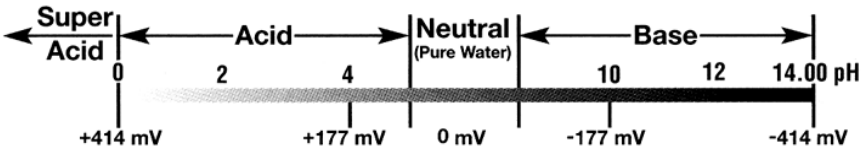
Introduction to pH and pH Measurement

Definition

The pH of a solution measures the degree of acidity or alkalinity relative to the ionization of water sample. Pure water dissociates to yield 10^{-7} M of $[H^+]$ and $[OH^-]$ at 25 °C; thus, the pH of water is neutral i.e. 7.

$$pH_{water} = - \log [H^+] = - \log 10^{-7} = 7$$

Most pH readings range from 0 to 14. Solutions with a higher $[H^+]$ than water (pH less than 7) are acidic; solutions with a lower $[H^+]$ than water (pH greater than 7) are basic or alkaline.



pH Measurement

Measuring pH involves comparing the potential of solutions with unknown $[H^+]$ to a known reference potential. pH meters convert the voltage ratio between a reference half-cell and a sensing half-cell to pH values.

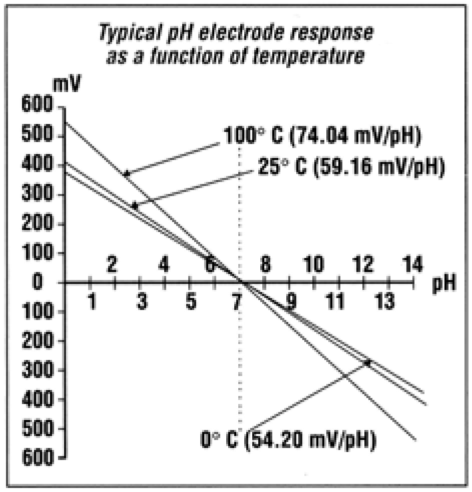
In acidic or alkaline solutions, the voltage on the outer membrane surface changes proportionally to changes in $[H^+]$. The pH meter detects the change in potential and determines $[H^+]$ of the unknown by the Nernst equation:

$$E = E^{o} + (2.3RT)/nF \log \{\text{unknown } [H^+]/\text{internal } [H^+]\}$$

where: E = total potential difference (measured in mV); E^{o} = reference potential; R = gas constant; T = temperature in Kelvin; n = number of electrons; F = Faraday's constant; $[H^+]$ = hydrogen ion concentration.

pH Temperature Compensation

The pH of any solution is a function of its temperature. Voltage output from the electrode changes linearly in relationship to changes in pH, and the temperature of the solution determines the slope of the graph. One pH unit corresponds to 59.16 mV at 25 °C, the standard voltage and temperature to which all calibrations are referenced. The electrode voltage decreases to 54.20 mV/pH unit at 0.0 °C and increases to 74.04 mV/pH unit at 100.0 °C.



Since pH values are temperature dependent, pH applications require some form of temperature compensation to ensure standardized pH values. Meters and controllers with automatic temperature compensation (ATC) receive a continuous signal from a temperature element and automatically correct the pH value based on the temperature of the solution. Manual temperature compensation requires the user to enter the temperature of the solution in order to correct pH readings for temperature. ATC is considered to be more practical for most pH applications.

pH System

A successful pH reading is dependent upon all components of the system being operational. Problems with any one of the three: electrode, meter or buffer will yield poor readings.

Electrodes: A pH electrode consists of two half-cells; an indicating electrode and a reference electrode. Most applications today use a combination electrode with both half cells in one body. Over 90% of pH measurement problems are related to the improper use, storage or selection of electrodes.

Meters: A pH meter is a sophisticated volt meter capable of reading small millivolt changes from the pH electrode system. The meter is seldom the source of problems for pH measurements. Today pH meters have temperature compensation (either automatic or manual) to correct for variations in slope caused by changes in temperature. Microprocessor technology has created many new convenience features for pH measurement; auto-buffer recognition, calculated slope and % efficiency, log tables for concentration of ions and more.

Buffers: These solutions of known pH value allow the user to adjust the system to read accurate measurements. For best accuracy:

- Standardization should be performed with fresh buffer solutions.
- Buffer used should frame the range of pH for the samples being tested.
- Buffers should be at the same temperature as the samples. (For example: if all your samples are at 50 °C, warm your buffers to 50 °C using a beaker in a warm bath.)

Buffer values are dependent upon temperature.