pH Measurement

Introduction

This technical bulletin provides information on how a pH electrode functions and how industry defines this functionality with respect to concentration. In addition, this bulletin describes pH measurements above 12 pH and its effects and special considerations.

pH Nomenclature

Water and water-based solutions, consist of charged particles called ions and uncharged particles called molecules. Some ions have a positive electrical charge and others have a negative charge. In every case, the number and magnitude of the charges balance so that there is no excess charge. In pure water, some of the water molecules, which consist of two hydrogen atoms and one oxygen atom (H_20), dissociate into ions:

$$H_20 \rightleftharpoons H^+ + OH^-$$

The H^+ hydrogen ions normally vary in concentration from 1.0 to 0.00000000000001 moles per liter. Such numbers are cumbersome to work with. Therefore, chemists sought an easier way to express hydrogen ion concentration. Several methods were tried, but the method universally adopted is the pH scale. To translate a hydrogen ion concentration to a pH value, the concentration (moles/liter) is expressed in scientific notation as a power of ten. For example:

$$0.000001 \text{ moles/liter} = 10^{-6} \text{ moles/liter}$$

Consequently, the power of ten exponent number (without negative sign) becomes the pH value. For this example, the H^+ (hydrogen ion) concentration is equal to 6 pH. Note that changing the hydrogen ion concentration by a factor of ten changes the pH value by one pH unit.

The pH scale provides a convenient way to express hydrogen ion concentrations of any magnitude. Usually, the pH scale spans 0 to 14, although it is possible to have a pH value of less than zero (negative) or greater than 14. Typical pH values of some common solutions are listed in Figure 1.

Solution	Value	Solution	Value
Hydrochloric acid (37%)	0 pH	Pure water	7 pH
Hydrochloric acid (1.4%)	1 pH	Milk of Magnesia	10 pH
Lemon juice	2 pH	Ammonia (1.7%)	11 pH
Beer	3 pH	Caustic soda (1%)	13 pH
Cheese	5 pH	Caustic soda (4%)	14 pH

FIGURE 1 Typical pH Values of Common Solutions

Pure water has a pH value of 7, which is considered neutral. When a solution has a pH value of less than 7.0, it has a hydrogen ion concentration greater than that of water and is referred to as an acid. Conversely, a solution with a pH value of more than 7.0 has a hydrogen ion concentration less than that of water and is referred to as a base.

The pH Electrode

A pH electrode is constructed with two types of glass. The stem of the electrode is a non-conductive glass. The tip, which is most often bubble-shaped, is a specially formulated “pH sensitive” lithium ion-conductive glass consisting of the oxides of silica, lithium, calcium, and other elements. The structure of the pH glass allows lithium ion electrons to be exchanged by hydrogen ions in aqueous solutions, forming a hydrated layer. A millivolt potential is created across the interface between the pH glass and the external aqueous solution. The magnitude of this potential is dependent on the pH value of the solution. The difference of potentials (V_1 minus V_2) created at the outer and inner hydrated layers of the pH glass can be measured using silver/silver chloride electrodes (see Figure 2 on next page).

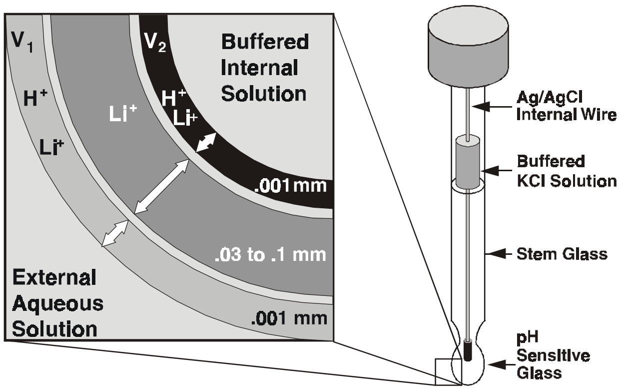

FIGURE 2 pH Glass Electrode Details

Since the internal solution of the glass electrode is buffered, its pH value is kept constant, making the measured potential difference dependent only upon the pH value of the external solution being measured.

The Nernst Equation

The millivolt potential across the glass electrode varies logarithmically with respect to hydrogen ion concentration. (Since the hydrogen ion may be influenced by its environment, the proper term for this relationship should be hydrogen ion "activity." In most applications, however, the terms "concentration" and "activity" are used interchangeably. This bulletin refers to the more common "concentration" expression.) The equation that defines the hydrogen ion concentration is known as the Nernst equation:

$$E = E_0 + 0.059 \log [H^+] \quad \text{or}$$

$$E = E_0 - 0.059 \text{ pH}$$

Where: E = Potential (volts)
E0 = Standard potential (volts)
$[H^+]$ = Hydrogen ion concentration

The value "0.059" is known as the "Nernst constant" which varies with temperature. At 25°C the Nernst constant value is 0.059 and at 80°C it is 0.070.

High pH Measurements

Although the pH glass electrode responds very selectively to H^+ ions, there is a small interference by similar ions like lithium (Li^+), sodium (Na^+), and potassium (K^+) which are illustrated by relative size in Figure 3.

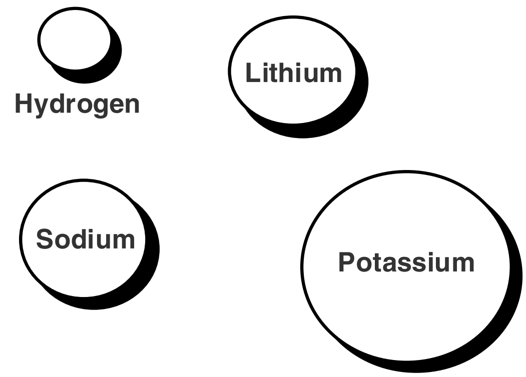

FIGURE 3 Relative Ion Sizes

The amount of interference decreases with increasing ion size. Since lithium ions are normally not in sample solutions and potassium ions cause very little interference, the most significant interference is from sodium ions.

Sodium ion interference only occurs when the hydrogen ion concentration is very low (10^{-12} or less). At 12 pH and higher, the sodium ion concentration, normally present because of sodium hydroxide (NaOH) addition, is in the range of 10^{-2}. Therefore, sodium ions will interfere when sodium ion concentration exceeds pH ion concentration by a factor of 10^{10} (ten thousand million times).

Depending on the exact glass formulation, sodium ion interference may take affect at a higher or lower pH value. Figure 4 graphically shows this phenomenon, known as "sodium ion error." It compares conventional pH electrode values with those of a standard hydrogen electrode that is not affected by sodium ion interference.

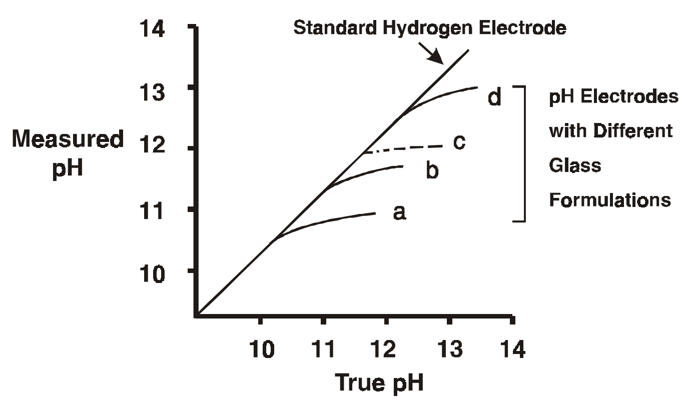

FIGURE 4 Sodium Ion Error

Electrode Considerations for High pH Measurements

There is no glass formulation currently available that has zero sodium ion error. Since there will be some error, it is important that the error be constant and reproducible. With many glass formulations this is not possible, because the electrode becomes sensitized to the environment it was in prior to the higher pH solution. For example, the exact start point of an electrode's sodium ion error might be 11.5 pH after immersion in tap water, but 12.5 pH after being in an alkaline solution. Additional considerations include temperature and electrode age.

The pH sensors manufactured by BI International use a specially formulated glass that, like all electrodes, exhibits a sodium ion error. This glass, however, is unique in that the sodium ion error is constant throughout the electrode's lifetime. This is accomplished by "controlled molecular etching" of the glass which purposely strips away one molecular layer at a time. This special characteristic provides a consistent amount of lithium ions available for exchange with the hydrogen ions to produce a similar millivolt potential for a similar condition.

Another consideration for high pH measurement applications is to measure the conductivity value instead of the pH value to attain the concentration of caustic.

Electrode Considerations for Hydrofluoric Acid Applications

Frequently, pH measurement applications involve the presence of hydrofluoric acid (HF). Hydrofluoric acid chemically attacks the glass electrode and renders it useless in a very short time. If the glass electrode remains in solution, it will eventually be dissolved. When a solution's pH value is less than 6 pH and hydrofluoric acid is present, it is recommended to use a pH electrode made of antimony instead of glass to avoid these problems.

Conclusion

There are many external influences that can affect the performance of a pH measuring system. To assure proper application of BI pH sensors, specific conditions of the process must be considered, including:

- Anticipated pH operating range
- Minimum and maximum process pH values
- Maximum temperature and pressure
- Composition of the process solution

It is also very useful to know about a previous measuring system's success or failure and any related circumstances.