digital voltmeter, there is one important difference, the ORP sensor electrode. The electrode (also called a “probe”) is constructed from an inert metal, usually platinum, that is resistant to oxidation and does not participate in reactions, and is designed to be immersed in a sample of water. When placed into water, this electrode, referred to as the “measurement electrode”, generates a voltage that corresponds to the substances dissolved in it. The probe also contains a second internal electrode (typically silver-silver chloride) referred to as the “reference electrode”, mounted inside the housing and isolated from the sample water. This electrode generates a constant reference voltage to which the voltage generated by the measurement electrode is compared.

While the ORP sensors of smaller, portable units are integrated into the meter’s waterproof housing, larger meters usually have probes that 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 measurement 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 amplify and process the voltage, compare it to the voltage generated by the internal reference electrode, and display the resulting ORP value in millivolts. Depending on the type of agents dissolved in the water, the polarity of the displayed voltage will either be positive or negative, indicating the water’s tendency to act as an oxidizer or a reducer. ORP meters are available at a wide range of prices, from inexpensive consumer-grade portable units to more sophisticated industrial and laboratory models.

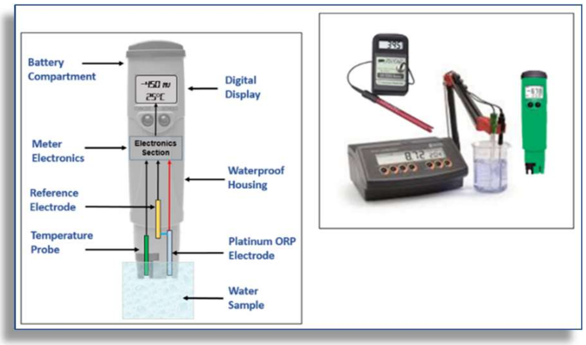


Figure 1

## Hydrogen water

When we say “hydrogen water”, we are referring to water containing dissolved molecular hydrogen gas ($H_2$). It is similar to carbonated beverages, which contain a different dissolved gas, carbon dioxide ($CO_2$), the gas responsible for their “fizziness”. It is important to note that the $H_2$ gas *dissolves* into the water, but does not bind chemically to the water molecules themselves, and does not form 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 that 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, it will eventually “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 other equivalent units such as parts per million (ppm) or parts per billion (ppb)[1]. Typical levels of dissolved $H_2$ are in the range of 0.5 to 2 mg/L. Although the saturation level of hydrogen at sea level is approximately

Hydrogen water may also be referred to as $H_2$-rich water, $H_2$ water, hydrogen-rich water, hydrogen-enriched water or hydrogen-infused water. For technical reasons, hydrogen water should not be called “hydrogenated water”.

1.6 mg/L, super-saturated levels in the 5-10 mg/L range can be produced by some products under the proper conditions of temperature and pressure.

## Hydrogen water products

Water containing dissolved hydrogen can be produced in many different ways, and over the last ten years, the number of hydrogen water products available to consumers has increased dramatically. **Figure 2** shows a variety of products that can now be purchased. Common methods for producing $H_2$ water include electrolyzers such as alkaline water ionizers, neutral-pH hydrogen-infusion machines (HIMs), pitchers, and portable bottles, as well as tablets and powders that produce $H_2$ gas either when placed into water or swallowed. Several prepackaged $H_2$ water products in aluminum cans and pouches are also available. While this paper will focus only on hydrogen drinking water, it should be noted that there are many other methods for administering hydrogen gas and receiving its therapeutic benefits (some that can only be administered in a clinical setting), including the inhalation of $H_2$ gas, intravenous injection of hydrogen-rich saline, hydrogen eye drops, and hydrogen baths.

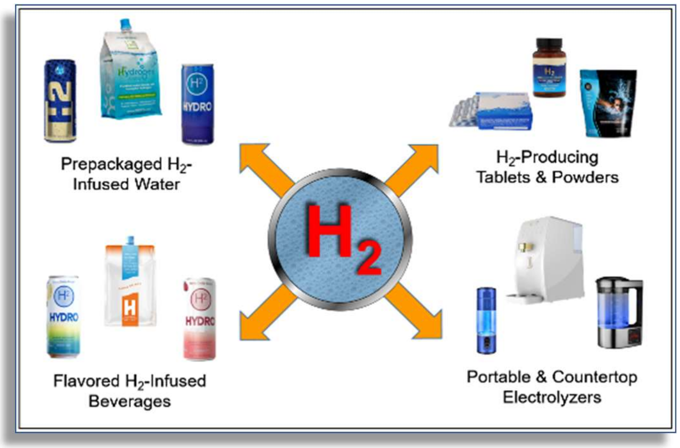


**Figure 2**

## Negative ORP and the source of the therapeutic benefit

Water containing dissolved $H_2$ gas will measure some level of negative ORP, typically in the range of -200 to -750 mV or more, depending on pH and temperature. Uninformed marketers often say this is an indication that various “special qualities” have been imparted to the water by the electricity during electrolysis. Statements 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 these claims persist and even proliferate. This has led to confusion among marketers and consumers alike about the actual source of hydrogen water’s benefit, as well as uncertainty about the proper method for evaluating its therapeutic efficacy. In hydrogen water, we know that the negative ORP is produced by the presence of dissolved hydrogen gas. During electrolysis, electricity (electron flow) 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. 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 it is produced *without the use of electricity* (e.g. using hydrogen-producing tablets or bubbling the gas into the water), will also have a negative ORP and can impart the same therapeutic benefits. 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 it is the dissolved $H_2$ gas, and not some other property of the water, that is responsible for the therapeutic benefits, regardless of how the $H_2$ was added to the water. As we will see later, the magnitude of the negative ORP measurement does not provide any conclusive information about either the level of the dissolved hydrogen gas in the water or the therapeutic benefits it may provide. It is also important to note that a negative ORP may not always indicate the presence of a therapeutic agent. There are many other substances, including some that are toxic (such as β-Mercaptoethanol) that can produce a negative ORP when dissolved in water. Therefore, it is always important to identify the substance responsible for the negative ORP before deciding to ingest the water.

## ORP and Voltage Potential

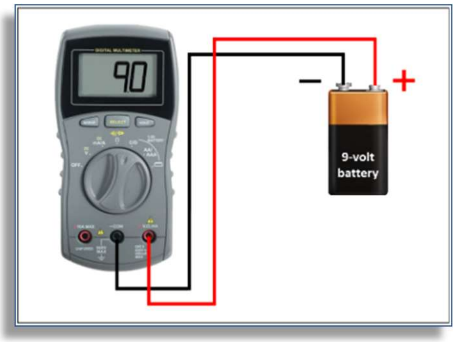


**Figure 3**

Discussions about ORP usually focus on the "O" and the "R" (oxidation & reduction), but detailed descriptions concerning the "P" component (potential) 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 tell us about the water? 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 3** 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. Just as elevation is referenced to sea level and temperature is referenced to the freezing and boiling points of water, voltage always represents the potential difference between two points, a *measured* point, and a *reference* point. Referring back to the ORP meter diagram in **Figure 1**, both of these "points", the platinum ORP electrode and the reference electrode can be seen.

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, but it isn't performing any work when sitting in a drawer. The type of 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 voltmeter can tell us the electrical potential stored in the battery, it cannot tell us whether the battery is 100% charged, or 25% charged; it may light a flashlight for an hour, or 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 the potential is depleted and the electron flow stops. When discussing voltage potential and electrons, we are referring only to the *tendency* of electrons to transfer between species, *not the number of electrons that will transfer;* the larger the measured potential, the greater the tendency. However, whether or not they ever do transfer, or if they do, *how many* will transfer when the battery is placed into a circuit, depends upon the resistance of the circuit to the flow of electrons. For example, if the wire connecting the

ORP measurements only represent "tendency" and do not guarantee that any oxidation or reduction reaction will occur in the body. Other factors such as temperature, activation energy, and reaction rates must also be favorable.

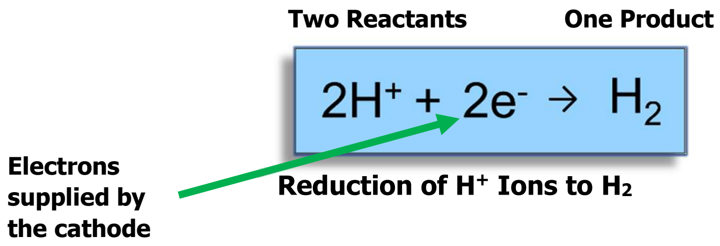
flashlight's light source to the battery became corroded, then the resistance of the circuit could become large enough that, regardless of how good the battery was, a potential of nine volts might not provide enough voltage potential for the electrons to overcome the resistance. Just like the electrons 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 (activation energy) before they can occur.

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 can 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 a *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 can occur.

During electrolysis, the electrons supplied to the water by the cathode quickly bond with hydrogen ions ($H^+$) to form hydrogen gas ($H_2$). They do not float in the water as free electrons.

## 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 that tends to accept electrons (has a deficiency of electrons), and another that tends to donate electrons (has a surplus of electrons). These transfer reactions, referred to as "redox" reactions, form the basis for an important branch of chemistry called *electrochemistry*. Oxidation and reduction reactions always occur together; i.e., when one species loses electrons, another must gain those same 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 $H_2$ and $O_2$ gas during the electrolysis of water are examples of oxidation and reduction reactions that occur simultaneously at the cathode and anode that are submerged in the water. During electrolysis, the cathode supplies the electrons that *reduce* hydrogen ions[2] to hydrogen molecules. **Equation 1** shows the reduction reaction describing the production of $H_2$ gas that occurs at the negative cathode.



**Equation 1**

The two reactants, $H^+$ ions (always present at some level in the water), and electrons (externally supplied to the water 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 each accept an electron from the cathode, and form two hydrogen atoms that then "pair up" to form one hydrogen molecule. **Figure 4** shows a pictorial representation of the reaction.

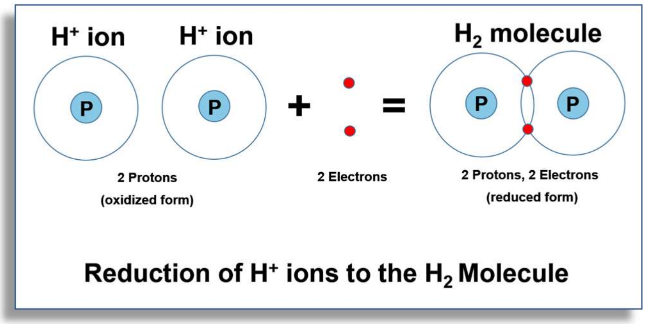


**Figure 4**

Notice that, before the reaction, the two $H^+$ ions start with no electrons (only protons), and, after the reaction is complete, the $H_2$ molecule contains two protons that share two electrons. Because electrons are charged particles, this disparity in electrons between the two species results in a measurable difference in energy potential. When water contains both $H_2$ gas and $H^+$ ions, the presence of these two species will give the water the potential to do work. And, just like when measuring a battery with a voltmeter, can be measured between two points, the meter's platinum electrode (submerged in the water) and its internal reference electrode (isolated from the water). Consequently, a change in the concentration[3] of either the $H_2$ or the $H^+$ will result in a change in the water's voltage potential relative to the meter's reference potential (which does not change).

A hydrogen atom (H) produced at the cathode is a strong free radical and has an unpaired electron. Therefore, it will quickly join with another hydrogen atom to form $H_2$ gas.

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 that occurs 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 that is connected to the positive terminal of the power supply.

**One Reactant** **Three Products**

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \longleftarrow$$

**Electrons return to the power supply through the anode**

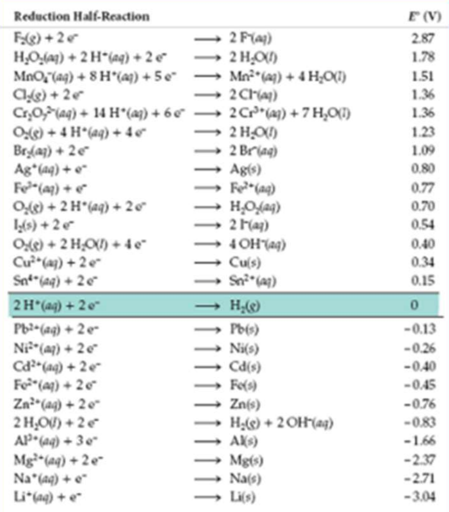
**Oxidation of $OH^-$ Ions to $O_2$ Gas**

**Equation 2**

During alkaline electrolysis, the waters produced at the anode and cathode are isolated from each other with a membrane so that they cannot mix. Therefore, the water from the secondary hose of an alkaline ionizer produced at the positive anode (lower, acid hose) will always measure a positive ORP. This is because, rather than containing the $H^+/H_2$ redox couple, this water will contain a different redox couple (usually an oxygen species), resulting in 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 gases, 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 or water having a positive ORP in detail.

## Redox potential and the redox couple

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).



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

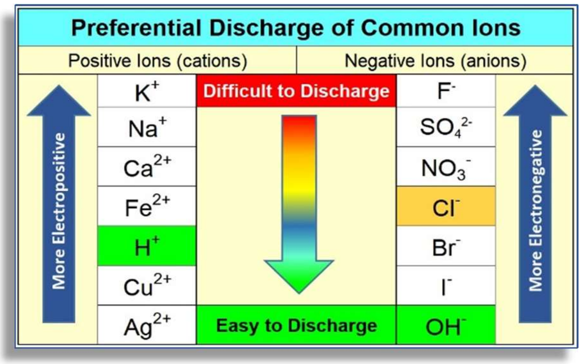
**Table 1**

The strongest reducing agents will have the most negative potentials and the highest tendency to transfer electrons, and the strongest oxidizing agents will have the most positive potentials and the highest tendency to receive electrons. 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 (the internal reference electrode). This potential, expressed in millivolts, is called **redox potential** (i.e. ORP) and is a measurement of the electrical potential energy or *charge separation* that exists between a *pair* of species, 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 redox potential, as well as the sign (either positive or negative), depends on which redox couple we are discussing, as well as the relative concentrations of each species, and other factors such as pH and temperature. A positive ORP indicates that the water will *tend* to act as an oxidizing agent, while a negative ORP indicates that the water will *tend* to act as a reducing agent.

A negative ORP does not indicate that the water has an electrical charge or that it contains free electrons, but rather that it contains $H_2$ gas, a reducing agent. Positive and negative charges must balance in water, ensuring that the water itself remains electrically neutral.

## Preferential discharge of ions during electrolysis

When electrons are transferred during electrolysis, this transfer of electrons (in either direction) is sometimes referred to as "discharge". The redox reactions at the anode and cathode previously described, during which $H^+$ ions are reduced to $H_2$ gas and $OH^-$ ions are oxidized to $O_2$ gas, are the ones *most likely* to occur, but not those that will necessarily occur. This is because not all ions have the same positive or negative reduction potential. Therefore, when two competing oxidizers or reducers are present in the water undergoing electrolysis, the redox reaction of one ion will be preferred over the other. This phenomenon is referred to as "preferential discharge". The reason for the preference can be seen in **Table 1**, which shows the reduction potentials for many redox reactions. The chart in **Figure 5** lists some common ions that might be present in drinking water in order of the ease with which they discharge. Among the positive ions, we can see that there are very few that can compete with $H^+$ (except copper and silver, which are unlikely to be present in drinking water), and among the negative ions, none are shown that can compete with $OH^-$.



**Preferential Discharge of Common Ions**

| Positive Ions (cations) | | Negative Ions (anions) |
|---|---|---|
| $K^+$ | Difficult to Discharge | $F^-$ |
| $Na^+$ | | $SO_4^{2-}$ |
| $Ca^{2+}$ | | $NO_3^-$ |
| $Fe^{2+}$ | | $Cl^-$ |
| $H^+$ | | $Br^-$ |
| $Cu^{2+}$ | | $I^-$ |
| $Ag^{2+}$ | Easy to Discharge | $OH^-$ |

Figure 5

Why are we discussing preferential discharge? The reason is that reduction potential does not always predict which ion will be reduced at the cathode or oxidized at the anode and, under some conditions, when the concentration of certain ions is high or electrolysis voltage is favorable, a more-positive ion could be reduced or a more-negative one oxidized instead. Although when producing drinking water, this would be a rare occurrence, some alkaline ionizers offer the option (available on some machines) to produce waters other than drinking water, and these machines either purposely take advantage of, or unknowingly experience the phenomenon of preferential discharge. One example of this is the option to produce a type of sanitizing water, during which a salt solution (sodium chloride, NaCl) is injected into the electrolysis chamber during electrolysis. This is done to purposely elevate the concentration of chloride ions ($Cl^-$) to such a degree that they will preferentially discharge at the anode instead of $OH^-$ and produce chlorine gas ($Cl_2$) instead of the oxygen gas ($O_2$) that would normally be produced. When producing sanitizing water, this is a desirable effect since the chlorine gas reacts with water to produce hypochlorous acid (HOCl), a very effective sanitizing agent used for wound care and to kill pathogens on a variety of surfaces. Another similar, but less-desirable effect can occur when these machines produce a type of acid water recommended for use in skincare. Although in this mode, a salt solution is not purposely injected into the electrolysis chamber by the machine, the water may already contain an adequate concentration of chloride ions from a number of sources: 1) naturally occurring in the source water; 2) produced by the charcoal filter during the reduction of chlorine to chloride in chlorinated water; 3) added by a water softener in the form of salt (sodium chloride, NaCl). As a result, this chloride may produce chlorine gas at the anode as described previously, and the skincare water may actually contain moderate to high levels of chlorine not necessarily beneficial for the skin. Any chlorine produced by electrolysis cannot be removed by the machine's chlorine filter because it is located *before* the electrolysis chamber where the chlorine is produced. Keep in mind that this is an unpredictable phenomenon that is dependent on the composition of the source water, and that for many it may not occur at all. But, users should always test their skincare water for chlorine using inexpensive test strips or test drops before applying it to their skin.

## The hydrogen redox couple

While there are many redox couples in chemistry, when discussing the ORP of water containing dissolved hydrogen, we are concerned with one particular redox couple, the **hydrogen redox couple, $H^+/H_2$**[4]. Earlier we showed the equation that describes the redox reaction during which two hydrogen ions ($H^+$) accept two electrons to form one molecule of $H_2$ gas. Referring back to **Equation 1**, you can see the two species that comprise the redox couple in blue.

$$2\enclose{circle}{H^+} + 2e^- \rightarrow \enclose{circle}{H_2}$$

"$H^+$" is the oxidized form of hydrogen, containing no electrons, and "$H_2$" is the reduced form, containing two electrons. Because an $H^+$ ion is a single proton that has no electrons to donate, it can only act as an oxidizing agent by accepting 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 of both $H_2$ gas and $H^+$ ions in the water produces a negative ORP.

## pH

For reasons that will be explained later, the pH of the hydrogen water being tested has a strong influence on the ORP reading. Therefore, it is important to first understand some basic concepts about pH. The term pH is an abbreviation that stands for "potential of hydrogen", and is a measure of the concentration of hydrogen ions ($H^+$) in water. When discussing the quantities and concentration of atoms, molecules, ions, etc., the numbers can be extremely small or large, and therefore rather cumbersome to use. The pH scale was devised as a convenient way to express these numbers as powers of ten (positive or negative exponents), instead of using equivalent mathematical expressions such as $1 \times 10^{-7}$ or 0.0000001. The pH scale, which goes from 0 to 14, is a logarithmic scale in which the concentration of $H^+$ ions is expressed as a negative power of 10. **Equation 3** is the equation used to calculate pH. 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 $H^+$ 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 a positive number, but also means that increases in the pH represent a *decrease* in the concentration (and vice-versa). Therefore, a pH of

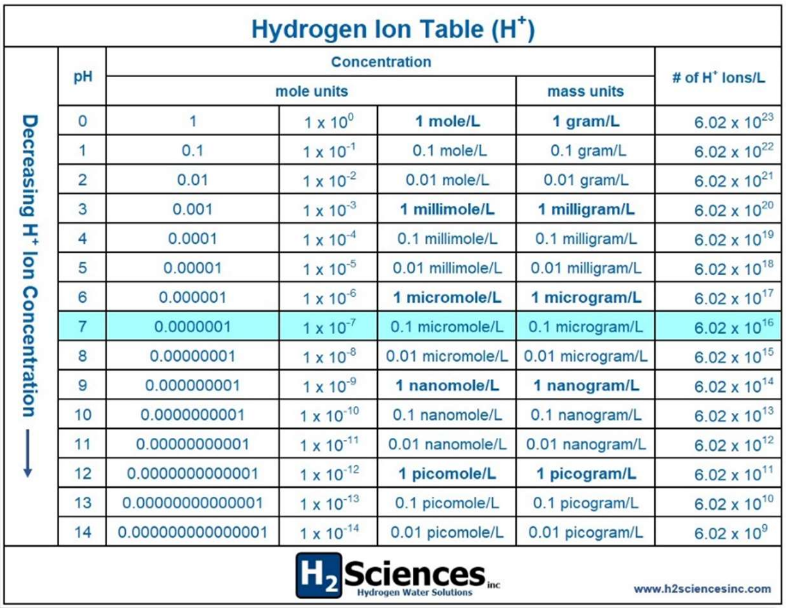
Although by convention the pH scale has a range of 0-14, pH measurements can be less than zero (very strong acids) or greater than 14 (very strong bases).

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

**Equation 3**

zero contains a very high concentration of $H^+$ ions, while a pH of 14 has a very low $H^+$ concentration. Because hydrogen ions represent the acid component in water, the lower the pH, the higher the $H^+$ ion concentration and the more acidic the water. The term “potential of hydrogen” is often misinterpreted to mean “the potential of hydrogen gas”. However, pH is not associated with dissolved $H_2$ gas. Adding pure $H_2$ gas to water (e.g. by bubbling) *will not* change the water’s pH significantly. However, certain methods used to produce hydrogen water may, while producing $H_2$ gas, *indirectly* change the water’s pH. For example, in an alkaline ionizer during the electrolysis of water (that reduces $H^+$ ions to $H_2$ gas at the cathode), the water’s pH is raised, not because $H_2$ gas was added to the water, but because, as the $H^+$ ions (acid) are consumed to produce $H_2$ gas, the level of $OH^-$ ions (base) increases. Recently, new hydrogen water technologies have emerged that focus on maximizing dissolved hydrogen levels while producing water whose pH is essentially the same as the source pH, typically close to neutral. Another type of product, the hydrogen-producing tablet, contains some amount of acid to promote the hydrogen evolution reaction and therefore can produce water with a pH lower that is lower than neutral.

**Table 2** shows the relationship between pH and the $H^+$ ion concentration. The concentration of $H^+$ 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 concentration of $H^+$ ions and includes some other concentration units as well as the actual number of $H^+$ ions the pH represents. It should come as no surprise that, because the $H^+$ 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 that will help us evaluate this influence in a variety of scenarios.



Hydrogen Ion Table ($H^+$)

Decreasing $H^+$ Ion Concentration ⟶

| pH | Concentration | | | | # of $H^+$ Ions/L |
|---|---|---|---|---|---|
| | mole units | | | mass units | |
| 0 | 1 | $1 \times 10^{0}$ | **1 mole/L** | **1 gram/L** | $6.02 \times 10^{23}$ |
| 1 | 0.1 | $1 \times 10^{-1}$ | 0.1 mole/L | 0.1 gram/L | $6.02 \times 10^{22}$ |
| 2 | 0.01 | $1 \times 10^{-2}$ | 0.01 mole/L | 0.01 gram/L | $6.02 \times 10^{21}$ |
| 3 | 0.001 | $1 \times 10^{-3}$ | **1 millimole/L** | **1 milligram/L** | $6.02 \times 10^{20}$ |
| 4 | 0.0001 | $1 \times 10^{-4}$ | 0.1 millimole/L | 0.1 milligram/L | $6.02 \times 10^{19}$ |
| 5 | 0.00001 | $1 \times 10^{-5}$ | 0.01 millimole/L | 0.01 milligram/L | $6.02 \times 10^{18}$ |
| 6 | 0.000001 | $1 \times 10^{-6}$ | **1 micromole/L** | **1 microgram/L** | $6.02 \times 10^{17}$ |
| 7 | 0.0000001 | $1 \times 10^{-7}$ | 0.1 micromole/L | 0.1 microgram/L | $6.02 \times 10^{16}$ |
| 8 | 0.00000001 | $1 \times 10^{-8}$ | 0.01 micromole/L | 0.01 microgram/L | $6.02 \times 10^{15}$ |
| 9 | 0.000000001 | $1 \times 10^{-9}$ | **1 nanomole/L** | **1 nanogram/L** | $6.02 \times 10^{14}$ |
| 10 | 0.0000000001 | $1 \times 10^{-10}$ | 0.1 nanomole/L | 0.1 nanogram/L | $6.02 \times 10^{13}$ |
| 11 | 0.00000000001 | $1 \times 10^{-11}$ | 0.01 nanomole/L | 0.01 nanogram/L | $6.02 \times 10^{12}$ |
| 12 | 0.0000000000001 | $1 \times 10^{-12}$ | **1 picomole/L** | **1 picogram/L** | $6.02 \times 10^{11}$ |
| 13 | 0.00000000000001 | $1 \times 10^{-13}$ | 0.1 picomole/L | 0.1 picogram/L | $6.02 \times 10^{10}$ |
| 14 | 0.000000000000001 | $1 \times 10^{-14}$ | 0.01 picomole/L | 0.01 picogram/L | $6.02 \times 10^{9}$ |

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Table 2

## 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. In this article we will use the Nernst equation to analyze[5] the contributions of temperature, dissolved hydrogen gas ($H_2$), and pH ($H^+$) and discover how much each one influences the ORP reading. **Equation 4** shows the general form of the Nernst equation (the brackets around “red” and “ox” indicate concentrations).

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

**Equation 4**

To use the Nernst equation to predict ORP values for hydrogen water, we need to modify its form slightly. Because $E^0$, the standard cell potential, is zero for hydrogen (see **Table 1**), we can eliminate that term. For the “[red]” and “[ox]” terms we will substitute the concentration of the reduced & oxidized species, $[H_2]$ and $[H^+]$. Because $H_2$ is a dissolved gas, the Nernst equation requires us to convert the $H_2$ concentration to its equivalent partial pressure, $PH_2$. But, for clarity and simplicity, we will use the term “$[H_2]$” instead. The R (gas constant), F (Faraday constant), and z (moles of electrons) are constants that do not change in our calculations. Finally, on the left side of the equation, the “$E_h$” term is the ORP calculated in units of millivolts. The final form of the Nernst equation we will use is shown in **Equation 5**.

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

**Equation 5**

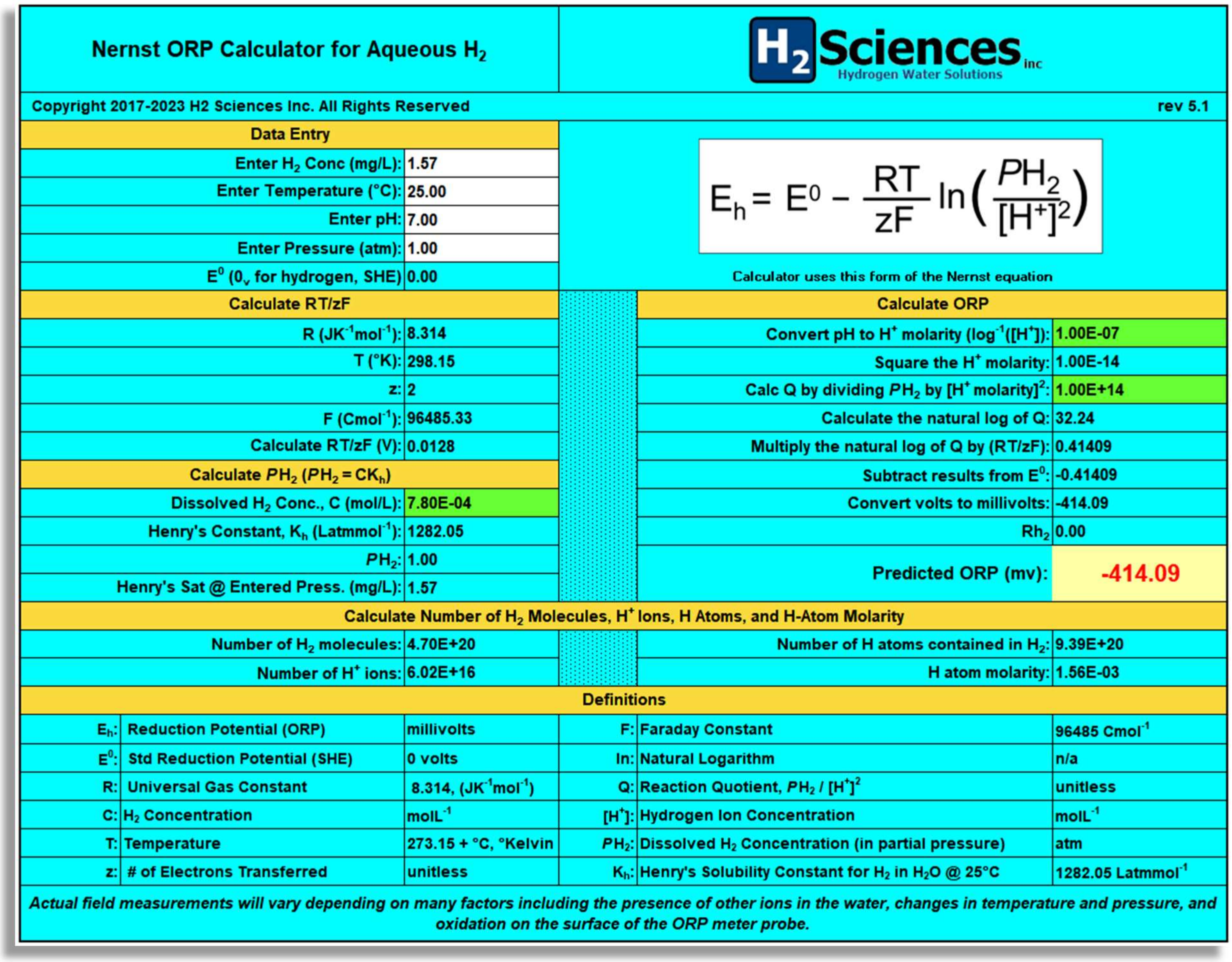
Since the hydrogen water we measure is unlikely to exist under standard conditions (0°C and 1 atm pressure), the Nernst equation allows us to substitute any values of temperature and pressure we choose, and, along with different pH values and concentrations of $H_2$, analyze their combined effects on the ORP.

The following are the definitions for the terms used in the Nernst equation:

- $E_h$, Nernst potential in millivolts (ORP);
- $E^0$, standard cell potential, 0.00v;
- R, universal gas constant, 8.31 $JK^{-1}mol^{-1}$;
- T, standard ambient temperature, 298.15°K (25°C);
- z, # of moles of electrons transferred in the reaction (2);
- F, Faraday constant, 96485 $Cmol^{-1}$ (electron charge per mole) ;
- $[H_2]$, hydrogen gas concentration (expressed in partial pressure);
- $[H^+]$, 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, $H_2$ temperature, and ORP as described will be accurate.

To automate the calculation of the ORP under a variety of different combinations of temperature, $H_2$, and pH scenarios, the Nernst equation was programmed into a calculator using MS Excel. The calculated results for each scenario were then used to create the $H_2$, pH, temperature, and ORP data tables required for plotting the various graphs used in this article. **Figure 6** shows the user interface for the Nernst calculator that displays not only the predicted ORP but most of the intermediate results.



**Nernst ORP Calculator for Aqueous $H_2$**

$H_2$Sciences inc
Hydrogen Water Solutions

rev 5.1

$$E_h = E^0 - \frac{RT}{zF} \ln\left(\frac{PH_2}{[H^+]^2}\right)$$

Calculator uses this form of the Nernst equation

| Data Entry | |
|---|---|
| Enter $H_2$ Conc (mg/L): | 1.57 |
| Enter Temperature (°C): | 25.00 |
| Enter pH: | 7.00 |
| Enter Pressure (atm): | 1.00 |
| $E^0$ ($0_v$ for hydrogen, SHE) | 0.00 |

| Calculate RT/zF | |
|---|---|
| R ($JK^{-1}mol^{-1}$): | 8.314 |
| T (°K): | 298.15 |
| z: | 2 |
| F ($Cmol^{-1}$): | 96485.33 |
| Calculate RT/zF (V): | 0.0128 |

| Calculate $PH_2$ ($PH_2 = CK_h$) | |
|---|---|
| Dissolved $H_2$ Conc., C (mol/L): | 7.80E-04 |
| Henry's Constant, $K_h$ ($Latmmol^{-1}$): | 1282.05 |
| $PH_2$: | 1.00 |
| Henry's Sat @ Entered Press. (mg/L): | 1.57 |

| Calculate ORP | |
|---|---|
| Convert pH to $H^+$ molarity ($\log^{-1}([H^+])$): | 1.00E-07 |
| Square the $H^+$ molarity: | 1.00E-14 |
| Calc Q by dividing $PH_2$ by $[H^+ \text{ molarity}]^2$: | 1.00E+14 |
| Calculate the natural log of Q: | 32.24 |
| Multiply the natural log of Q by (RT/zF): | 0.41409 |
| Subtract results from $E^0$: | -0.41409 |
| Convert volts to millivolts: | -414.09 |
| $Rh_2$ | 0.00 |
| Predicted ORP (mv): | -414.09 |

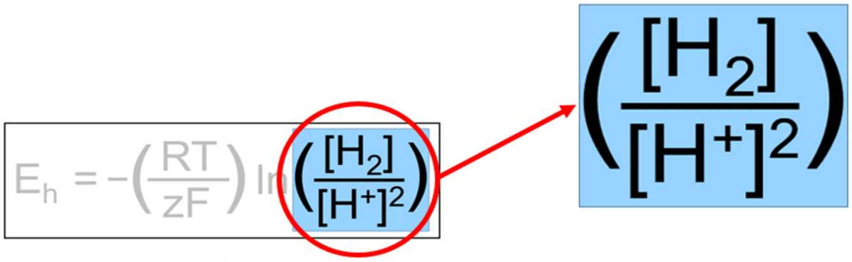
| Calculate Number of $H_2$ Molecules, $H^+$ Ions, H Atoms, and H-Atom Molarity | | | |
|---|---|---|---|
| Number of $H_2$ molecules: | 4.70E+20 | Number of H atoms contained in $H_2$: | 9.39E+20 |
| Number of $H^+$ ions: | 6.02E+16 | H atom molarity: | 1.56E-03 |

| Definitions | | | | | |
|---|---|---|---|---|---|
| $E_h$: | Reduction Potential (ORP) | millivolts | F: | Faraday Constant | 96485 $Cmol^{-1}$ |
| $E^0$: | Std Reduction Potential (SHE) | 0 volts | In: | Natural Logarithm | n/a |
| R: | Universal Gas Constant | 8.314, ($JK^{-1}mol^{-1}$) | Q: | Reaction Quotient, $PH_2 / [H^+]^2$ | unitless |
| C: | $H_2$ Concentration | $molL^{-1}$ | $[H^+]$: | Hydrogen Ion Concentration | $molL^{-1}$ |
| T: | Temperature | 273.15 + °C, °Kelvin | $PH_2$: | Dissolved $H_2$ Concentration (in partial pressure) | atm |
| z: | # of Electrons Transferred | unitless | $K_h$: | Henry's Solubility Constant for $H_2$ in $H_2O$ @ 25°C | 1282.05 $Latmmol^{-1}$ |

*Actual field measurements will vary depending on many factors including the presence of other ions in the water, changes in temperature and pressure, and oxidation on the surface of the ORP meter probe.*

**Figure 6**

While a detailed discussion of the Nernst equation is beyond the scope of this article, a closer look at the last term in **Equation 5** will give us some important insight into how the ORP is calculated. **Figure 7** shows the two hydrogen species contained within the Nernst equation which represent our redox couple of interest.



**Equation 5**

**Figure 7**

As we discussed earlier, the reduced and oxidized forms of hydrogen represent the two hydrogen species in the water whose *combined* presence contributes 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 predominant $H^+/H_2$ redox couple. The "$[H^+]$" term represents the concentration of hydrogen ions (which we calculate from the water's pH) and the "$[H_2]$" term represents the concentration of dissolved hydrogen gas ("$PH_2$" in the calculator). Therefore, because the ORP reading is calculated using the quotient, its value is dependent not only on the concentration of the dissolved hydrogen gas (the value of the numerator) but on the concentrations of *both* the $H_2$ *and* $H^+$ (the values of the numerator *and* denominator). As we will see, each of these species contributes something to the ORP reading. Since we have seen that the dissolved $H_2$ is responsible for producing the negative ORP, this raises a few questions:

- What concentration of dissolved $H_2$ is required to produce a negative ORP?
- To what degree does the ORP respond to changes in the temperature, $H_2$, or $H^+$ concentrations?
- Can we use the ORP reading to measure the level of dissolved $H_2$?
- Can we use the ORP readings from two different samples to compare their relative dissolved $H_2$ concentrations?

The Nernst equation will help us answer these questions by permitting us to analyze how changes in temperature and the concentrations of $H^+$ and $H_2$ influence the ORP reading.

## What dissolved $H_2$ concentration is required to produce a negative ORP?

You might be wondering, "What level of dissolved $H_2$ is required to produce a negative ORP"? Because of the difficulty in measuring extremely low levels of dissolved $H_2$, this question can be hard to answer experimentally. But, to determine the amount of $H_2$ required to produce even a "moderate" level of negative ORP, we can use the Nernst equation to theoretically predict the ORP at various $H_2$ concentrations (even extremely low ones), while eliminating the influences of pH and temperature by keeping them constant (*the answer may surprise you!)*

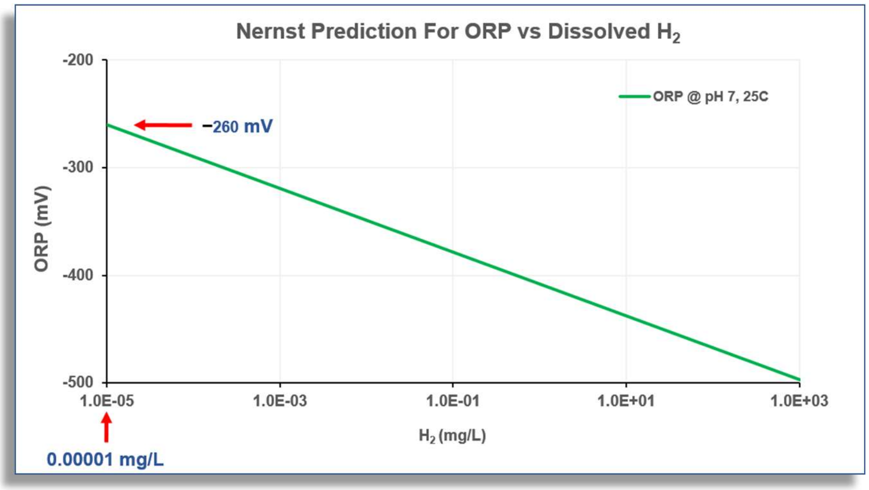


**Figure 8**

The graph in **Figure 8** shows that, at a pH of 7, an $H_2$ concentration of only 1 x $10^{-5}$ mg/L (0.00001 mg/L), or *one hundred-thousandth of a milligram per liter* (50,000 times less than the level considered to be therapeutic), is all that is necessary to produce a negative ORP of -260 mV. Keep in mind that a dissolved $H_2$ level this small will only produce this value of negative ORP when using our Nernst equation calculator, which does not consider any other redox couples that may be in the water. If we were to do a laboratory experiment using water containing such an extremely low level of dissolved $H_2$, not only would this level of dissolved $H_2$ likely be undetectable, but other *oxidizing* redox couples also present in the water (e.g. an oxygen species) would overpower the negative redox potential generated by the $H^+/H_2$ redox couple, and the water would instead measure a positive ORP. However, this demonstrates the very low level of $H_2$ required to produce a negative ORP, and, as we shall see, shows us how little the negative ORP reading can actually tell us about the amount of dissolved $H_2$ in the water.

## The relationship between dissolved $H_2$ concentration and ORP

Many variables can influence the ORP of water. In this article, we are focusing on the three primary variables, temperature, pH ($H^+$ ion concentration), and dissolved $H_2$ concentration. To determine their separate contributions, we must change only one while keeping the values of the other two unchanged. In this way, we can observe the individual effect of each on ORP. Therefore, to examine the effect that a change in *only* the $H_2$ concentration has on the ORP, we will experiment with different values for the $H_2$ concentration, while holding the pH and the temperature constant. Later we will use the same technique to analyze the individual effects of pH and temperature on ORP.

Because Earth's atmosphere contains a small amount of $H_2$ gas (0.00005%), any water exposed to the air will also contain an extremely small concentration of dissolved $H_2$, about 8.65 x $10^{-7}$ mg/L.

The graph in **Figure 9** shows the predicted ORP readings for an $H_2$ concentration range typical for hydrogen water machines, 0.5 to 2 mg/L, at a pH of 7 and temperature of 25°C.

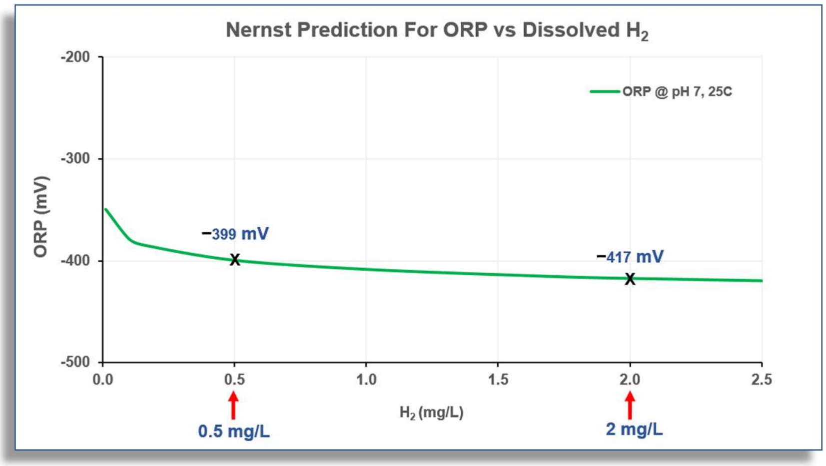


Figure 9

As the dissolved $H_2$ concentration increases from 0.5 mg/L to 2 mg/L, the ORP response is somewhat "flat", falling from -399 mV to -417 mV, only *18 millivolts more negative!* This means that each change in $H_2$ concentration of 1 mg/L (a large change in terms of potential therapeutic benefit) will change the ORP reading *by only 12 millivolts!* To emphasize just how small of an influence the dissolved $H_2$ has on ORP, we can expand the graph's dissolved $H_2$ range by a massive amount. The graph in **Figure 10** shows the negative ORP readings for dissolved $H_2$ levels in the range of 0.5 to **50 mg/L.**

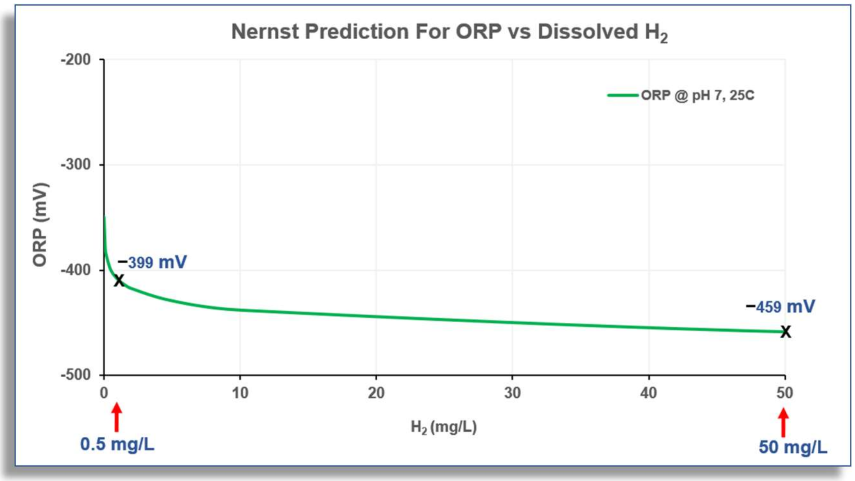


Figure 10

As you can see, even over this extremely large range, the negative ORP increases from -399 mV to -459 mV, ***only 60 millivolts more negative!*** Although such a high dissolved $H_2$ level could likely only be achieved under extreme laboratory conditions of temperature and pressure, nevertheless, this shows us just *how little* the ORP responds to even extremely large changes in the $H_2$ concentration.

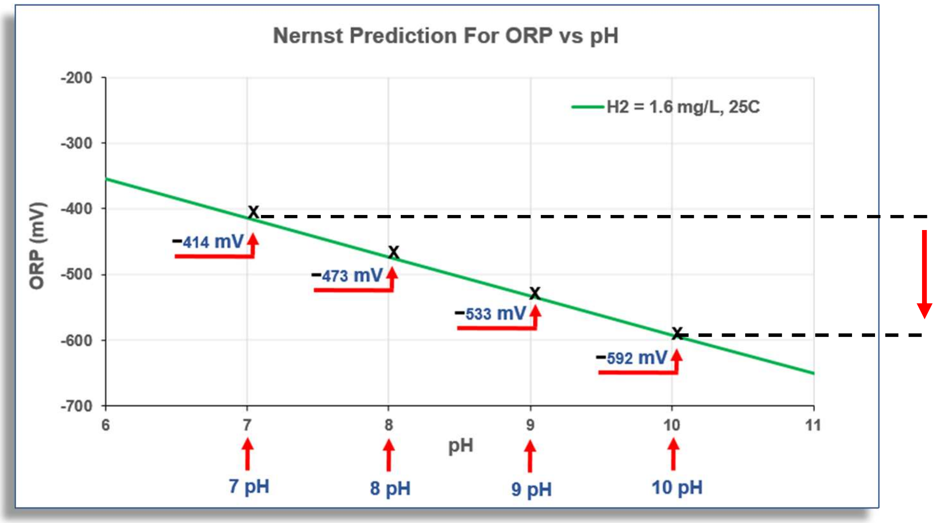
## The relationship between pH and ORP

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

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 7 and the temperature at 25°C. To examine the impact that a change in only the pH has on the ORP, we will change the pH while maintaining the $H_2$ concentration at 1.6 mg/L and temperature at 25°C. 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 $H_2$ on ORP that occurs over a typical $H_2$ concentration range of 0.5 to 2 mg/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 the amounts of change we might normally expect to see in the pH and $H_2$ concentration contribute *equally* to the ORP?" To answer this question, let's now take a look at how changes in pH impact the ORP. To do a valid comparison, again we will use, as we did with $H_2$, a typical range of pH values.

The graph in **Figure 11** 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 and 25°C.



**ORP becomes 178 mV more negative as the pH increases from 7 to 10**

**Figure 11**

The graph shows the degree to which a rise in *only* the pH while maintaining a constant temperature and dissolved $H_2$ level, influences the ORP reading. At a pH of 7, hydrogen water having a concentration of 1.6 mg/L measures an ORP of -414 mV. As the pH increases from 7 to 10, 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 this increase in the negative ORP is the result of only the rise in pH, while the $H_2$ concentration and temperature remain the same. **Figure 12** shows this ORP change graphically.

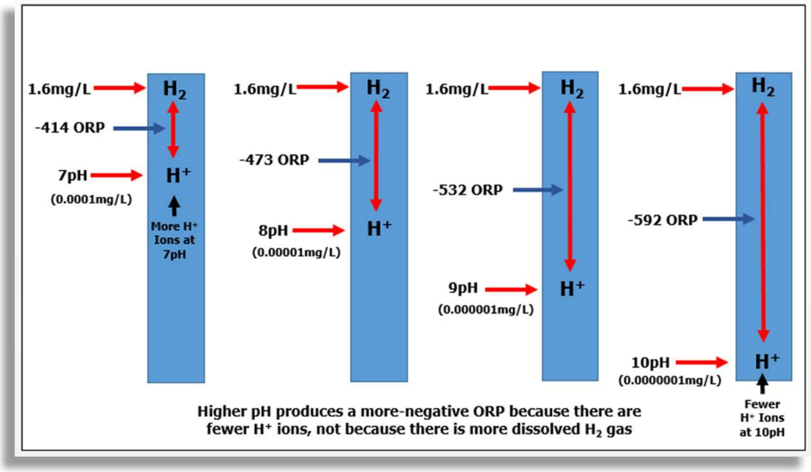


**Figure 12**

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, the more negative reading occurred not because something was added to the water, but because **something was *removed from* the water, $H^+$ ions!** This large increase in the negative ORP occurs with no change in the $H_2$ concentration. Therefore, because ORP responds mostly to changes in pH, the magnitude of the ORP reading does not provide any useful information about the level of dissolved $H_2$ in the water.

The product of $H^+$ and $OH^-$ ions is always the same. Therefore, as $H^+$ (acid) decreases, $OH^-$ (base) must increase. This product is called the "ionic product" of water, and explains why a water ionizer elevates the water's pH (basicity).

## 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 on one graph. **Figure 13** shows a special type of graph that plots the lines for both ORP vs $H_2$ concentration and ORP vs pH. Notice that this graph has two horizontal axes, each with a different title and labeled values. These two axes represent *both* the $H_2$ concentration (in blue) and pH values (in red), each covering their respective typical ranges, 0.5 to 2 mg/L for $H_2$, and 7 to 10 for pH. As before, the graph showing ORP vs pH (red line) maintains the $H_2$ concentration at 1.6 mg/L, while the graph of ORP vs $H_2$ (blue line) holds the pH constant at 7. Rather than displaying the results separately on two graphs, using one graph to plot both relationships permits us to easily see just how differently the ORP responds to each over typical ranges of dissolved $H_2$ and pH.

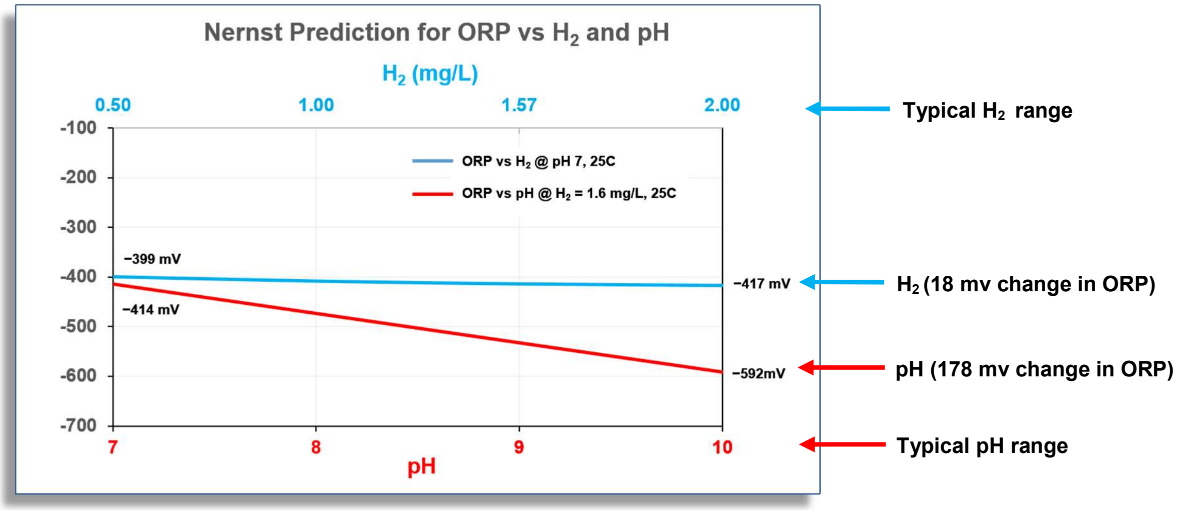


Figure 13

By comparing the slope of each line, we can clearly see the relatively flat response of the ORP to changes in $H_2$ (blue line) compared to the much steeper response of ORP to changes in pH (red line). The graphic in **Figure 14** allows us to see how both $H^+$ and $H_2$ impact the ORP reading in terms of the percentage of their contributions over each of their typical ranges. Viewing their relative contributions this way, it can be seen that, over a typical range of $H_2$ concentrations, the ORP will change by a total of only 18 mV. In contrast, over a typical range of 3 pH units, the ORP will change by 178 mV. While the pH contributes about 90% of the ORP reading, the $H_2$ 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.

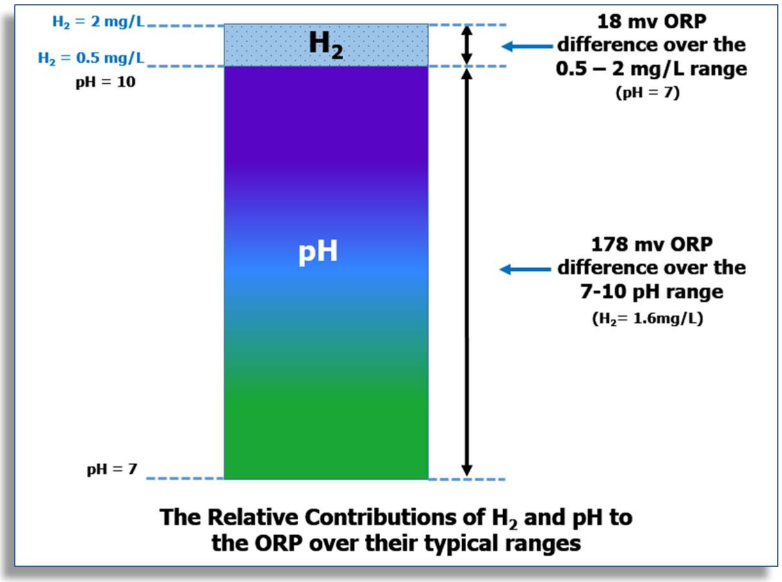
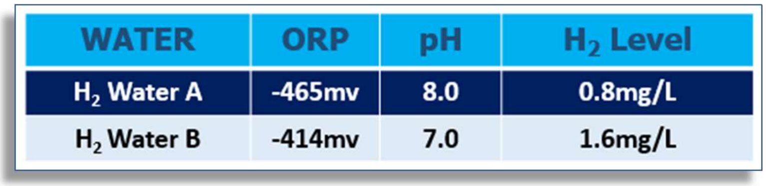


Figure 14

## A larger negative ORP reading does not mean more dissolved $H_2$

We have shown that the negative ORP reading cannot be directly correlated with any particular level of dissolved $H_2$. But, is it possible to use the ORP measurements from two different water samples to compare the *relative* amounts of dissolved $H_2$ they contain? Let's look at an example that shows why the ORP reading cannot be used *even to compare* dissolved $H_2$ levels. While the logical assumption might be that the water with the more negative ORP will also contain the highest level of dissolved $H_2$, the following example shows why this assumption is *not necessarily* true. **Table 3** shows the predicted ORP for two hydrogen water samples, A and B, having different pH and dissolved $H_2$ levels.



| WATER | ORP | pH | $H_2$ Level |
|---|---|---|---|
| $H_2$ Water A | -465mv | 8.0 | 0.8mg/L |
| $H_2$ Water B | -414mv | 7.0 | 1.6mg/L |

**Table 3**

Water A, with a pH of 8 and an $H_2$ level of 0.8 mg/L, measures an ORP of -465 mV. But, water B, with a pH of 7 and an $H_2$ level of 1.6 mg/L (twice as much $H_2$ as A), has an ORP of only -414 mv. 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 $H_2$. This scenario demonstrates why it is incorrect to assume that water having a more negative ORP reading has more dissolved $H_2$. 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 $H_2$; in fact, the water with the more negative ORP could easily contain *less* $H_2$.

## Why does pH have more influence on ORP than $H_2$?

As we have seen, the concentrations of $H_2$ and $H^+$ both contribute to the ORP measurement, and, as the $H^+$ concentration changes, the ORP will also change, even with no change in $H_2$ concentration. In our analysis of the relationship between $H_2$, $H^+$, and ORP, we have seen that the ORP reading responds *in a much greater way* to a typical change in pH than it does to a typical change in the level of dissolved $H_2$. However, "*Why* is this true?" Here is a summary of our findings:

### 1) The pH scale expresses $H^+$ concentrations as powers of 10.

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

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

The pH scale expresses changes in $H^+$ using powers of 10. When the pH increases by one unit, it represents a ten-fold *decrease* in the $H^+$ 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 $H^+$ ($10^3 = 1000$). Because changes in pH represent *exponential* changes in the $H^+$ concentration, even changes in pH that seem to be small can represent *very substantial changes* in the $H^+$ concentration. And, since the pH of hydrogen water can easily span 4 units of pH (6-10), the $H^+$ concentration of various types of $H_2$ water 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 $H^+$ concentration (notice that pH is unitless), but the ORP electrode responds to the concentration of $H^+$ ions, ***not the pH***.

The name "hydrogen" can refer to any one of four different hydrogen species:

1) $H^+$, positive hydrogen ion

2) H, hydrogen atom

3) $H^-$, negative hydrogen ion

4) $H_2$, hydrogen molecule

"pH" always refers to $H^+$ ions

### 2) Concentrations of $H_2$ are expressed using a linear scale.

Unlike $H^+$ concentrations, which are expressed using a logarithmic scale (pH), $H_2$ concentrations are expressed using a *linear* scale, milligrams per liter (mg/L), and typically cover a much smaller concentration range than $H^+$. Consequently, compared to the large changes possible in $H^+$, changes in $H_2$ typically represent relatively small changes. For example, if we were to express $H_2$ concentrations as powers of ten like pH, then our concentration range of 0.5 to 5 mg/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 $H_2$ and $H^+$ again helps to explain why $H_2$ has a much smaller impact than pH on the ORP reading. It is important to note here that, although a change in $H_2$ level of only 1 or 2 mg/L appears to be small, and does have an imperceptible impact on the ORP reading, it is, nevertheless, from the standpoint of therapeutic benefit, *very* significant.

### 3) The Nernst equation performs an exponential math operation on the $[H^+]$ 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:

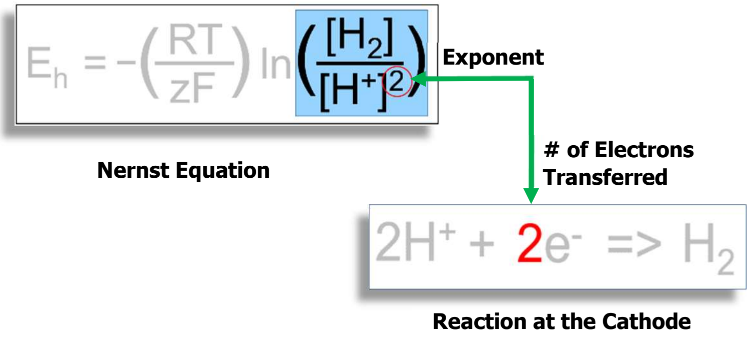


Figure 15

In **Figure 15**, notice that the bottom term in the blue box, “[$H^+$]”, includes the exponent “2” outside of the brackets (circled in red), while the top term, [$H_2$], does not. The cathode reaction equation shows 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 ($H^+$) to its reduced form ($H_2$), must be expressed as an *exponent* for the [$H^+$] term. The explanation for this is beyond the scope of our discussion. However, since, by definition, reduction is a gain of electrons, it makes sense that the number 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 $H^+$ concentration (multiply the [$H^+$] term by itself), whose value *is already an exponential representation of the $H^+$ concentration!* (because pH is an exponential scale). However, no similar exponential function is performed on the [$H_2$] 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 $H_2$ 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 $H^+$ concentration. Consequently, the large influence of pH on the ORP measurement overpowers the small influence of $H_2$, and essentially “controls” the ORP.

## The Relationship between water temperature and ORP

Although pH has the predominant influence over the ORP, water temperature also influences the measurement. Nevertheless, most consumer-grade ORP meters do not include the water’s temperature when calculating the ORP, and therefore they do not compensate for changes in the temperature of the water, which can vary significantly. Looking at **Equation 6**, we can see that the temperature dependence of ORP is an intrinsic part of the Nernst equation, represented as the “T” in the RT/zF term.

$$E_h = -\left(\frac{R\boxed{T}}{zF}\right) \ln\left(\frac{[H_2]}{[H^+]^2}\right)$$

**Equation 6**

When calculating ORP as a function of temperature, an increase in the water temperature of 20°C (approximately the difference between ice water and room-temperature water) will make the ORP 30 mv more negative, even if the $H_2$ concentration and the pH remain unchanged. For comparison, the $H_2$ concentration would need to increase by a very significant factor of 10 (e.g., from 0.1 mg/L to 1 mg/L), to produce the same 30 mv increase on ORP. As we saw in our earlier discussion about the large impact of pH on ORP, to produce the same 30 mv change, the pH would only need to increase by ½ a unit. The change in ORP as a function of only a temperature change is illustrated in **Figure 16**, where the $H_2$ and pH are held constant ($H_2$ = 1.6 mg/L, pH = 7). As the temperature increases from 5°C to 25°C, the magnitude of the negative ORP will increase from -384 mv to -414 mv, even though the $H_2$ concentration and pH remain the same.

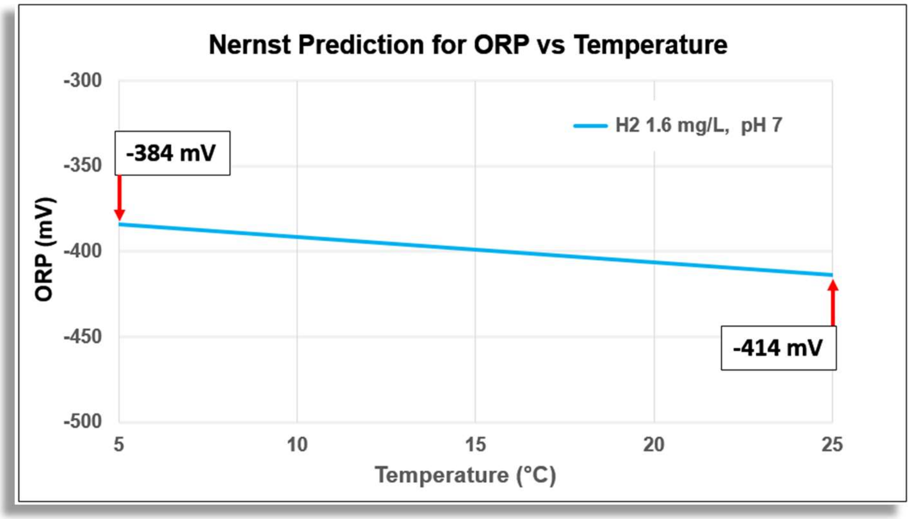


Figure 16

Unfortunately, the influence of temperature on the ORP has not gone unnoticed by some marketers, who, in an attempt to drive the ORP more negative, will not only slow the water flow to elevate the pH, but will also supply their machines with warm or even hot water to increase the negative ORP even more, a practice that can damage the main filter and is therefore not recommended by water ionizer manufacturers.

## The Relationship between water temperature and pressure on dissolved $H_2$ concentration

We have completed our analysis of how $H_2$, pH, and temperature affect ORP, so this is a good place to discuss two factors that influence the dissolved $H_2$ concentration, water temperature and pressure. According to Henry's Law, the maximum amount of $H_2$ that can dissolve in water (saturation level) is related to both water temperature and pressure. The equation for calculating the saturation level of hydrogen gas is shown in **Equation 7**:

$$C = P/Kh$$

Equation 7

"C" is the $H_2$ concentration in moles/liter (which we convert to mg/L) and "P" is the pressure in atmospheres (atm). The term "Kh" is called the "Henry's constant", and its value has been experimentally determined by scientists as 1282.05 Latm/mol at 25°C. But, as the temperature rises above or falls below 25°C, the Henry's constant will change. The calculated value for the saturation level of dissolved $H_2$ at 25°C and 1 atmosphere of pressure (sea level) is 1.6 mg/L.

## Temperature

The influence of temperature is of interest to us because hydrogen gas can be added, not only to room-temperature water, but to very cold (ice water) and very hot (coffee/tea) water as well. The graph in **Figure 17** shows how water temperature influences the maximum amount of $H_2$ that can dissolve in water at a pressure of 1 atm.

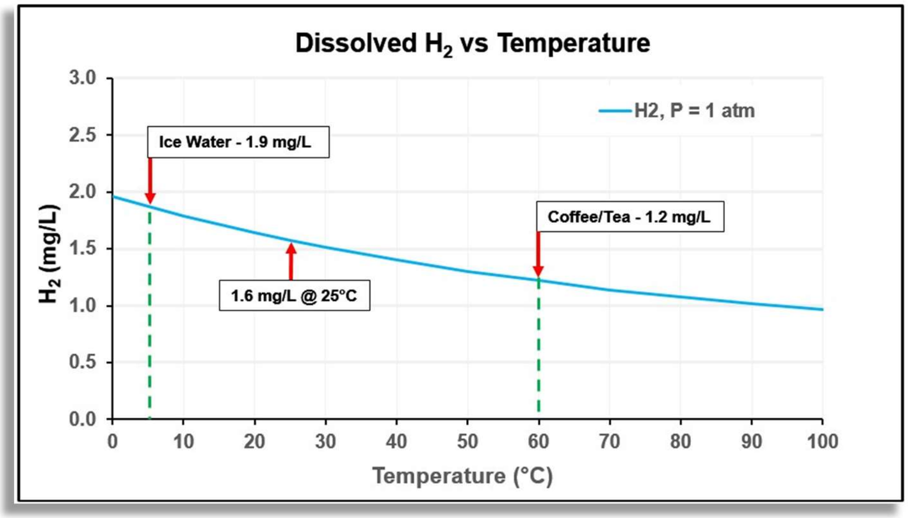


Figure 17

As you can see, over the largest range of temperatures we would normally expect to find hydrogen water, 5°C (41°F) to 60°C (140°F), the saturation level for $H_2$ changes from 1.9 mg/L @ 5°C to 1.2 mg/L @ 60°C, a drop of approximately 35%. Depending on the device and the concentration it can produce, this can be considered significant. Notice also that this relationship is an inverse one, where an increase in temperature results in a decrease in the saturation level of $H_2$.

## Pressure

The atmosphere above us has weight, and the amount of pressure we experience from the weight of the atmosphere changes with elevation. This atmospheric pressure (measured in units of atmospheres, atm) has a direct influence on the performance of products that produce hydrogen water when produced by the same device at different altitudes. Therefore, a hydrogen water device that is capable of producing saturated $H_2$ water at 1.6 mg/L in Los Angeles (sea level, 1 atm of pressure) will only be capable of producing 1.3 mg/L in Denver (5000 ft., 0.8 atm). Because most hydrogen water devices including countertop water ionizers and hydrogen infusion machines are "open systems" (open to the atmosphere), the hydrogen water concentrations they can produce are limited by atmospheric pressure to 1.6 mg/L. But some devices are designed as "closed systems" and allow the pressure to build above 1 atm using either an internal water pump or by simply preventing the $H_2$ gas from escaping. By increasing the gas pressure, these products can increase their dissolved $H_2$ level far above that which can be attained at 1 atm, sometimes by very significant amounts. Anyone who has opened a carbonated soda or a bottle of champagne has seen how manufacturers take advantage of this principle to increase the dissolved level of another gas, carbon dioxide ($CO_2$), using high pressure.

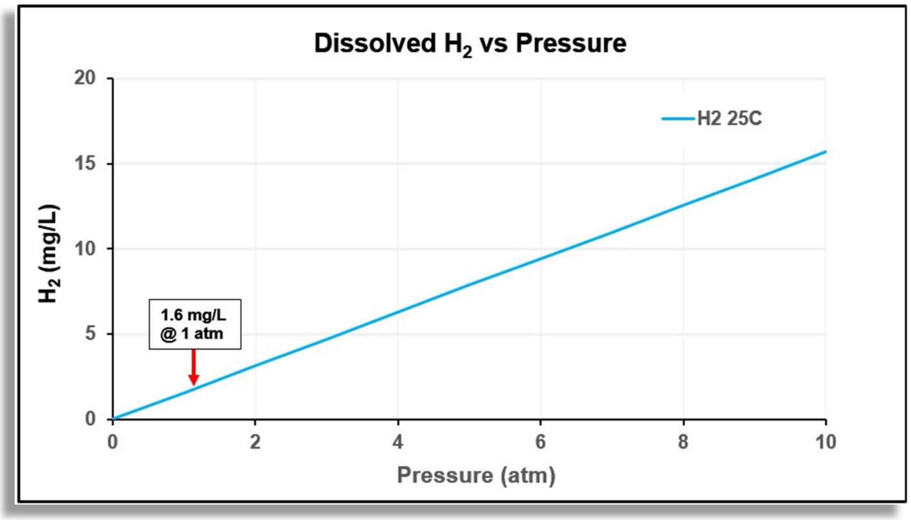


Figure 18

The graph in Figure 18 shows how the pressure influences the maximum amount of $H_2$ that can dissolve in water at a temperature of 25°C. Notice that, in contrast to temperature, the relationship between dissolved $H_2$ and pressure is a direct one, where an increase in pressure results in an increase in $H_2$ concentration. As hydrogen water manufacturers continue to scale up their designs to safely produce higher pressures, we can expect to see a continued rise in the concentration of dissolved $H_2$ water they produce. An example of a hydrogen water device that takes advantage of pressure to elevate the dissolved $H_2$ is the rechargeable portable hydrogen water bottle shown in Figure 19. The bottle is composed of three main components:

1) A **base unit** containing the platinum electrodes, a rechargeable battery that provides the power for electrolysis and other functions, and the associated electronics. A USB connector is included for charging the battery, and some models also have an adapter to permit the user to attach a generic water bottle. The bottom of the base typically includes a very small vent hole that permits oxygen generated at the anode to escape.
2) A threaded **bottle** made of strong plastic (typically Tritan® or polycarbonate) that attaches to the base;
3) A screw-on **cap** that seals tightly to the bottle preventing the $H_2$ gas from escaping. The cap often includes a pressure relief valve to permit a certain amount of pressure to build while preventing it from rising to an unsafe level.

Figure 19

To make hydrogen water, the bottle is filled with any type of water, sealed with the screw-on cap, and then run on a timed cycle, typically for 5-15 minutes. As the hydrogen gas is produced in the sealed bottle, it cannot escape and, as the internal pressure continues to rise, the gas is forced to dissolve into the water at a higher level than would normally be achieved. Depending on the design and cycle time, these bottles are capable of pressures in the 2-4 atm range (29-59 psi), which corresponds to a dissolved $H_2$ concentration in the 3-6 mg/L range. Although they typically contain only 250-300 mL of water, their higher concentration means that they are capable of providing the same amount of $H_2$ as a liter of water whose concentration is 1.6 mg/L. Other products that take advantage of pressure to increase dissolved $H_2$ are also available, including flow-through machines that use an internal water pump to elevate the pressure and prepackaged $H_2$ water in factory-pressurized cans.

## Dissolved hydrogen meters

**Figure 20**

Relatively inexpensive consumer-grade digital hydrogen meters costing approximately $500 or less are available on the consumer market. 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, use non-selective ORP electrodes to measure the water's reduction potential. But, these meters should not be confused with more sophisticated technologies (see **Figure 20**) which *can* accurately measure hydrogen. For example, gas chromatography is the "gold standard" for measuring dissolved hydrogen, but can easily cost $15,000 or more. Also, there are less expensive digital hydrogen meters incorporating ultra-sensitive hydrogen gas probes (polarographic/voltammetric) that can still cost $5,000 or more. These technologies, designed primarily for scientific and industrial use, are very expensive, require a trained expert to use, and are therefore beyond the reach of the average consumer. In this section, we will assess, based on our previous discussions about the relationship between $H_2$, pH, temperature, and ORP, the ability of the ORP-based dissolved hydrogen meter to accurately measure dissolved $H_2$. These meters attempt to determine the dissolved $H_2$ level by measuring the water's redox potential which, as we have seen, is influenced mostly by the concentration of the $H^+$ species of the $H^+/H_2$ redox couple, (represented by pH), somewhat by the water's temperature, and, to a relatively insignificant degree, by the concentration $H_2$. The meter attempts to determine the $H_2$ concentration from the ORP measurement using the following process:

**1)** The Nernst predictions for the ORP of $H_2$ water assuming a pH of 7 are factory-programmed into the meter's firmware or calculated using an algorithm.

**2)** The redox potential of the sample water (in mV) is determined by the meter's ORP, compared to a voltage generated by the reference electrode, and processed by the electronics section.

**3)** The dissolved $H_2$ level of the sample is calculated by comparing the redox potential of the sample (whose pH is assumed to be *exactly* 7.0) to its internal Nernst predictions for the ORP of 7-pH hydrogen-infused water.

**4)** The $H_2$ level (in ppm, ppb, or mg/L) is displayed on the meter's LCD screen.

For example, we can see from the graph in **Figure 21** that, at a pH of 7, water samples containing two different dissolved $H_2$ levels, 0.1 mg/L and 2 mg/L, are predicted by the Nernst equation to have ORP values of -379 mV and -417 mV respectively. Therefore, it seems logical to assume that, if the water sample has a pH of 7, and if its ORP measures -379 mV, it should have a dissolved $H_2$ level of 0.1 mg/L; likewise, if its ORP measures -417 mV, it should have a dissolved $H_2$ level of 2 mg/L. And, if the measured ORP falls somewhere in between these two, then it should be simple for a computer algorithm to interpolate the reading and display the corresponding $H_2$.

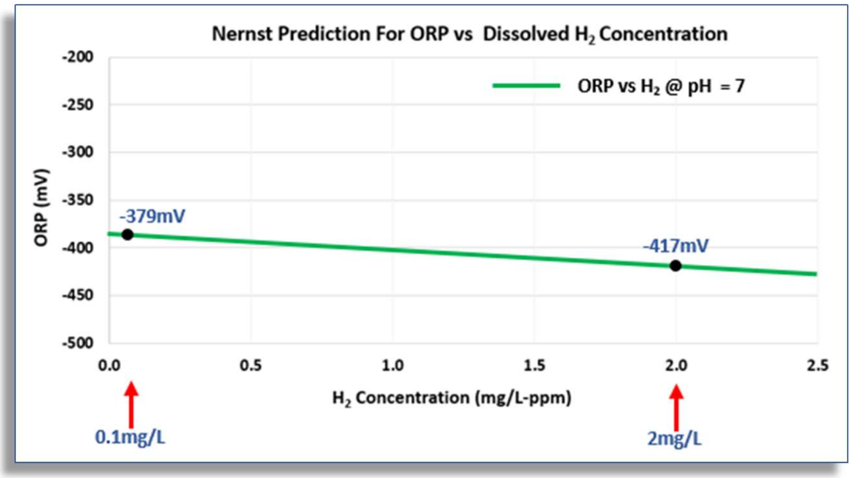


**Figure 21**

However, this is not so simple. Consider the following points:

**1)** Water will rarely have a pH of *exactly* 7.0, 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 $H_2$* over the range of 0.1 to 2 mg/L (30 mV vs 38 mV). Because the meter does not measure and compensate for the pH, this inevitable variance in the water's pH will prevent using the redox potential to accurately measure $H_2$.

**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* contain other redox couples, which will almost always 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 unpredictably influence the ORP measurement and skew the $H_2$ measurement.

**3)** These meters are limited in the maximum dissolved $H_2$ they can read, typically only 3 mg/L., and therefore not capable of measuring the higher concentrations of newer technologies.

## Observations about the shortcomings of ORP technology

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.

Our analysis of the relationship between $H_2$ concentration, pH, and ORP used the results predicted by the Nernst equation when entering selected values for both pH and $H_2$ 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 the ORP measurement cannot be used to measure $H_2$, ORP meters also have many inherent shortcomings, limiting their usefulness for even their designed purpose, *measuring ORP*.

- ORP meter probes will accumulate organic matter/minerals and produce inaccurate readings if not kept clean.
- ORP meters can measure both positive and negative values, but only positive calibration fluids are commercially available.
- Depending on the presence of ions or other chemical species in the water that 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.
- ORP probes must be properly conditioned using an oxidizer to optimize performance when measuring negative ORP values.
- Stirring may be required to stabilize the reading, but there is no standard amount of time to stir.
- ORP probes may last for years, but they do have a lifespan and will eventually fail to give accurate readings as they degrade.
- As the pH rises, the concentration of $H^+$ 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 $H_2$, any hydrogen meter based on the ORP platform will also be subject to these additional inherent weaknesses.

Does this mean that those involved in the sales and marketing of hydrogen water should throw their ORP meters in the trash? Not necessarily! The ORP meter can still be a useful tool when it is properly used and the results are correctly explained. Some examples of valid ways to use an ORP meter include:

- Use the negative ORP to show that the water contains some level of dissolved hydrogen gas and compare it to the ORP of other so called “antioxidant” waters that do not contain hydrogen gas.
- Use the ORP meter to demonstrate $H_2$’s ability to permeate the cell membrane by measuring the ORP of a small sealed zip bag of positive ORP water after it has been submerged in a container of hydrogen water. After enough time has elapsed, the $H_2$ gas will travel through the bag and the water will then measure a negative ORP.
- If your machine produces sanitizing water, a high positive ORP is a good indication of the sanitizing power of the water.

## Applying these results to other hydrogen-water devices

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".

In recent years, many new types of hydrogen water technologies have emerged with designs that differ significantly from the alkaline ionizer. Newer electrolytic devices that utilize proton-exchange membranes with solid polymer electrolyte (PEM/SPE) do not alter the pH of the drinking water, while methods such as hydrogen-producing tablets may actually lower the pH. But, regardless of the method used to create the hydrogen water, the relationships we have seen between temperature, $H_2$, 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 1.6 mg/L is -414 mV. The same 1.6 mg/L water at 9.5 pH will measure -562 mV. Marketers of alkaline water devices might seek to exploit this ORP difference (due solely to the higher 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 $H_2$ or its associated therapeutic benefits.

## 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 electronic 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 and laypeople alike often use titration to determine the concentration. Titration is commonly used to measure properties such as pH or chlorine levels. In a titration, precise amounts (drops) of a solution of known concentration (the titrant) are slowly added to a precise amount of a test sample 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


Methylene Blue Powder

For a redox reagent to measure the concentration of a particular dissolved compound, the reagent must be carefully selected to ensure 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 that we know will: 1) under the expected conditions of temperature, pH, etc., react with hydrogen; 2) give us some type of visible indication that a reaction is occurring; 3) let us know when we have measured all of the dissolved $H_2$ (the titration endpoint). A good choice for measuring dissolved hydrogen is methylene blue (MB), a dark green powder that turns deep blue when dissolved in a solvent such as ethanol or water.

Methylene blue is used in medicine as a biological tissue dye and an agent to treat a variety of medical conditions. As an oxidizing agent and when dissolved in an appropriate solvent, it is known to react with molecular hydrogen (aided by a platinum catalyst) to produce the clear form of methylene blue, leucomethylene blue (leucoMB). **Figure 22** shows the reaction between methylene blue and $H_2$. Because the reduced form of methylene blue is “clear” when dissolved in water, it satisfies the requirement that the titrant must provide some “visible indication” that a reaction with $H_2$ has occurred.

**Oxidized Form** **Reduced Form**

$$\text{MB (blue)} + H_2 \overset{\text{Pt}}{=>} \text{leucoMB (clear)}$$

Figure 22

Because the platinum acts only as a catalyst and does not participate in the reaction, it is shown above the “=” sign. **Figure 23** shows the oxidized and reduced forms of the MB molecule.

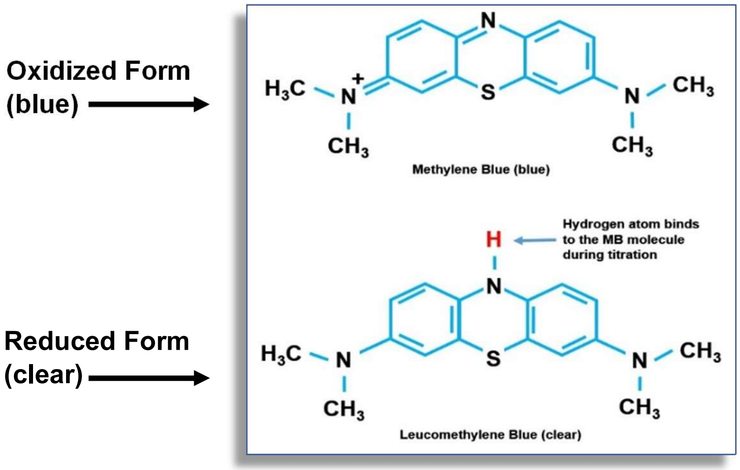


Figure 23

As you can see, the only difference between the structures of the two molecules is the addition of the hydrogen atom (red "**H**") in the bottom diagram that binds to the MB molecule during the reaction. This atom comes from the hydrogen molecule, which starts as two hydrogen atoms bound together ($H_2$). During the reaction, $H_2$ splits into two hydrogen atoms (H), which then bind to the MB molecules contained in the reagent to form LMB. Therefore, as the methylene blue reagent is added to the sample containing dissolved $H_2$, the $H_2$ molecules are split and slowly "consumed" as they react with MB. As more drops are added, all of the $H_2$ in the sample will eventually be depleted. At this point, any titrant added to the water sample will cause the sample to remain blue, indicating that the titration endpoint has been reached. Therefore, knowing the molecular weights, it becomes a straightforward matter to design a reagent that consumes a known amount of dissolved $H_2$ per drop (1 drop typically represents 0.1 mg/L of dissolved $H_2$) when using a precisely calculated volume of test water (typically ≈ 6 mL). This allows us to add up the total number of drops required to consume all of the $H_2$ in the test sample (reach the titration endpoint), and thereby determine the concentration of dissolved $H_2$ in the test sample.

Just as with any reagent, care must be taken to ensure that the water being tested is appropriate for titration. Some precautions include:

- The reaction between $H_2$ and methylene blue does have some sensitivity to the pH of the water; the recommended test sample pH range is 6 to 9.5;
- The water and reagent should be used at or near room temperature;
- The water should not contain any other redox agents (e.g. copper, vitamin C, or chloramines) that could interfere with the action of the reagent or platinum catalyst.

But, because this method does not rely upon the measurement of redox potential like an ORP-based device, the reagent's response is accurate and fairly "flat" well beyond the pH range of most, if not all, hydrogen drinking waters. A popular methylene blue redox titration reagent, **H₂Blue®**, provides consumers with a simple, reliable, and inexpensive method for accurately measuring dissolved $H_2$.

## How much $H_2$ do I need?

Like most therapeutic agents, the benefits of $H_2$ are related to dose, and ingested levels below a particular threshold will not produce the desired therapeutic benefits. But, because there are so many different disease models and ways to ingest hydrogen, it will take time for researchers to determine dosages for specific diseases, administration methods, age groups, etc. In the meantime, based on the amounts of hydrogen typically administered during research studies, the Molecular Hydrogen Institute (MHI) recommends ingesting between 1 and 3 milligrams of $H_2$ per day. How can we determine the amount of hydrogen we are ingesting? The ingested dose is related to two parameters, the dissolved $H_2$ concentration and the volume of water you drink. To calculate the amount of $H_2$ you will ingest:

- Determine the dissolved $H_2$ concentration (in units of mg/L) using an accepted method. If your units are in ppm or ppb, then convert them to mg/L as follows: 1000 ppb = 1 ppm = 1 mg/L.
- Multiply the concentration in mg/L by the volume of water you drink in units of liters.

Example: If you drink 2 liters whose $H_2$ concentration is 0.5 mg/L, then 0.5 x 2 = 1 mg of ingested $H_2$. In order to achieve this dose, the International Hydrogen Standards Association (IHSA) recommends that your product be capable of producing a liter of hydrogen water whose concentration is at least 0.5 mg/L.

## Is molecular hydrogen a "conventional antioxidant"?

This article has focused on the relationship between dissolved hydrogen gas and the negative ORP reading, and we have not discussed hydrogen's therapeutic properties. However, because the negative ORP of $H_2$ water is so often associated with the water's therapeutic benefit or its "antioxidant" properties, and many alkaline ionized water companies and sellers commonly refer to it as "antioxidant water", some discussion about $H_2$ as an antioxidant is warranted. When comparing the ORP readings from various types of hydrogen water, an assumption is usually made that a more negative reading is indicative of a higher antioxidant capacity and/or therapeutic benefit. Additionally, because alkaline ionized water contains higher levels of hydroxide (a negatively-charged ion, $OH^-$), some, perhaps unaware of the presence of $H_2$, contend that hydroxide is responsible for the negative ORP reading, and even go so far as to identify it, rather than $H_2$, as the antioxidant agent in the water (hydroxide is not a biological antioxidant). Although most source water can contain beneficial minerals, and water itself may be considered therapeutic, research studies conclusively show that the added antioxidant benefits of alkaline ionized water are due solely to the dissolved $H_2$, not the pH or other properties, and, when the $H_2$ is removed from the water, so are the benefits.

In light of the many myths surrounding water containing $H_2$, we should ask, "is there any evidence to support the claim that water containing dissolved $H_2$ can act as an antioxidant *inside the body*, or is this just another myth?" After 15 years of research, approximately 2000 research articles have been published that confirm the ability of $H_2$ to reduce the levels of some free radicals (particularly the hydroxyl radical, $^{\bullet}OH$), resulting in a corresponding reduction in the level of oxidative stress and inflammation in the body. Therefore, based on the research, it is legitimate to say that $H_2$ acts as an antioxidant in the body. However, there are at least two reasons why some scientists are skeptical that $H_2$'s antioxidant mechanism is the same as that of other conventional antioxidants such as vitamin C, whose antioxidant properties are based on free-radical scavenging:

In a test tube, when there are no other antioxidants present, $H_2$ can indeed scavenge hydroxyl radicals. But in the human body, $H_2$ cannot compete with other antioxidants which have much more favorable reaction kinetics.

1) The reaction kinetics between $H_2$ and the $^{\bullet}OH$ radical are extremely unfavorable. Therefore, it is more likely that the body's own antioxidants (SOD, CAT, glutathione, etc.), or even other biomolecules (DNA, proteins, etc.), whose reaction kinetics are much more favorable, would preferentially neutralize free radicals rather than $H_2$.
2) $H_2$'s antioxidant benefits can continue for hours or even days after $H_2$ has completely left the body. A conventional antioxidant would need to be present to act as a free-radical scavenger.

It now appears more likely that, rather than acting as a free-radical scavenger like other conventional antioxidants, $H_2$ instead acts *to inhibit the formation* of $^{\bullet}OH$ radicals (the precise mechanism is still being investigated). Therefore, while the result is still a reduction in free radicals, oxidative stress, and inflammation, the role of $H_2$ appears to be more of 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. Since it is becoming clearer that $H_2$ does not fit the biochemistry definition of an antioxidant (electron donor), we believe that it is more technically correct to refer to $H_2$, not as an antioxidant, but rather as having "antioxidant-like" properties.

## Summary

For many years the negative ORP of alkaline ionized water was not understood, and, in an attempt to explain it, marketers developed many false narratives about its significance, including that the water had undergone structural changes during electrolysis, contained free electrons, or possessed other enigmatic therapeutic properties. We now know that any hydrogen water, regardless of whether or not it was produced using electricity, will measure a negative ORP. Because many other substances besides dissolved $H_2$ can also produce a negative ORP, some of which can be toxic, it is important to always identify the substance producing the negative ORP to ensure that it is safe and can impart therapeutic benefits when ingested. Our analysis of the influence that water temperature, pH, and dissolved $H_2$ concentration have on the oxidation-reduction potential has shown that, while the dissolved $H_2$ gas is responsible for the negative ORP reading and therefore it is an indication that *some level* of dissolved hydrogen is present, the ORP measurement cannot be used to accurately measure its concentration. Inherent fluctuations in the ORP meter, combined with the large impact that even small changes in pH and temperature can have on the ORP, will always dominate the ORP reading, obscuring the relatively small contribution from the dissolved $H_2$ and preventing us from using the magnitude of the ORP reading to determine how much $H_2$ the water contains.

Because we now know that $H_2$'s therapeutic benefits are dose-dependent and that ingested levels below a certain threshold level do not provide therapeutic benefits, the accurate measurement of $H_2$ has become essential. While the negative ORP is usually a valid indication that the water contains dissolved $H_2$ gas, to determine the actual level of dissolved $H_2$ we must use a method that specifically measures the $H_2$ gas independent of the water's pH, rather than one that relies on the measurement of the redox potential and its inevitable influence from pH. While laboratory-grade devices such as gas chromatography or meters that have $H_2$-specific probes are available, they can cost thousands of dollars and require a high level of technical expertise to calibrate, operate, and maintain. In contrast, the inexpensive portable "dissolved hydrogen" meters are based on ORP technology and measure only redox potential, not the dissolved $H_2$, and do not take into account the influence of temperature or pH. While consumers have become conditioned to trust measurements produced by digital electronic devices, these are not always the best choice. For hundreds of years, chemists have used titration to measure the levels of a wide variety of dissolved compounds. A redox reagent such as **$H_2$Blue®** offers a simple, accurate, and inexpensive method for determining dissolved hydrogen levels over a broad range of water pH.

## About the Author

Randy Sharpe is the President/CEO of H2 Sciences Inc., the manufacturer and worldwide distributor of the **$H_2$Blue®** hydrogen test reagent, and the Director of Testing at H2 Analytics, a company that provides performance testing and certification for hydrogen water products. His background includes chemistry, computer programming, satellite communications systems design, and electrical engineering. He is a co-author of the following peer-reviewed publications:

1. Tyler W. LeBaron and Randy Sharpe, "*ORP should not be used to estimate or compare concentrations of aqueous H2: An in silico analysis and narrative synopsis*" published in Frontiers in Food Science and Technology; https://www.frontiersin.org/articles/10.3389/frfst.2022.1007001/full.

2. Tyler W. LeBaron, Randy Sharpe, and Kinji Ohno, *"Electrolyzed Reduced Water: I. Molecular hydrogen is the Exclusive Agent Responsible for the Therapeutic Effects";* published in the International Journal of Molecular Sciences; https://www.mdpi.com/1422-0067/23/23/14750

3. Tyler W. LeBaron, Randy Sharpe, and Kinji Ohno, "*Electrolyzed Reduced Water: II. Safety Concerns and Effectiveness as a Source of Hydrogen Water";* published in the International Journal of Molecular Sciences; https://www.mdpi.com/1422-0067/23/23/14508

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For more information on therapeutic hydrogen, visit the Molecular Hydrogen Institute (MHI) at: www.molecularhydrogeninstitute.com

## About H2 Sciences Inc.

H2 Sciences Inc., a US corporation located in Henderson, NV, manufactures and distributes the **$H_2$Blue®** hydrogen test reagent, a simple, reliable, and inexpensive method for measuring the dissolved hydrogen concentration in hydrogen-infused water. Website: www.h2sciencesinc.com

## About H2 Analytics

H2 Analytics, a US company located in Henderson, NV, provides consulting, testing, and certification services to manufacturers, distributors, and retailers in the hydrogen water industry using gas chromatography. They are currently the only company in North America approved by the International Hydrogen Standards Association (IHSA) to test and certify hydrogen water products.
Website: www.h2-analytics.com

***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 is referred to as* $H^+/H_2$ *for simplicity.*

*5. Nernst calculations and graphing performed using MS Excel 2013*

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