

The Relationship Between pH and Deionized Water

Basics of pH

Water and variable pH has been well documented as a topic; however, confusion persists about its significance in high purity water applications.

The pH scale encompasses 14 orders of magnitude based on Hydrogen (H+) ion concentrations 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 the pH scale is backwards and an acidic solution has a lower pH value even though the acid concentration increases. Anything on the scale between 0 and 7 is considered acidic, and anything on the scale from 7 to 14 is considered basic. A pH value of 7 is neutral.

pH Scale **BASIC** ACIDIC **NEUTRAL** 2 3 4 7 10 12 13 Baking Battery Lemon Wine Rain Deionized Soap Ammonia Caustic Acid Juice Water Soda Soda

Remember, the pH scale is logarithmic, not linear. A small change in pH represents a tremendous change in chemistry.

Why pH is critical

The pH value gives us insight into many water treatment correlations 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 and diagnosing poor ion exchange performance downstream.

Measuring pH 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. Getting an accurate pH value for deionized water with very low conductivity often proves difficult and leads to unnecessary corrective actions.¹

¹ Conductivity and resistivity are reciprocal values. Ultra-pure water conductivity is 0.055 Microseimens which equals a resistivity of 18.2 Mega ohm.

Placing pH meter electrodes into a beaker full of deionized water will result in a somewhat meaningless value because deionized water has a very low ionic strength (most, if not all, of the dissolved ions have been removed) and is an extremely aggressive solvent in this state.

As a result, large differences in the ionic strength of the sample and the buffer solution of the pH electrode, when using a pH meter, 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, rapid contaminant adsorption into pure water samples can compromise pH readings because it has little, if any, buffering capacity.

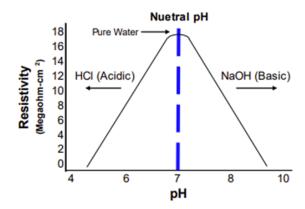
For example, a sample of deionized water exposed to air can quickly absorb C02 and form carbonic acid (H2CO3), which can alter the 7.0 pH of neutral water to drop as low as 5.6. Remember, the pH scale is logarithmic, and this represents a significant change in chemistry!

Handheld or bench top pH meters often present challenges because they are usually calibrated for samples with much higher ion concentrations than those found in ultra-pure water. To compensate, a more accurate (but not completely reliable) pH reading can be obtained by diluting the standard buffer with one 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. Yet even those are not suggested for monitoring changes in deionized water systems. These pH meters have the advantage of avoiding 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, which is 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 μ 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 7. Determining which way the pH will swing requires knowing 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), and when these 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 adding 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 produces both water and salts. The resulting pH depends on what salt is formed after the acid and base neutralize each other. For example, sodium carbonate (Na2CO3) gives Na+ ions and CO3 2- ions. The positive ion, Na+, is released by the strong base, NaOH. The negative ion, CO3 2-, is released by the weak acid, H2CO3.

As a result, the salt sodium carbonate is formed from this weak acid and a strong base neutralization, and ultimately yields 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. The type of salts present, and the resulting acid and base that are formed from the salts' reaction with water, 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 in Table 1 which has a partial list of minimum and maximum pH at given Resistivity values for reference.

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

Resistivity	Conductivity	Max possible pH	Min possible pH
18.2	0.055	7.0	7.0
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: Water pH at the given resistivity reading can fall between the given pH ranges depending on 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 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 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 H+ to form H20. 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 trace presence of weak acids lowers 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 the ability 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 H+ to form H20.

The problem is the Strong Acid Cation inevitably leaks trace amounts of sodium during the service cycle which enters the Strong Base Anion. Sodium then combines with OH- to form sodium hydroxide (NaOH), a strong base. The trace presence of NaOH will elevate the pH above neutral.

However, effluent samples from a Strong Acid Cation-Strong Base Anion when exposed to the atmosphere and then tested for pH, generally show a lower value closer to neutral. Again, this is due to the introduction of C02 into the water producing carbonic acid (H2CO3) which lowers 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 sodium leakage problem is solved due to the exponential number of cation/anion exchanges taking 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, if the mixed bed produces a high pH reading, this could mean the Strong Acid Cation was regenerated poorly and was unable to neutralize the hydroxyl produced by the Strong Base Anion.

Keep in mind, 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 theoretical pH values from 5.2 all the way up to 8.8.

Conclusion

If it is necessary to achieve pure water with a neutral pH, or within a certain pH range, it may be easier to use different physicochemical methods to infer pH values rather than struggle with obtaining an accurate pH meter reading.

In many applications, purchasing specialized equipment to obtain more accurate deionized water pH readings 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, producing water with an 18.2 Mega ohms Resistivity value ensures water with 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 water pH within a 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.

For more information, please visit our site at www.purewater.com

References

Fundamentals of Chemistry, 2nd ed., R.A. Burns 1995

Betz Handbook of Industrial Water Conditioning, 9th Ed., 1991

Ion Exchange Deionization for Industrial Users, William E. Bornak, Tall Oaks Publishing, 2003

Chemistry Demystified, Linda Williams, McGraw-Hill, 2003

High-Purity Water and pH, Estelle Riche, Aude Carrie, Nicolas Andin, and Stephane Mabic, American Laboratory News, June/July 2006