

# pH Reference Section

## Introduction to pH

### INTRODUCTION

pH is a unit of measure which describes the degree of acidity or alkalinity of a solution. It is measured on a scale of 0 to 14. The term pH is derived from "p", the mathematical symbol of the negative logarithm, and "H", the chemical symbol of Hydrogen. The formal definition of pH is the negative logarithm of the Hydrogen ion activity.

$$\text{pH} = -\log[\text{H}^+]$$

pH provides the needed quantitative information by expressing the degree of the activity of an acid or base in terms of hydrogen ion activity.

The pH value of a substance is directly related to the ratio of the hydrogen ion  $[\text{H}^+]$  and the hydroxyl ion  $[\text{OH}^-]$  concentrations. If the  $\text{H}^+$  concentration is greater than  $\text{OH}^-$ , the material is acidic; i.e., the pH value is less than 7. If the  $\text{OH}^-$  concentration is greater than  $\text{H}^+$ , the material is basic, with a pH value greater than 7. If equal amounts of  $\text{H}^+$  and  $\text{OH}^-$  ions are present, the material is neutral, with a pH of 7.

Acids and bases have free hydrogen and hydroxyl ions, respectively. Since the relationship between hydrogen ions and hydroxyl ions in a given solution is constant for a given set of conditions, either one can be determined by knowing the other. Thus, pH is a measurement of both acidity and alkalinity, even though by definition it is a selective measurement of hydrogen ion activity. Since pH is a logarithmic function, a change of one pH unit represents a ten-fold change in hydrogen ion concentration. Table 1 shows the concentration of both the hydrogen ion and the hydroxyl ion at different pH values.

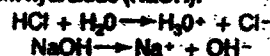
### THE MOLAR CONCEPT

A mole of a compound is defined as Avogadro's number of molecules ( $6.02 \times 10^{23}$  molecules), which has a mass approximately equal to the molecular weight, expressed in grams. For example, sodium hydroxide, NaOH, which has a molecular weight of  $23 + 16 + 1 = 40$ , would have 40 grams in a mole. Since the atomic weight of the hydrogen ion ( $\text{H}^+$ ) is one (1), there is one gram of hydrogen ions in a mole of hydrogen. A solution with a pH of 10 has  $1 \times 10^{-10}$  moles of hydrogen ions, or  $10^{-10}$  grams in a one liter solution.

### IONIZATION

An ion is a charged particle, created by an atom or molecule which has either gained or lost electron(s). The presence of ions in solution allows electrical energy to be passed through the solution as a conductor. Different compounds form ions in solution in different amounts, depending on the ability of the atoms to gain or lose electrons. They will dissociate (or ionize) in solution to form hydrogen ( $\text{H}^+$ ) or hydroxyl ( $\text{OH}^-$ ) ions in the solution.

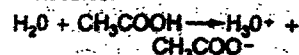
Molecules that dissociate easily will form strong acids or bases when in aqueous solution (water solvent). Examples of these are hydrochloric acid (HCl) or sodium hydroxide (NaOH):



In an aqueous solution, hydrogen ions normally combine with the water solvent to form the hydronium ion ( $\text{H}_3\text{O}^+$ ). pH measurements of these solutions are therefore measurements of the hydronium ion concentration. Normally, the terms "hydronium ion" and

"hydrogen ion" are used interchangeably in pH measurement applications.

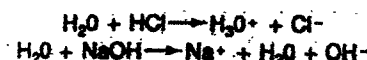
Some compounds form weak acids or bases; only a very small percentage of the compounds dissociates into its constituent ions, so very few hydrogen or hydroxyl ions are formed. An example of this is acetic acid, which forms less than one hydrogen ion for every one hundred molecules:



Pure water also dissociates weakly, with  $10^{-7}$  hydrogen and  $10^{-7}$  hydroxyl ions formed for every water molecule at  $25^\circ\text{C}$ :



The addition of acid to water increases the concentration of hydrogen ions and reduces the concentration of hydroxyl ions. A base added to water has the opposite effect, increasing the concentration of hydroxyl ions and reducing the concentration of hydrogen ions:



There is a wide variety of applications for pH measurement. For example, pH measurement and control is the key to the successful purification of drinking water, the manufacture of sugar, sewage treatment, food processing, electroplating, and the effectiveness and safety of medicines, cosmetics, etc. Plants require the soil to be within a certain pH range in order to grow properly, and animals can sicken or die if their blood pH level is not within the correct limits. Figure 1 gives pH values for some common industrial and household products.

### pH MEASUREMENT

A rough indication of pH can be obtained using pH papers or indicators, which change color as the pH level varies. These indicators have limitations on their accuracy, and can be difficult to interpret correctly in colored or murky samples.

More accurate pH measurements are obtained with a pH meter. A pH measurement system consists of three parts: a pH measuring electrode, a reference electrode, and a high input impedance meter. The pH electrode can be thought of as a battery, with a voltage that varies with the pH of the measured solution. The pH measuring electrode is a hydrogen ion sensitive glass bulb, with a millivolt output that varies with the changes in the relative hydrogen ion concentration inside and outside of the

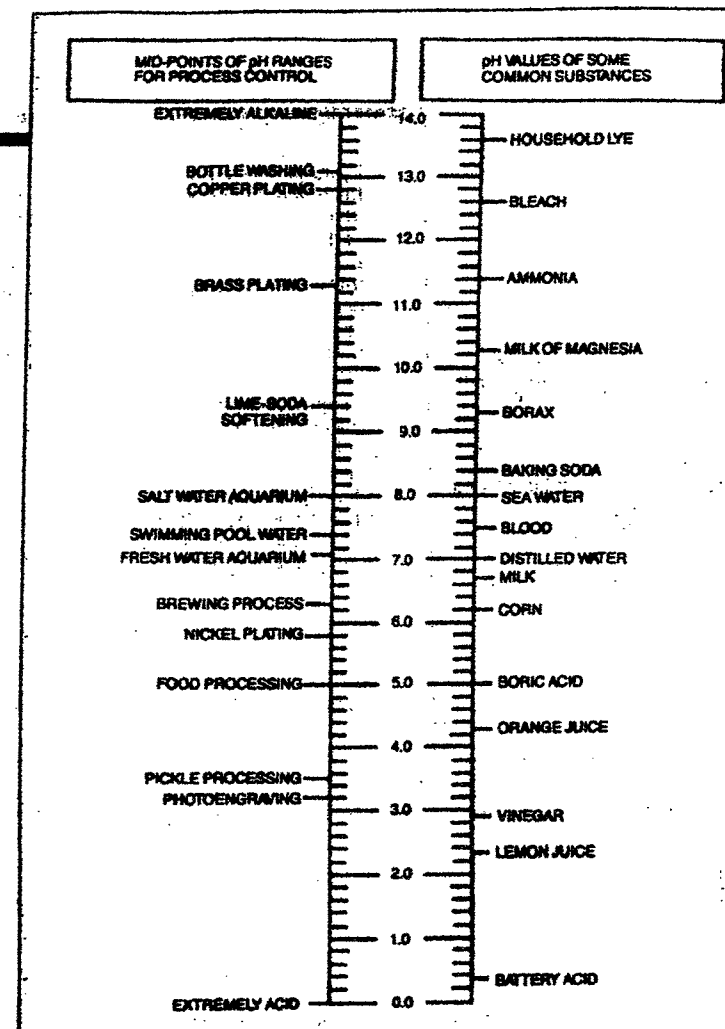


Figure 1

bulb. The reference electrode output does not vary with the activity of the hydrogen ion. The pH electrode has very high internal resistance, making the voltage change with pH difficult to measure. The input impedance of the pH meter and leakage resistances are therefore important factors. The pH meter is basically a high impedance amplifier that accurately measures the minute electrode voltages and displays the results directly in pH units on either an analog or digital display. In some cases, voltages can also be read for special applications or for use with ion-select or Oxidation-Reduction Potential (ORP) electrodes.

### TEMPERATURE COMPENSATION

Temperature compensation is contained within the instrument, because pH electrodes and measurements are temperature sensitive. The temperature compensation may be either manual or automatic. With manual compensation, a separate temperature measurement is required, and the pH meter manual compensation control can be set with

the approximate temperature value. With automatic temperature compensation (ATC), the signal from a separate temperature probe is fed into the pH meter, so that it can accurately determine pH value of the sample at that temperature.

### BUFFER SOLUTIONS

Buffers are solutions that have constant pH values and the ability to resist changes in that pH level. They are used to calibrate the pH measurement system (electrode and meter). There can be small differences between the output of one electrode and another, as well as changes in the output of electrodes over time. Therefore, the system must be periodically calibrated. Buffers are available with a wide range of pH values, and they come in both premixed liquid form or as convenient dry powder capsules. Most pH meters require calibration at several specific pH values. One calibration is usually performed near the isopotential point (the signal produced by an electrode at pH 7 is 0 mV at  $25^\circ\text{C}$ ), and a second is typically

performed at either pH 4 or pH 10. It is best to select a buffer as close as possible to the actual pH value of the sample to be measured.

### TEMPERATURE EFFECTS

As previously stated, the pH electrode is temperature dependent, and may be compensated for in the pH meter circuitry. The circuitry of the pH meter utilizes the Nernst equation, which is a general mathematical description of electrode behavior.

$$E = E_x + \frac{2.3RT_K}{nF} \log(a_i)$$

where:

$E_x$  = constant depending upon reference electrode  
 $R$  = constant  
 $T_K$  = absolute temperature (Kelvin)  
 $n$  = charge of the ion (including sign)  
 $F$  = constant  
 $a_i$  = activity of the ion

For pH measurement, we are interested in the hydrogen ion for  $\text{H}^+$ :

$$\frac{2.3RT_K}{nF} = 59.16 \text{ mV}$$

where:  $n = 1$  and  $T = 25^\circ\text{C}$ . This term is commonly known as the Nernst coefficient. Since pH is defined as the negative logarithm of the hydrogen ion activity, the general equation at any temperature can be expressed as:

$$E = E_x - 1.96 T_K \text{ pH}$$

Changes in temperature of a solution will vary the millivolt output of the glass pH electrode in accordance with the Nernst equation. Its variation in the electrode sensitivity versus temperature is a linear function, and most pH meters have circuitry designed to compensate for this effect (refer to Temperature Compensation). Figure 2 shows the effect on the glass pH electrode signal at various temperatures.

In figure 2, all three slopes intersect at the point of 0 mV and pH 7.0; this implies no millivolt change with temperature at this, the isopotential point. Also, it can be seen that when working near 7.0 pH, temperature compensation is not a significant factor. However, when working at pH levels of 3.0 or 11.0, a temperature change of  $15^\circ\text{C}$  can result in an error of 0.2 pH. Since the temperature effect on the electrode has been shown to be linear, the temperature dependence of pH can then be expressed as:

$$0.03 \text{ pH error/pH unit}/10^\circ\text{C}$$

The actual pH of the sample can change with temperature due to a change in the hydrogen ion activity in the solution, because ionization of compounds and

HYDROGEN ION CONCENTRATION IN MOLES/LITER AT 25°C		
pH	$\text{H}^+$	$\text{OH}^-$
0	$(10^0) 1$	$0.0000000000001 (10^{-14})$
1	$(10^{-1}) 0.1$	$0.0000000000001 (10^{-13})$
2	$(10^{-2}) 0.01$	$0.0000000000001 (10^{-12})$
3	$(10^{-3}) 0.001$	$0.0000000000001 (10^{-11})$
4	$(10^{-4}) 0.0001$	$0.0000000000001 (10^{-10})$
5	$(10^{-5}) 0.00001$	$0.0000000000001 (10^{-9})$
6	$(10^{-6}) 0.000001$	$0.0000000000001 (10^{-8})$
7	$(10^{-7}) 0.0000001$	$0.0000000000001 (10^{-7})$
8	$(10^{-8}) 0.00000001$	$0.0000000000001 (10^{-6})$
9	$(10^{-9}) 0.000000001$	$0.0000000000001 (10^{-5})$
10	$(10^{-10}) 0.0000000001$	$0.0000000000001 (10^{-4})$
11	$(10^{-11}) 0.00000000001$	$0.001 (10^{-3})$
12	$(10^{-12}) 0.000000000001$	$0.01 (10^{-2})$
13	$(10^{-13}) 0.0000000000001$	$0.1 (10^{-1})$
14	$(10^{-14}) 0.00000000000001$	$1 (10^0)$

Table 1

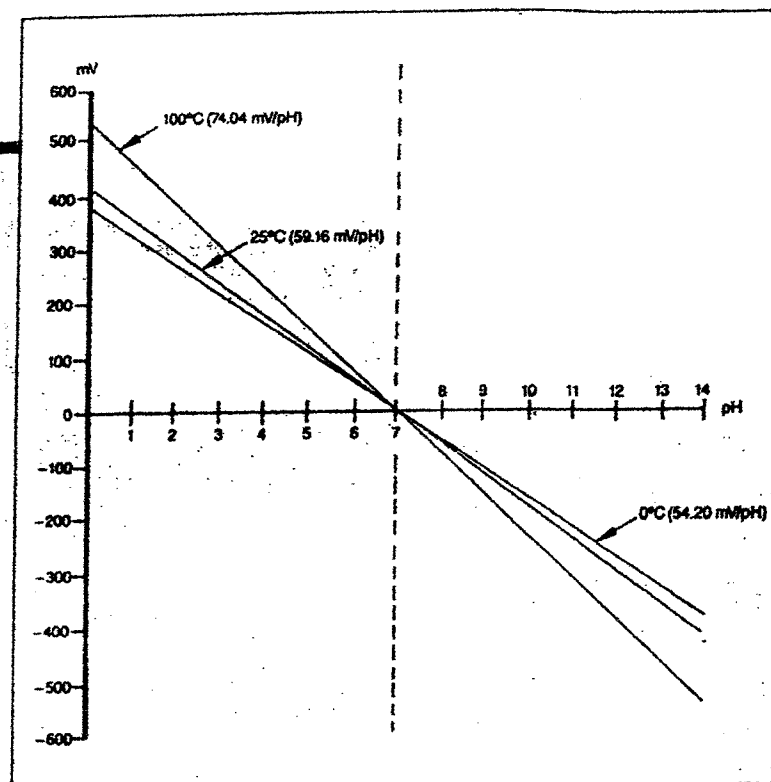


Figure 2

hydrogen ion activity in the solution may be temperature dependent. Temperature compensation does not correct for this, and is not desirable, because an accurate pH measurement is desired at that particular temperature. Temperature compensation only corrects for the change in the output of the electrode, not for the change in the actual solution pH.

Temperature will also affect the glass membrane's impedance. For each 8° below 25°C, the specified impedance approximately doubles. Depending on the original impedance of the glass membrane, the meter will have to handle a higher impedance at a lower temperature. **CE**

Written by: OMEGA ENGINEERING, INC.

## Measurement of pH

The measurement of pH is one of the most common analytical techniques used in chemistry laboratories today. Nonetheless, pH measurements often suffer from the effects of incorrect materials or incorrect maintenance. The purpose of this paper is to help simplify the choice of materials, methods, and maintenance protocols for pH measurements.

### pH MEASUREMENT SYSTEM

A pH measurement system always consists of four parts: a pH sensing electrode, an amplifier that translates the signal into something the user can read, a reference electrode, and the sample being measured. Each part of the system plays a critical role in the measurement process.

A glass electrode is actually a small battery (technically, a transducer). This battery displays a varying voltage, depending upon the pH of the solution in which it is immersed. A reasonable representation of that voltage is given in Figure 1. The potential of the glass electrode is a function of the activity of the free-hydrogen ions and a value  $E_0$  which is supposed to be the 0 or rest

potential of the system. This is actually the voltage of the system when the pH is 0.

The reference electrode is also a battery; however, unlike the pH electrode, its voltage does not vary with the activity of hydrogen ion or any other ion solution, but is a function only of the value  $E_0$  or the rest potential.

There are nine actual voltages in the system. Inside the body of the electrode is a wire — normally a silver wire coated with silver chloride. On that wire is some matrix that should present a constant voltage to the wire. At the interface of the wire and solution is a voltage which we can call  $E_1$ . Between the wire and the inner surface of the glass is another voltage, on the inner surface of the glass is a voltage ( $E_2$ ), and across the glass membrane there is a voltage ( $E_3$ ), which is called the asymmetry potential. There is a voltage on the outer surface of the electrode, a voltage between the pH electrode and the reference electrode; another voltage, referred to as the liquid junction potential or streaming potential, at the point where the filling solution of the reference electrode contacts the

sample ( $E_7$ ); a voltage between the inner surface of the reference electrode and the metal wire that connects the inner filling solution of the reference electrode to the lead wire, and, of course, another voltage on the surface of the connecting wire ( $E_9$ ).

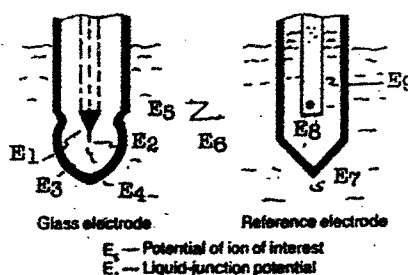


Figure 1. Flow chart of selection process for reference electrodes.

When making a pH measurement, one assumes that all of those voltages remain constant except the voltage on the outer surface of the pH electrode. If that assumption is correct, legitimate pH measurements can be made; if not, then incorrect pH measurements will certainly result. In other words, it is

assumed that the pH electrode delivers a varying voltage to the pH meter, while the reference electrode delivers a constant voltage to the meter.

### THE REFERENCE ELECTRODE

The reference electrode is the most complicated part of a pH measurement system. When application problems arise, they normally devolve to the reference electrode. When difficulties in pH measurements are encountered, the source of the problem is typically the reference electrode. In our experience the reference electrode accounts for 70% of the problems that arise in the pH measuring process.

A reference electrode consists of three principal parts: an internal element, which is normally either a silver wire coated with silver chloride or a platinum wire covered with a mixture of calomel ( $\text{Hg}_2\text{Cl}_2$ ), some filling solution, and a permeable junction through which the filling solution escapes the electrode (called the fluid junction or liquid junction). The liquid junction can come in several forms, but its principal function is to allow small quantities of the reference electrode's filling solution to slowly leak or migrate into the sample being measured. There are three common forms of this junction: 1) ceramic or other frit material, 2) a fibrous material (the best of which is quartz fiber) or 3) a sleeve junction.

Fritted materials are usually white and are composed of small particles pressed closely together. The filling solution leaks through the open cells between these particles. Since the cells vary considerably in size, the flow rate across the surface is quite variable. In some areas, there is almost no net outward flow of filling solution. At those points the junction is considered to be a "diffusion junction." In the areas where the net outward migration of filling solution is rapid, the electrode is considered to have a flowing junction.

Fiber references come in two types: woven fibers and straight fibers. Woven fibers, such as asbestos fiber, have cells of varying size because of the structure of the woven material. Some of these cells are very small and tightly packed together; at those points there is a diffusion junction. Where the fibers are loosely packed, the flow rate is high and a flowing junction exists.

The quartz fiber reference electrode consists of straight fibers of quartz laid next to each other with straight channels of filling solution passing between them. This junction generally is considered to have no diffusion properties and to be strictly a flowing junction.

The sleeve junction reference electrode is constructed by putting a hole in the side of a glass or plastic tube, grinding the surface around that tube, and covering it with a tapered glass or plastic sleeve. Such a junction is similar in its overall function to a frit junction in that certain areas are pressed tightly and other areas are not, so that both diffusion and flowing junctions exist. A sleeve junction electrode is much faster flowing and much easier to clean than the others.

Reference electrodes are available in a variety of types to accommodate many types of samples. Certain samples require reference electrodes that flow very slowly, whereas other samples require reference electrodes that are easy to clean. The flow chart in Figure 2 should serve as a guide in selecting the reference electrode most appropriate for the application.

The best way to understand the purpose of a reference electrode is to imagine measuring the voltage on a battery with a voltmeter. A voltage measurement cannot be made if only one end of the battery is connected to the meter. If, however, two leads are plugged into the voltmeter and both ends of the battery are touched, a reading is possible.

A pH electrode can be compared to the battery in this example. The wire inside the pH electrode serves the same purpose as the first lead from the voltmeter. The reference electrode can be compared to the second lead, which completes the circuit and enables the measurement of the voltage, or voltage changes, at the pH electrode.

In reality, the pH and reference electrodes are immersed in the same solution with the filling solution of the reference electrode flowing into the sample and completing the circuit with the pH electrode. If the reference electrode is not immersed in the sample, a legitimate measurement is not possible. If the reference electrode is immersed in the sample but is completely dry, no reading would be forthcoming. If it were filled with filling solution but completely occluded, then it would not establish good consistent electrical connection with the sample, and the readings would vary. A reference electrode that is partially plugged up allows the sample ions to migrate into the junction of the electrode and set up new potentials: voltages that are measured by the system and interpreted as changing pH readings. This is the most common source of problems in a pH measuring system.

The first indication of difficulty in the reference electrode usually is a very long stabilization time. This can be caused by changes in temperature, by reactions taking place in the solution, or by pickup of  $\text{CO}_2$  from the atmosphere. Generally, however, a long stabilization time is caused by either the incompatibility of the reference electrode with the sample being measured or by a faulty reference electrode.

It is usually possible to differentiate between drift caused by a faulty electrode and drift caused by other factors (incompatibility between electrode and sample, temperature changes, or reaction within the sample) by moving a hand quickly toward and then away from the electrode. If the reading on the pH meter changes significantly in response to the hand movement, and if the change in the meter reading reverses when retracting the hand, then it would be very safe to assume that the reference electrode is either plugged up or otherwise defective. If the drift continues undisturbed by the movement of the hand toward and away from the electrode, then the problem is probably in the sample. Although this is not a foolproof method, it works most of the time.

There are other ways to check for improperly functioning reference electrodes. The most positive checks are performed using a magnetic stirrer.

- If stirring a sample seems to cause an unstable reading; turn the stirrer off. If the reading changes significantly (by one or two tenths of a pH unit), then there is a reference electrode problem.
- If, while stirring, there is a fair amount of noise (variation in the reading), and turning the stirring motor down to a slower speed reduces the amount of noise, it is safe to assume that there is a reference electrode problem.

If the reference electrode is so dirty that it is completely occluded, it may be just like an open circuit. If this is the case, it exhibits the typical slow, never-ending drift. There are a number of other sources of this same problem (including the electrode's not being plugged in to the meter!), such as: broken wires within the pH or reference electrode; a broken lead wire from the pH or reference electrode; or an open circuit within the meter. A quick way to check whether the problem is in the electrodes or the meter is to substitute new electrodes or, using a wire, paper clip, or shorting plug, short between the reference electrode input and the pH electrode input on the meter. If shorting the electrode inputs does