

## The Relationship between pH and Deionized Water

## The basics of $\mathbf{p H}$

The topic of pH and water has been well documented over the years; however, there is still much confusion about its significance in high purity water applications.

The pH scale encompasses 14 orders of magnitude of the concentration of the Hydrogen $(\mathrm{H}+$ ) ion on a scale of 0 to 14 . This scale is used to measure the relative acidic or basic level of a solution. It is important to note that the pH scale is backwards. Therefore, an acidic solution would have a lower pH value even though the acid concentration increases. Anything on the scale between 0 and 7 is considered acidic and likewise anything on the scale from 7 to 14 is considered basic. A pH value of 7 is neutral.

| ACIDIC |  |  |  |  | pH Scale |  |  |  |  | BASIC |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | NUETRAL |  |  |  | B |  |  |  |
| 01 | 2 | 3 | 4 | 5 | 6 | 7 | $8 \quad 9$ | 10 | 11 | 12 | 13 | 14 |
| Battery Acid | Lemon Juice |  | Wine | Rain |  | Deionized Water | Baking Soda | Soap | Ammon |  | Caust | Soda |

It is very important to remember that the pH scale is logarithmic and not linear. A small change in pH represents a tremendous change in chemistry.

## Why pH is so important

The pH value gives us insight into many elaborate correlations in water treatment such as corrosion and scaling potential. Interpreting pH values is critical in both designing and troubleshooting high purity water treatment
systems, from optimizing coagulants upstream to assessing poor ion exchange performance downstream.

## Measurement of $\mathbf{p H}$ in high purity water

There are many affordable high quality pH meters on the market today that do an outstanding job of measuring the pH of a given solution. Many of these are handheld and offer great mobility, durability and ease of use and calibration. It is gaining an accurate pH value of deionized water with a very low conductivity that can often prove difficult and lead to unnecessary corrective actions. ${ }^{1}$

Placing the electrodes of a pH meter into a beaker full of deionized water will result in a somewhat meaningless value. This is because deionized water has a very low ionic strength (most if not all of the dissolved ions have been removed) and it is an extremely aggressive solvent when in this state. As a result, when using a pH meter, large differences in the ionic strength of the sample and the buffer solution of the pH electrode can cause unreliable readings. The required electron transport between the measuring and reference sides of the pH electrode is difficult to achieve in these conditions.

Furthermore, the quick adsorption of contaminants into the pure water sample can compromise a pH reading because it has little, if any, buffering capacity. For example, a sample of deionized water exposed to air can quickly adsorb $\mathrm{CO}_{2}$ and form carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ which can alter the pH of neutral water at 7.0 to drop as low as 5.6. Remember that the pH scale is logarithmic and this represents a very large change in chemistry!

Often the problem with a handheld or bench top pH meter is that they are usually calibrated for samples that have a much higher concentration of ions than those that are found in ultra pure water. In order to compensate for this, a more accurate (but not completely reliable) pH reading can be obtained by diluting the standard buffer by adding drop of potassium chloride ( KCl ) per 100 ml of sample before it is measured.

The most accurate pH measurements come from a more sophisticated inline pH meter and even those are not suggested for monitoring changes in deionized water systems. These pH meters have the advantage of avoiding

[^0]atmospheric contamination and using special high resistivity meters with a temperature compensation for a more accurate reading. However, there is still contamination potential from the chemicals necessary for the reference electrodes, usually a strong salt solution.

## An alternative

A practical and often overlooked solution to obtaining the pH value of high purity deionized water is to use an online Resistivity meter to find the corresponding pH value of deionized water. High purity water with a Resistivity of 18.2 Mega ohm (or a conductivity value $0.055 \mu \mathrm{~S}$ ) will have a neutral pH . The graph below shows the relationship between resistivity and pH .


As the Resistivity value drops, the possible pH values move away from a neutral value of 7 . In order to determine which way the pH will swing, it is necessary to know which salt is present in the water. If you take a water molecule and split it in half, you have hydrogen (acidic) and hydroxyl (basic). When these two acid and base species combine they form a water molecule with a neutral pH of 6.998.

## As the Resistivity drops

However, it is not safe to assume that if we add any acid and a proportional amount of base together, the two will neutralize and form pure water with a neutral pH . This is far from true. Adding an acid and a proportional amount of base will produce both water and salt. The resulting pH will depend on what salt is formed after the acid and base neutralize each other. For example, sodium carbonate $\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)$ gives $\mathrm{Na}^{+}$ions and $\mathrm{CO}_{3}{ }^{2-}$ ions. The positive ion, $\mathrm{Na}^{+}$, is released by the strong base, NaOH . The negative ion,
$\mathrm{CO}_{3}{ }^{2-}$, is released by the weak acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$. As a result, sodium carbonate is the salt that is formed from a weak acid and a strong base neutralization and therefore will ultimately yield a slightly basic solution.

The pH of water depends greatly on what types of salts are present in the water. As the Resistivity begins to drop (or the conductivity begins to rise) this translates into a greater presence of dissolved salts in the water. It is the type of salts present and the resulting acid and base that are formed from the salts' reaction with water that dictate what range the pH may fall into at a given Resistivity value. This reaction of salts with water is called hydrolysis and can be summed up below. Table 1 contains a partial list of minimum and maximum pH values at given Resistivity values for reference.

- The salt of a strong acid and a strong base gives a neutral solution
- The salt of a strong acid and a weak base gives an acidic solution
- The salt of a weak acid and a strong base gives a basic solution
- The salt of a weak acid and a weak base gives either an acidic, neutral or basic solution.

| Resistivity | Conductivity | Max pH possible | Min pH possible |
| :--- | :--- | :--- | :--- |
| 18.2 | 0.055 | 7 | 7 |
| 18.0 | 0.056 | 7.8 | 6.2 |
| 16.0 | 0.063 | 7.9 | 6.1 |
| 10.0 | 0.10 | 8.1 | 5.9 |
| 5.0 | 0.2 | 8.4 | 6.5 |
| 2.0 | 0.5 | 8.8 | 5.2 |

Table 1: The pH of water at the given resistivity readings can fall between the given pH ranges depending on the type of salt present.

## Why does a Strong Acid Cation + Weak Base Anion dual bed configuration produce a lower than neutral pH value and a Strong Acid Cation + Strong Base Anion dual bed produce a higher than neutral pH value?

The SAC resin in the $\mathrm{H}+$ form will convert positively charged ions into their respective strong and weak acids. This is why the effluent of a Strong Acid Cation in the $\mathrm{H}+$ form will have a low pH value.

The strong acids are removed by the Weak Base Anion in the OH- form. The resulting OH - is combined with $\mathrm{H}+$ to form H 20 ; however the weak acids will remain in the effluent because they are not removed by the Weak Base Anion resin. The water is demineralized (or partially demineralized) but the presence of trace amounts of weak acids lower the pH to less than neutral. These weak acids also prevent the SAC-WBA configuration from obtaining a high Resistivity. Of course, the advantage to a SAC-WBA system is that you are able to produce a high volume of water relatively inexpensively.

Conversely, in a SAC-SBA configuration a more complete demineralization takes place. The Strong Base Anion neutralizes both the strong and weak acids produced by the Strong Acid Cation and releases OH- which combines with $\mathrm{H}+$ to form H20. The problem is that the Strong Acid Cation inevitably leaks a trace amount of sodium during the service cycle and enters the Strong Base Anion. Sodium then combines with OH - to form sodium hydroxide $(\mathrm{NaOH})$, a strong base. The trace presence of NaOH will elevate the pH above neutral.

However, if you were to take a sample of effluent from a Strong Acid Cation-Strong Base Anion, expose it to the atmosphere and then test for pH , it would most likely show a lower value closer to neutral. Again, this is due to the introduction of $\mathrm{CO}_{2}$ into the water and producing carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ which will lower the pH .

A mixed bed polisher contains both Strong Acid Cation and Strong Base Anion resins mixed together. The resulting pH is neutral at a high resistivity because the problem of sodium leakage is solved due to the exponentially large number of cation/anion exchanges that take place throughout the bed. If the mixed bed shows an extremely low pH value immediately after being placed into service, this could mean that the Strong Base Anion was regenerated poorly and is unable to neutralize the strong and weak acids
produced by the Strong Acid Cation. Likewise, in the same scenario, if the mixed bed gave a high pH reading, this could mean that the Strong Acid Cation was regenerated poorly and was unable to neutralize the hydroxyl produced by the Strong Base Anion.

Keep in mind that even when the Strong Acid Cation and Strong Base Anion resins are regenerated properly, the mixed bed will inevitably exhaust and a pH swing in one direction or the other will happen depending on the Resistivity reading and feed water composition. For example, a mixed bed producing deionized water with a Resistivity of 2 Mega ohms could have a theoretical pH value of 5.2 all the way up to 8.8.

## Conclusion

If it is necessary to achieve pure water with a neutral pH or to fall within a certain pH range, it may be easier to use different physicochemical methods to infer pH values rather than struggle with the challenges of obtaining an accurate reading with a pH meter. For many applications the option of purchasing specialized equipment to obtain a more accurate pH reading of deionized water is cost prohibitive and unpractical. Using a handheld or bench unit can lead to skewed values due to changes in ionic strength and buffer capacity. However, obtaining water with a Resistivity value of 18.2 Mega ohms ensures that the water has a pH that is neutral or very close to neutral. Reading high resistivity values requires an inline resistivity meter to avoid atmospheric contamination. As the Resistivity drops the range of minimum and maximum pH values can still be accurately inferred. If the application calls for the pH to be within certain high/low range, then Table 1 will prove useful. In separate bed demineralizer systems the high and low pH values during normal service can be explained by the resins intended purpose and limitations.

## References:

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[^0]:    ${ }^{1}$ Conductivity and Resistivity are reciprocal values. Conductivity of ultra pure water is 0.055 Microseimens which equals a resistivity of 18.2 Mega ohm.

