FUNDAMENTALS OF pH

Definition of pH

Just as the kilometer is a measure of distance, and the hour a measure of time, the pH unit measures the degree of acidity or basicity of a solution.

To be more exact, pH is the measurement of the *hydrogen ion concentration,* $[H^+]$. Every aqueous solution can be measured to determine its pH value. This value ranges from 0 to 14 pH. Values below 7 pH exhibit acidic properties, and values above 7 pH exhibit basic (also known as caustic or alkaline) properties. Since 7 pH is the center of the measurement scale, it is neither acidic nor basic and is, therefore, called "neutral."

pH is defined as the *negative logarithm of the hydrogen ion* concentration. This definition of pH was introduced in 1909 by the Danish biochemist, Soren Peter Lauritz Sorensen. It is expressed mathematically as:

$$pH = -\log [H^+]$$

where: $[H^+]$ is hydrogen ion concentration in mol/L.

The pH value is an expression of the ratio of $[H^+]$ to $[OH^-]$ (hydroxide ion concentration). Hence, if the $[H^+]$ is greater than $[OH^-]$, the solution is acidic. Conversely, if the $[OH^-]$ is greater than the $[H^+]$, the solution is basic. At 7 pH, the ratio of $[H^+]$ to $[OH^-]$ is equal and, therefore, the solution is neutral. As shown in the equation below, pH is a logarithmic function. A change of one pH unit represents a 10-fold change in concentration of hydrogen ion.

In a neutral solution, the $[H^+] = 1 \times 10^{-7}$ mol/L. This represents a pH of 7.

$$
\begin{aligned}
pH &= -\log (1 \times 10^{-7}) \\
&= -(\log 1 + \log 10^{-7}) \\
&= -(0.0 + (-7)) \\
&= 7.0
\end{aligned}
$$

Since the concentration of hydrogen ions and hydroxide ions are constant in a stable solution, either one can be quantified if the value of the other is known. Therefore, when determining the pH of a solution, (even though the hydrogen ion concentration is being measured), the hydroxide ion concentration can be calculated:

$$[H^+][OH^-] = 10^{-14}$$

pH Values and Hydrogen/Hydroxide Concentrations

In *Figure 3,* the pH value corresponds to the number of decimal places under the column for "hydrogen ion concentration." The pH of the solution equals the exponential form of the $[H^+]$, with the minus sign changed to a plus. It is much easier to write or say "10 pH" than it is to communicate "a hydrogen-ion concentration of 0.0000000001mol/L."

[OH⁻] concentration (mol/L)		pH	[H⁺] concentration (mol/L)		
1×10^{-14}	0.00000000000001	0	1	1×10^{0}	
1×10^{-13}	0.0000000000001	1	0.1	1×10^{-1}	
1×10^{-12}	0.000000000001	2	0.01	1×10^{-2}	
1×10^{-11}	0.00000000001	3	0.001	1×10^{-3}	Increasing
1×10^{-10}	0.0000000001	4	0.0001	1×10^{-4}	acidity
1×10^{-9}	0.000000001	5	0.00001	1×10^{-5}	
1×10^{-8}	0.00000001	6	0.000001	1×10^{-6}	
1×10^{-7}	0.0000001	7	0.0000001	1×10^{-7}	Neutral
1×10^{-6}	0.000001	8	0.00000001	1×10^{-8}	
1×10^{-5}	0.00001	9	0.000000001	1×10^{-9}	
1×10^{-4}	0.0001	10	0.0000000001	1×10^{-10}	Increasing
1×10^{-3}	0.001	11	0.00000000001	1×10^{-11}	basicity
1×10^{-2}	0.01	12	0.000000000001	1×10^{-12}	
1×10^{-1}	0.1	13	0.0000000000001	1×10^{-13}	
1×10^{0}	1	14	0.00000000000001	1×10^{-14}	

FIGURE 3 Table of Relative [OH⁻] and [H⁺] Mol/Liter Concentrations

How Is pH Measured?

The measurement of pH in an aqueous solution can be made in a variety of ways. The most common way involves the use of a pH sensitive glass electrode, a reference electrode and a pH meter. Alternative methods for determining the pH of a solution are:

Indicators: Indicators are materials that are specifically designed to change color when exposed to different pH values. The color of a wetted sample paper is matched to a color on a color chart to infer a pH value. pH paper is available for narrow pH ranges (for example, 3.0 to 5.5 pH, 4.5 to 7.5 pH and 6.0 to 8.0 pH), and very wide pH ranges of 0.0 to 14.0 pH.

NOTE: pH paper is typically used for preliminary and small volume measuring. It cannot be used for continuous monitoring of a process. Though pH paper is fairly inexpensive, it can be attacked by process solutions which may interfere with the color change.

Colorimeter: This device uses a vial filled with an appropriate volume of sample, to which a reagent is added. As the reagent is added, a color change takes place. The color of this solution is then compared to a color wheel or spectral standard to interpolate the pH value.

> The colorimeter can be used for grab sample measuring, but not continuous on-line measuring. It is typically used to determine the pH value of water in swimming pools, spas, cooling towers, and boilers, as well as lake and river waters.

A pH meter is always recommended for precise and continuous measuring. Most laboratories use a pH meter connected to a strip chart recorder or some other data acquisition device so that the reading can be recorded or stored electronically over a user-defined range.

Activity versus Concentration

Glass electrodes are sensitive to the hydrogen ion *activity* in a solution. Consequently, the concentration of hydrogen ion is not the only factor influencing the pH of a solution. The concentration of other chemicals in the solution, or the *ionic strength* of the solution, is also a major influence in the measurement of pH.

The term "ionic strength" is used to describe the amount of ionic species in a solution, as well as the magnitude of charge on those species. Examples of ion species compounds are sodium (Na^+)sulfate (SO_4^{2-}) $[Na_2SO_4]$, Calcium (Ca^{2+}) chloride(Cl^-) $[CaCl_2]$, and potassium (K^+) nitrate (NO_3^-) $[KNO_3]$. The presence of these ions in solution tend to limit the mobility of the hydrogen ion, thereby decreasing the activity of H^+.

The concept of limited mobility of the hydrogen ion is analogous to a person entering a shopping mall. If the shopping crowd is small, the person is free to move about the mall in any direction. However, if the mall is very crowded, the shopper has a difficult time moving from store to store which severely limits their activity. It is this same principle of a "crowded environment" that limits the activity of the hydrogen ion.

The following equation mathematically describes this effect on the activity of H^+:

> pH = -log $\{[H^+]$ x $[f]\}$
> where: f is the activity coefficient

In solutions where the ionic strength is very low, the activity coefficient is 1.00 making the activity of hydrogen ion equal to its concentration. As the ionic strength of a solution increases, the activity coefficient decreases. This has the effect of lowering the activity of hydrogen ion which is seen as an increase in pH. The following example illustrates this point:

Example: The pH of a 0.00002 M solution of nitric acid can be calculated using this equation:

> pH = - log $\{[H^+]$ x $[f]\}$
> pH = - log $\{[0.00002]$ x $[1]\}$
> pH = 4.70

The value of $[f]$ can be derived from various equations, or found in tables published in:

CRC Handbook of Chemistry and Physics by Robert C West, Ph.D., Ed., CRC Press, Inc., Boca Raton, FL

Lange's Handbook of Chemistry by John A. Dean, Ph.D., Ed., McGraw-Hill Book Company, NY, NY

The product of the activity coefficient and hydrogen ion concentration is equal to 0.00002. This means that the ionic strength of the solution has no effect on the pH calculation.

If the ionic strength were 0.1, the new pH can be calculated using this equation:

$$pH = -\log\{[H^+] \times [f]\}$$
$$pH = -\log\{[0.00002] \times [0.75]\}$$
$$pH = 4.82$$

If the ionic strength of the solution were 0.1, the activity coefficient, $[f]$, would then be 0.75. The product of the activity coefficient and hydrogen ion concentration is now less than 0.00002. This causes the pH calculation of the nitric acid solution to increase by 0.12 pH unit. In this case, the ionic strength has a major influence on the pH of the solution.

The Nernst Equation

The general mathematical description of electrode behavior was described by the 19th century German chemist, Hermann Walther Nernst (1864-1941). He introduced the Nernst equation in 1889. It is expressed as:

$$E = E_o - \frac{2.3RT}{nf}\log a_i$$

where: E = total potential (in millivolts) between two electrodes
E_o = standard potential of the ion
R = universal gas constant (in Joules/mol-Kelvin)
T = absolute temperature (in Kelvin)
n = charge of the ion
F = Faraday constant (in Coulcombs/mol)
a_i = activity of the ion

The entire term "2.3RT/nF" is called the Nernst factor, or slope factor. This term provides the amount of change in total potential for every ten-fold change in ion concentration. For hydrogen ion activity, where n = 1, the Nernst factor is 59.16 mV for every ten-fold change in activity at 25°C. This means that for every pH unit change, the total potential will change 59.16 mV.

The following general equation may be stated for any temperature (since pH is defined as the negative logarithm of the hydrogen ion activity):

$$E = E_o + (1.98 \times 10^{-4})\, T_K\, pH$$

However, the Nernst factor will change when temperature changes (T is not constant). At 25°C the slope of the PH electrode is 59.16 mV/pH unit. At 0°C the slope value is approximately 54 mV/pH, and at 100°C the slope value is approximately 74 mV/pH. The millivolt output of the

glass pH electrode will change with temperature in accordance with the Nernst equation. As the temperature increases, so does the millivolt output. Specifically, the slope of the electrode is what changes.

The change in electrode output versus temperature is linear which can be compensated in the pH meter. The linear function for temperature vs. pH change can be expressed as:

0.003 pH error/pH unit/C

If an uncompensated pH system were standardized in pH 7 buffer at 25°C, and then a sample at 23°C measured 4.00 pH, the error would be 0.018 pH unit (0.003 x 2°C x 3 units). For a measurement of 4.00 pH at 75°C (probably close to a typical worst case), an uncompensated pH system would read 4.45 pH.

The Standard Hydrogen Electrode

The glass measuring electrode has its electrochemical roots planted in the earlier use of the standard hydrogen electrode(SHE). The SHE is the universal reference for reporting relative half-cell potentials. It is a type of gas electrode and was widely used in early studies as a reference electrode, and as an indicator electrode for the determination of pH values. The SHE could be used as either an anode or cathode depending upon the nature of the half-cell it is used with.

The SHE consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.00M. The platinum electrode is made of a small square of platinum foil which is platinized (known as platinum black). Hydrogen gas, at a pressure of 1 atmosphere, is bubbled around the platinum electrode. The platinum black serves as a large surface area for the reaction to take place, and the stream of hydrogen keeps the solution saturated at the electrode site with respect to the gas.

It is interesting to note that even though the SHE is the universal reference standard, it exists only as a theoretical electrode which scientists use as the definition of an arbitrary reference electrode with a half-cell potential of 0.00 volts. (Because half-cell potentials cannot be measured, this is the perfect electrode to allow scientists to perform theoretical research calculations.) The reason this electrode cannot be manufactured is due to the fact that no solution can be prepared that yields a hydrogen ion activity of 1.00M.