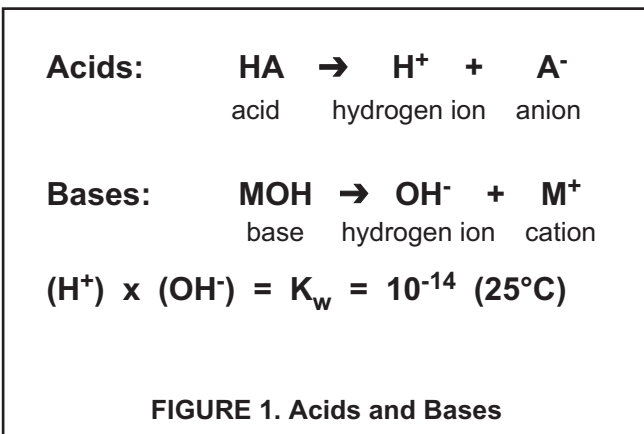# The Theory of pH Measurement

pH measurement has a wide variety of industrial applications in virtually every industry. These range from water conditioning to specific process related measurements to waste treatment.

WHAT IS pH?

pH is a measure of the acidity or alkalinity of a water solution. The acidity or alkalinity of a water solution is determined by the relative number of hydrogen ions (H^+) or hydroxyl ions (OH^-) present. Acidic solutions have a higher relative number of hydrogen ions, while alkaline (also called basic) solutions have a higher relative number of hydroxyl ions. Acids are substances which either dissociate (split apart) to release hydrogen ions or react with water to form hydrogen ions. Bases are substances that dissociate to release hydroxyl ions or react with water to form hydroxyl ions.

In water solutions, the product of the molar concentrations[1] of hydrogen and hydroxyl ions is equal to a dissociation constant (K_w). Knowing the value of the constant and the concentration of hydrogen ions makes it possible to calculate the concentration of hydroxyl ions, and vice versa. At 25°C, the value of K_w is 10^{-14} (see Figure 1).

Acids: $\quad HA \;\rightarrow\; H^+ \;+\; A^-$

$\qquad\qquad$ acid $\qquad$ hydrogen ion $\quad$ anion

Bases: $\quad MOH \;\rightarrow\; OH^- \;+\; M^+$

$\qquad\qquad$ base $\quad$ hydrogen ion $\quad$ cation

$(H^+) \;x\; (OH^-) \;=\; K_w \;=\; 10^{-14} \; (25°C)$

FIGURE 1. Acids and Bases

The concentration of hydrogen and hydroxyl ions can

[1] Molar concentration is a measurement of the number of atoms, molecules or ions in a solution.
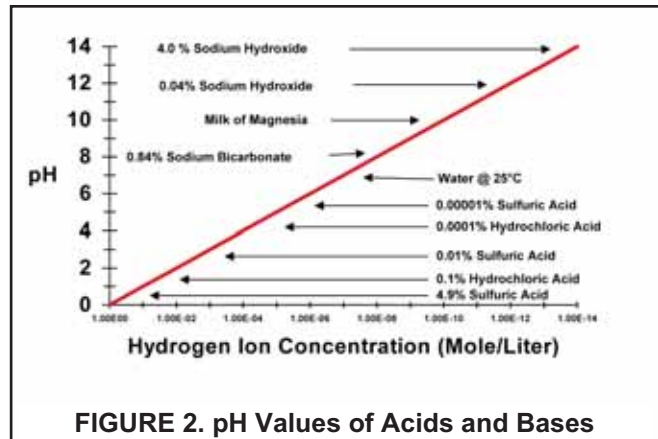

FIGURE 2. pH Values of Acids and Bases

vary over 15 orders of magnitude in water solutions. Even common household items can reflect this wide variation (Figure 2).

pH is strictly defined as the negative logarithm of the hydrogen ion activity (a_H):
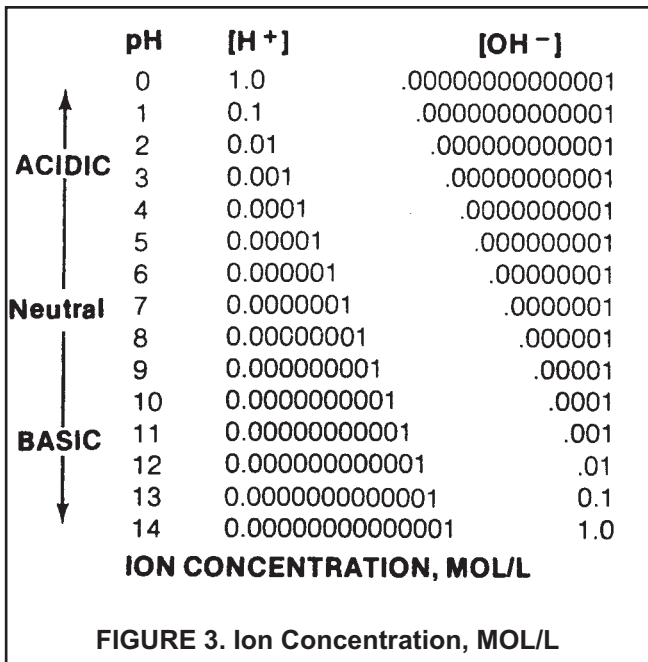
$$pH \;=\; -\log_{10} a_H$$

The hydrogen ion activity is defined as the molar concentration of hydrogen ions multiplied by an activity coefficient, which takes into account the interaction of hydrogen ions with other chemical species in the solution.

In practice, pH is often assumed to be the negative logarithm of the hydrogen ion concentration:

$$pH = -\log_{10} [H^+]$$

In this form, the usefulness of pH as a convenient shorthand for expressing hydrogen ion concentration can be seen on page 2, Figure 3:

At 25°C, a neutral solution has a pH of 7.0, while solutions with pH < 7 are acidic and solutions with pH > 7

ROSEMOUNT®
Analytical

EMERSON
Process Management

pH	[H+]	[OH−]
0	1.0	.00000000000001
1	0.1	.0000000000001
2	0.01	.000000000001
3	0.001	.00000000001
4	0.0001	.0000000001
5	0.00001	.000000001
6	0.000001	.00000001
7	0.0000001	.0000001
8	0.00000001	.000001
9	0.000000001	.00001
10	0.0000000001	.0001
11	0.00000000001	.001
12	0.000000000001	.01
13	0.0000000000001	0.1
14	0.00000000000001	1.0

ACIDIC — Neutral — BASIC

ION CONCENTRATION, MOL/L

FIGURE 3. Ion Concentration, MOL/L

are alkaline. The normal overall pH range is 0 to 14 pH, although solutions containing non-water solvents can have pH values outside this range.

THE MEASUREMENT OF pH

pH measurement is based on the use of a pH sensitive electrode (usually glass), a reference electrode, and a temperature element to provide a temperature signal to the pH analyzer.

The pH electrode uses a specially formulated, pH sensitive glass in contact with the solution, which develops a potential (voltage) proportional to the pH of the solution. The reference electrode is designed to maintain a constant potential at any given temperature, and serves to complete the pH measuring circuit within the solution. It provides a known reference potential for the pH electrode. The difference in the potentials of the pH and reference electrodes provides a millivolt signal proportional to pH.

Most pH sensors are designed to produce a 0 mV signal at 7.0 pH, with a (theoretically ideal) slope (sensitivity) of -59.16 mV / pH at 25°C.
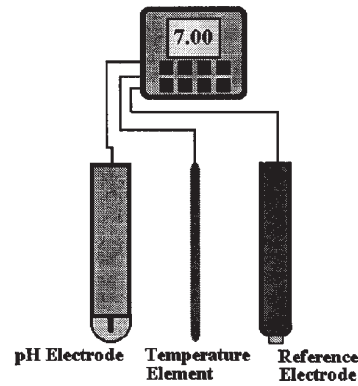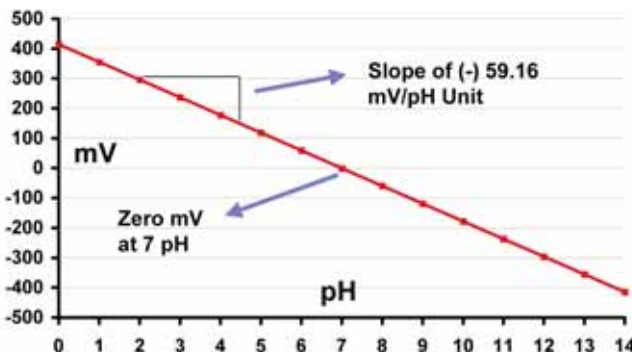
pH and reference electrode combination exhibits an isopotential point, which is a pH and millivolt potential at which the potential is constant with temperature changes. The isopotential point is most frequently designed to be at 7.0 pH and 0 mV. Using the isopotential point with a theoretical knowledge of electrode behavior makes it possible to compensate (correct) the pH measurement at any temperature to a reference temperature (usually 25°C), using a temperature signal from the temperature element. This makes the pH measurement independent of changes in the electrodes' output with temperature.

pH MEASUREMENT IN PROCESS SOLUTIONS

The potential effects of process solutions on pH sensors
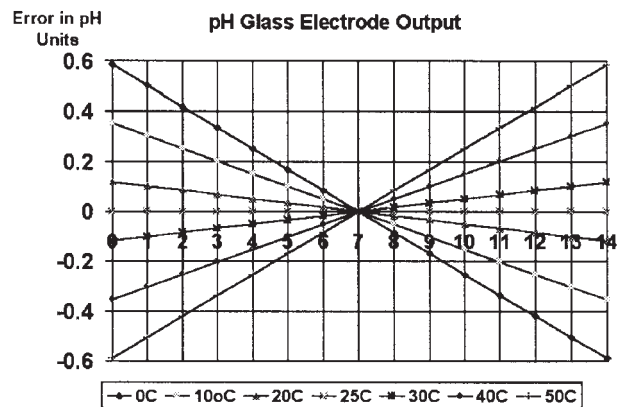
will require a more detailed look at the construction of pH and reference electrodes. But first, some basic properties of the pH of water solutions need to be examined.

pH IN AQUEOUS SOLUTIONS

Practical pH Measurement Range

Although the range of pH measurements is defined to be 0 to 14 pH, solutions with pH values near the extremes of this range are often better measured using conductivity.

At pH values below 1.0 pH, the glass pH electrode can be subject to acid errors, and the sensor can be

subject to chemical attack. Solutions with a pH in this range have an acid concentration at, or approaching the percent by weight range, which will have conductivity likely to be large in comparison to other electrolytes in the solution. A toroidal conductivity measurement, with a read-out in percent acid, can often be successfully applied in these cases and will be a far more accurate measurement of acid concentration than pH.

In the case of high pH, the reason for switching to a
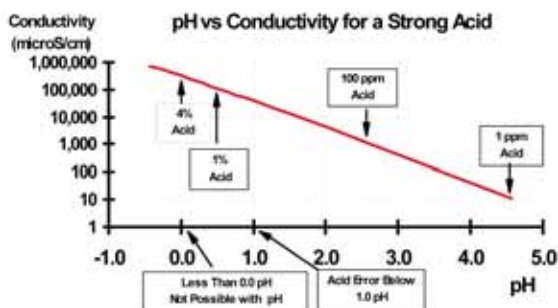
conductivity measurement is more compelling: highly alkaline solutions quickly destroy glass pH electrodes. If the nominal pH is expected to be above 13 pH, a conductivity measurement should be considered.

Solution pH Changes with Temperature
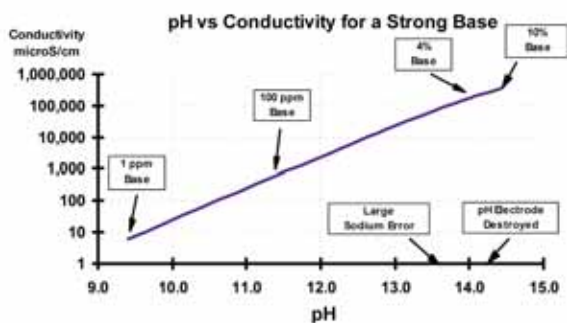
The pH of a solution can change with temperature, due to the effect of temperature on the dissociation of weak acids and bases, and the dissociation of water itself. In fact, any solution with a pH of 7 or above will have some degree of temperature dependence. How much this will affect the measurement will depend upon the composition of the solution and how high the nominal process temperature is above 25°C. This behavior is frequently the explanation for discrepancies between laboratory and on-line pH measurements.

Modern pH analyzers allow their temperature compensation routines to be modified to take into account solution pH changes with temperature as well as changes in the millivolt output of the electrodes. Simply entering the temperature coefficient of the solution (pH change per degree C) into the analyzer does this. While the temperature coefficient can be calculated for simple cases, it is often necessary to measure it in the laboratory by noting the pH at various temperatures. If the composition of a process changes, the temperature coefficient can also change;

therefore, the final product composition should be used for determining the solution coefficient.

Processes with Mixed Solvents

The conventional pH analyzer and sensor are designed to measure the pH in water solutions. When a non-water solvent is present in appreciable quantities, the pH reading will be shifted from the expected value by effects of the non-water solvent on the pH and reference electrodes, and effects on the activity of hydrogen ion itself. Since pH sensor components are designed for use in water, the non-water solvent may attack seals and O-rings.

There are a few mixed solvent cases that can be considered:

(1) A solvent that is miscible with (mixes with) water may cause a shift in the pH reading, but if the solvent's concentration is above 15% by weight, it may dry the pH electrode, requiring periodic rewetting of the sensor by water.

(2) A solvent that is non-miscible with water will likely not have an appreciable concentration of hydrogen ions; most will be in the water phase. It is better to make the measurement in a place in the process where the water and solvent phases separate and keep the pH sensor in the water phase.

(3) Completely non-water process measurements may only be possible with periodic rewetting of the pH sensor with water, and may also require a specially designed reference electrode.

In all of the above cases, pH measurement of the mixed solvent solution should be studied in the laboratory before going on-line, and the study should include prolonged exposure of the pH sensor to the process sample.

PROCESS EFFECTS ON THE GLASS pH ELECTRODE

A glass pH electrode consists of an inert glass tube with a pH sensitive glass tip, either hemispherical (bulb) or flat in shape, blown onto it. The tip contains a fill solution with a known pH, and it is the influence of this solution on the inside of the glass tip versus the influence of the process solution on the outside that gives rise to its millivolt potential. Ideally, the pH electrode will have a slope (response) of -59.16 mV/pH, but in practice, a new electrode may only have a slope
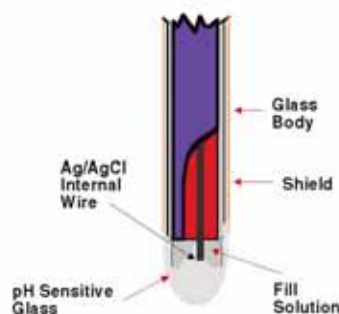
of -57 to -58 mV/pH. As the electrode ages, its slope decreases.

Temperature Effects

In addition to changing millivolt output of the pH electrode, elevated temperatures accelerate the aging of the electrode. Extremely high or low temperatures can alternatively boil the fill solution or freeze it, causing the electrode tip to break or crack. Elevated temperatures can also affect the interior and exterior of the pH electrode differently, giving rise to asymmetry potential, which shifts the zero point of the pH electrode and changes its temperature behavior, which leads to temperature compensation errors.

Sodium Error

More correctly called alkali ion error, sodium ion error occurs at high pH, where hydrogen ion concentration is very low in comparison to sodium ion concentration. The sodium ion concentration can be so high relative to hydrogen ion contration that the electrode begins to respond to the sodium ion. This results in a reading that is lower than the actual pH. Depending on the pH glass formulation, this can occur as low as 10 pH. Where accurate high pH readings are required, the upper pH limit of the pH electrode should be checked and a specially formulated, high pH electrode used if necessary. Compared to sodium, lithium ions will produce a larger error, while the effect of potassium ions is negligible.

Components Attacking pH Electrodes Caustic

As noted earlier, high concentrations of hydroxyl ions shorten the life of pH electrodes. Solutions, that reach a pH in excess of 14 pH (equivalent to 4% caustic soda) can destroy a pH electrode in a matter of hours. There is nothing that can be done to prevent this, short of simply avoiding pH measurements in these solutions and using conductivity instead.

Hydrofluoric Acid

Hydrofluoric acid (HF) also dissolves pH glass, but there are pH glass formulations designed to resist destruction by HF, which when used within their limits can give satisfactory electrode life.

It is important to note that, while only hydrofluoric acid (HF) attacks glass and not fluoride ion ($F-$), hydrofluoric acid is a weak acid. Therefore, a solution can contain a relatively high concentration of fluoride ion at a high pH and do no damage to the electrode. But if the pH of the solution decreases, the fluoride ion will combine with hydrogen ion to form HF, which will damage the electrode. So, it is important to look at the extremes of the pH measurement (even in process upset conditions) and the total concentration of fluoride in the solution to determine what the maximum concentration of HF will be.

PROCESS EFFECTS ON REFERENCE ELECTRODES

The common reference electrode used in pH measurements consists of a silver wire coated with silver chloride in a fill solution of potassium chloride. The purpose of the potassium chloride is to maintain a reproducible concentration of silver ions in the fill solution, which in turn, results in a reproducible potential (voltage) on the silver-silver chloride wire. For the reference electrode to maintain a reproducible potential, the fill solution must remain relatively uncontaminated by certain components in the process solution.

At the same time, the reference electrode must be in electrical contact with the pH electrode through the process solution. A porous liquid junction of ceramic, wood, or plastic, which allows ions to pass between the fill solution and the process, typically does this. This passage of ions between the reference electrode and the process is necessary to maintain electrical contact, but also creates the potential for contamination of the reference fill solution by components in the process solution.

Reference Poisoning

REFERENCE ELECTRODE COMPONENTS

- Internal element- Ag\AgCl
- Electrolyte fill - KCl/AgCl
- Liquid Junctions
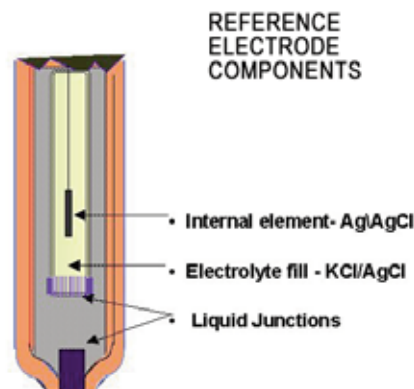
The mechanism of reference poisoning is a conversion of the reference from a silver-silver chloride based electrode to an electrode based on a different silver compound. The ions, which typically cause this form less soluble salt with silver than does chloride. These ions include bromide, iodide, and sulfide ions. When these ions enter the fill solution, they form insoluble precipitates with the silver ions in the fill solution. But there is no initial effect on the potential of the reference, because the silver ions lost to precipitation are replenished by silver ions dissolving off the silver chloride coating of the silver wire. It is not until the silver chloride coating is completely lost that a large change in the potential (and temperature behavior) of the reference occurs. At this point, the reference electrode must be replaced.

Poisoning can also occur by reducing agent (bisulfite) or complexing agents (ammonia), which reduce the concentration of silver ion in the fill solution by reducing it to silver metal or complexing it.

To counter this effect, multiple junction reference electrodes are used, which consist of two or more liquid junctions and fill solutions to slow the progress of the poisoning ions. Gelling of the reference fill solution is also used to prevent the transport of poisoning ions by convection.
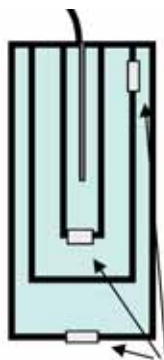
Liquid Junctions

A new approach is the use of a reference with a long tortuous path to the silver-silver chloride wire, along with gelling of the fill solution.

Plugging of the Liquid Junction

To maintain electrical contact between the reference electrode and the pH electrode, there must be a relatively free diffusion of ions between the reference fill solution and the process solution. In some cases, large concentrations of an ion that forms an insoluble precipitate with silver ion (most notably sulfide ion) will precipitate within the liquid junction and plug it. Metal ions that form insoluble salts with chloride ion (typically the heavy metals: silver, lead, and mercury) will also precipitate in the liquid junction.

When the liquid junction is closed to migration, the pH reading will drift aimlessly.

To counter these effects, multiple junction reference electrodes have been used with the outermost fill solution containing potassium nitrate, rather than potassium chloride.This lowers the concentration of chloride available for precipitation by heavy metals, as well as lowers the concentration of free silver ion, which can precipitate with sulfide.

Liquid Junction Potential

Potassium chloride is chosen for the fill solution not only for its ability to solubilize silver ion, but also because it is equitransferent. Equitransferent means that the positive potassium ion and the negative chloride ion diffuse through a water solution at nearly the same rate. When diffusing through the liquid junction of a reference electrode, both the positive and negative

ions tend to move together and maintain a net zero charge at all points within the liquid junction.

However, not all solutions are equitransferent, and when the process solution is not, a liquid junction potential can result. When a positive ion diffuses through the liquid junction faster than a negative ion, or vice versa, a charge imbalance will result. This gives rise to an opposing potential, which is liquid junction potential. The magnitude of this potential depends upon the composition and concentrations in the process solution and the design of the liquid junction.

This potential gets added to the potentials of the pH and reference electrodes and causes an offset to the pH measurement of typically a few tenths of a pH. This phenomenon normally takes 15 to 20 minutes to develop after the pH sensor is put on line. pH buffer solutions, used to calibrate pH measurements, are by and large equitransferent, so returning a freshly buffer-calibrated pH sensor to a buffer solution from the process will show an offset in the buffer until the liquid junction potential subsides.

The remedy for liquid junction potential is to standardize the pH measurement after the sensor has been put on-line and has stabilized.

LIQUID JUNCTION POTENTIAL

$$E = E_{pH} - E_{REF} + E_j$$
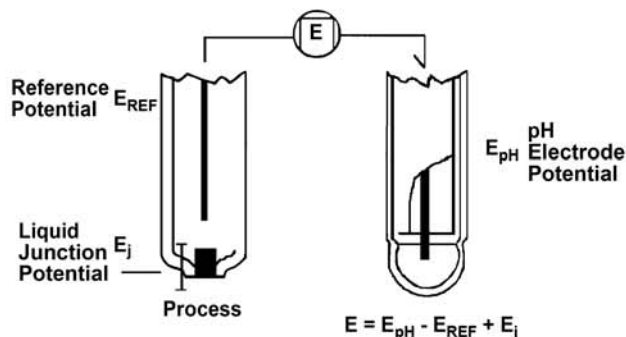
pH SENSOR COATING AND CLEANING

Undissolved solids and liquids in a process can coat a pH sensor, drastically increasing its response time or even plugging the liquid junction of the reference electrode. Depending upon rate of fouling, the sensor can either be cleaned manually or on-line.

Manually cleaning the sensor should be done with the mildest effective cleaning solution possible. Alkaline deposits can be removed with weak acid solutions (5% HCl or vinegar), while acid deposits may be removed with mild caustic (1% caustic soda). Organic deposits (oil and grease) can often be removed with a detergent solution, but a more tenacious coating may require the use of a solvent. The solvent used should be carefully chosen to avoid attack on the sensor's O-rings and seals.

In all cases, the exposure to the cleaning solution should be minimized to limit the amount of cleaning

solution entering the liquid junction. Cleaning solution that enters the liquid junction can create a liquid junction potential, which will persist until the cleaning solution components diffuse out of the liquid junction.

On-line cleaning reduces maintenance in processes that quickly foul the sensor. Ultrasonic cleaning was the first approach to on-line cleaning, but was ineffective on soft or gelatinous coating, and only marginally effective with hard crystalline coatings, which it was designed to address. It has, for the most part, been abandoned as a cleaning method.

One of the most fruitful methods for on-line cleaning has been the jet spray cleaner. This method directs a spray of water or cleaning solution at the face of the pH sensor at timed intervals or based on a high refer-ence impedance alarm (see Reference Electrode Impedance [next page]).

A new liquid junction design, the hydrolysis reference junction (TUpH™), has proved effective in avoiding the effects of severe coating. The TUpH junction uses extremely small pores, difficult to penetrate by most particulates and suspensions, over a relatively wide area. Use of this junction can drastically reduce the required frequency of manual cleaning and, in most cases, eliminates the need for on-line cleaning.

CALIBRATION
Buffer Calibration

Buffers are standard solutions formulated to maintain a known pH in spite of small amounts of contamination. Buffer calibrations use two buffer solutions, usually at least 3 pH units apart, which allows the pH analyzer to calculate a new slope and zero value to be used for deriving pH from the millivolt and temperature signals.

The slope and zero value derived from a buffer calibration provide an indication of the condition of the glass electrode from the magnitude of its slope, while the zero value gives an indication of reference poisoning or asymmetry potential. Overall, the buffer calibration can demonstrate how well the pH sensor responds to pH.

Buffer Calibration Errors

Buffer solutions have a stated pH value at 25°C, but when that value is 7 pH or above, the actual pH of the buffer will change with temperature. The values of the buffer solution at temperatures other than 25°C are usually listed on the bottle. The pH value at the cali-bration temperature should be used or errors in the slope and zero values, calculated by the calibration, will result. An alternative is to use the "buffer recogni-tion" feature on modern pH analyzers, which automati-cally corrects the buffer value used by the analyzer for the temperature.

Another type of calibration error can be caused by buffer calibrations done in haste, which may not allow the pH sensor to fully respond to the buffer solution. This will cause errors, especially in the case of a warm pH sensor not being given enough time to cool down to the temperature of the buffer solution. Current pH analyzers have a "buffer stabilization" feature, which prevents the analyzer from accepting a buffer pH reading that has not reached a prescribed level of stabilization.

Grab Sample Standardization of pH

Standardization is a simple zero adjustment of a pH analyzer to match the reading of a sample of the pro-cess solution made using a laboratory or portable pH analyzer. It is most useful for zeroing out a liquid junc-tion potential, but some caution should be used when using the zero adjustment. A simple standardization does not demonstrate that the pH sensor is respond-ing to pH, as does a buffer calibration. In some cases, a broken pH electrode can result in a believable pH reading, which can then be standardized to a grab sample value.

A sample can be prone to contamination from the sample container or even exposure to air; high purity water is a prime example. A reaction occurring in the sample may not have reached completion when the sample was taken, but will have completed by the time it reaches the lab. Discrepancies between the labora-tory measurement and an on-line measurement at an elevated temperature may be due to the solution pH being temperature dependent; adjusting the analyzer's temperature compensation (not a zero adjustment) is the proper course of action. Finally, it must be remem-bered that the laboratory or portable analyzer used to adjust the on-line measurement is not a primary pH standard, as is a buffer solution, and while it is almost always assumed that the laboratory is right, this is not always the case.

pH Diagnostics

The most straightforward way to validate the accuracy of a pH analyzer and sensor is by a buffer calibration. This is not possible during on-line operation, and, in general, the only clue to an on-line problem is a pH reading that is clearly impossible, given what is known about the process.

Over the years, on-line pH diagnostics came into use with the advent of the microprocessor driven analyz-ers. But these early diagnostics were restricted to the pH analyzer only. They provided self-checking of the analyzer and detection of electrode and temperature sensor inputs that were out of range due to shorts or open circuits.

pH Sensor Impedance Diagnostics

The pH sensor is the most maintenance intensive part of the pH measurement, and with the widespread use of disposable pH sensors, it is likely to fail after 6 to 12 months of use, or even sooner in severe applications. Failures can occur slowly, such as the gradual loss of pH electrode slope or poisoning of the reference electrode. Or they can occur suddenly or catastrophically, as in the case of pH electrode breakage or coating and plugging of a reference electrode. In either case, failure might go undetected until the next routine buffer calibration. The purpose of impedance diagnostics is to detect these problems in real time.

Glass pH Electrode Impedance

Glass pH electrode impedance is in the range of 10's to 100's of megOhms and is strongly temperature dependent. A crack or break in the glass electrode creates a short, which results in an impedance of 1 megOhm or less. Detecting broken or cracked pH electrodes requires impedance measurement circuitry with temperature compensation and the simple setting of a low impedance alarm.

Reference Electrode Impedance

The overall impedance of a reference electrode is a sum of the resistances of its components with the largest being the liquid junction. This is due to the limited volume of current carrying electrolyte within the liquid junction. Coating or blockage of the liquid junction further increases the impedance of the liquid junction. Detection of coating or blockage involves setting a high reference impedance alarm.

SUMMARY

pH measurements are based on the response of a pH sensor to the logarithmic concentration of hydrogen ions in solution and are a measure of the acidity or alkalinity of a solution. There are a number of factors that should be considered for on-line pH measurements. These involve the temperature behavior of the solution pH, the composition of the process solution, and the potential for fouling of the sensor by undissolved material in the process. Contemporary pH analyzers offer the user calibration routines to improve the accuracy of calibrations, as well as diagnostics to detect pH sensor failure on-line.
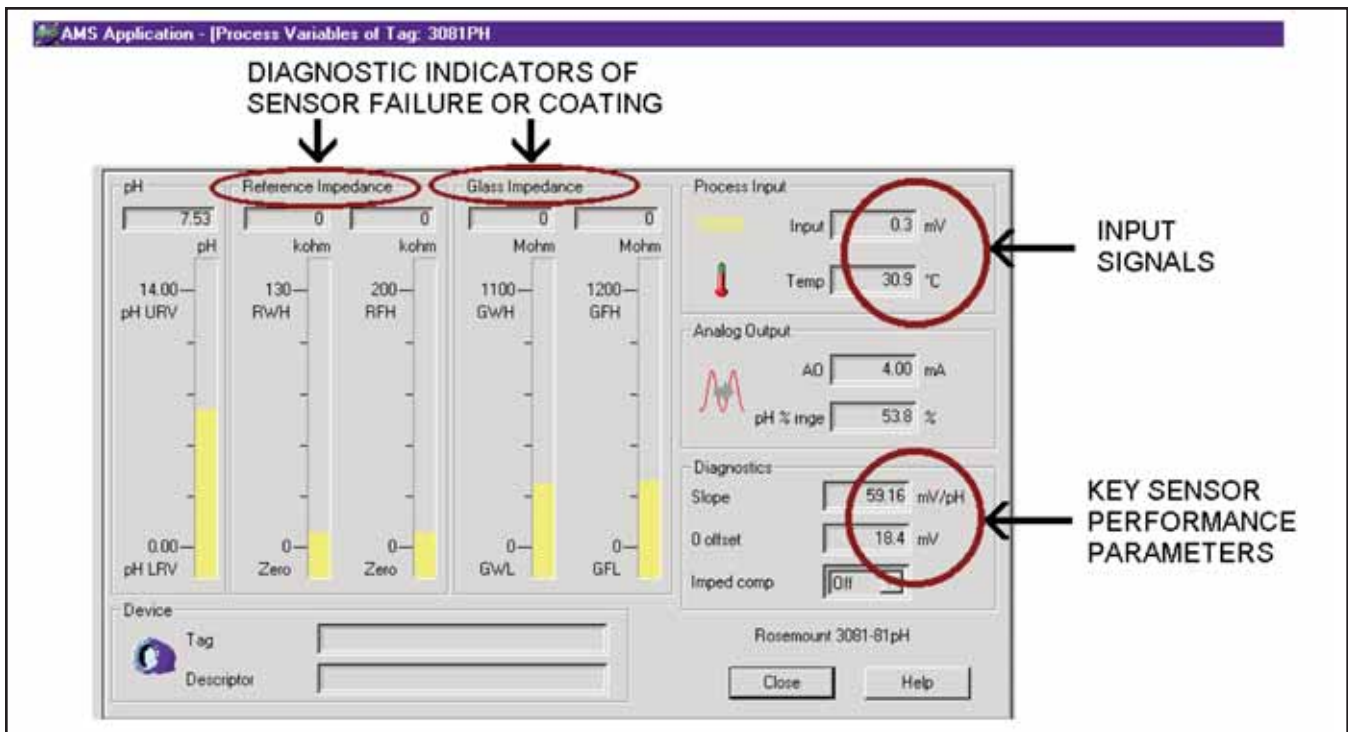
Emerson's Asset Management Solutions software is an excellent tool for tracking changes in the condition of the pH sensor. The Windows-based software can continuously display live values of sensor diagnostic variables when used with a compatible HART device. For more information, see Application Data Sheet 43-017.

INSTRUMENTATION

Model 54e pH Microprocessor Analyzer

- NEMA 4X (IP65) weatherproof, corrosion-resistant enclosure.
- Comprehensive pH glass and reference diagnostics.
- Fully descriptive diagnostic messages.
- Two independent outputs.
- Back-lit dot-matrix display.
- HART and AMS aware.
- Optional TPC relays and PID current outputs.

Model 5081 pH/ORP Smart Two-Wire Transmitter

- Hand-held infrared remote control link to activate all the transmitter functions.
- Large custom LCD display.
- NEMA 4X (IP65) weatherproof, corrosion-resistant enclosure.
- Comprehensive pH glass and reference diagnostics.
- Non-volatile EEPROM memory to hold data in event of power failure.
- Compatible with FOUNDATION fieldbus and HART communication protocol and AMS software.

Model 396P pH/ORP TUpH Sensor

- Polypropylene reference junction and helical pathway mean longer sensor life in process solutions containing heavy solids.
- Disposable, one-piece construction is convenient and economical where minimal troubleshooting and maintenance downtime are of prime importance.
- Versatile. Can be used in numerous loop configurations with all Rosemount Analytical and other manufacturers' instruments.

Model 396R Retractable pH/ORP TUpH Sensor

- Rugged titanium and polypropylene construction for maximum chemical resistance.
- Longer sensor life and reduced maintenance.
- Retractable version for greater insertion depths.

EMERSON™
Process Management