pH Measurement Electrode Basics

pH electrode technology hasn't changed much in the past 50 to 60 years. With all the technological advancements of the last 30 to 40 years, pH electrode manufacturing remains an art. The special glass body of the electrode is blown to its configuration by glass blowers. Not a terribly advanced nor "high tech" process but a very critical and important step in the electrode manufacturing. In fact, the thickness of the glass determines its resistance and affects its output.

MDS37, $750, see page B-29.

pH electrodes are constructed from a special composition glass which senses the hydrogen ion concentration. This glass is typically composed of alkali metal ions. The alkali metal ions of the glass and the hydrogen ions in solution undergo an ion exchange reaction generating a potential difference. In a combination pH electrode, the most widely used variety, there are actually two electrodes in one body. One portion is called the measuring electrode, the other the reference electrode. The potential that is generated at the junction site of the measuring portion is due to the free hydrogen ions present in solution. The potential of the reference portion is produced by the internal element in contact with the reference fill solution. This potential is always constant. In summary the measuring electrode delivers a varying voltage and the reference electrode delivers a constant voltage to the meter.

The voltage signal produced by the pH electrode is a very small, high impedance signal. The input impedance requires that it only be interfaced with equipment with high impedance circuits. The input impedance required is greater than 10^{13} ohms. This is the reason why pH electrodes do not interface directly will all equipment.

pH electrodes are available in a variety of styles for both laboratory and industrial applications. No matter their status, they are all composed of glass and are therefore subject to breakage. Electrodes are designed to measure mostly aqueous media. They are not designed to be used in solvents, such as CCl_4, which does not have any free hydrogen ions.

The pH electrode due to the nature of its construction needs to be kept moist at all times. In order to operate properly the glass needs to be hydrated. Hydration is required for the ion exchange process to occur. If an electrode should become dry, it is best to place it in some tap water for a half hour to condition the glass.

pH electrodes are like batteries; they run down with time and use. As an electrode ages, its glass changes resistance. This resistance change alters the electrode potential. For this reason, electrodes need to be calibrated on a regular basis. Calibration in a pH buffer solution corrects for this change. Calibration of any pH equipment should always begin with buffer 7.0 as this is the "zero point." The pH scale has an equivalent mV scale. The mV scale ranges from +420 to -420 mV. At a pH of 7.0 the mV value is 0. Each pH change corresponds to a change of ±60 mV. As pH values become more acidic, the mV values become greater. For example a pH of 4.0 corresponds to a value of 180 mV.

PHB-212, $420, see page B-23.

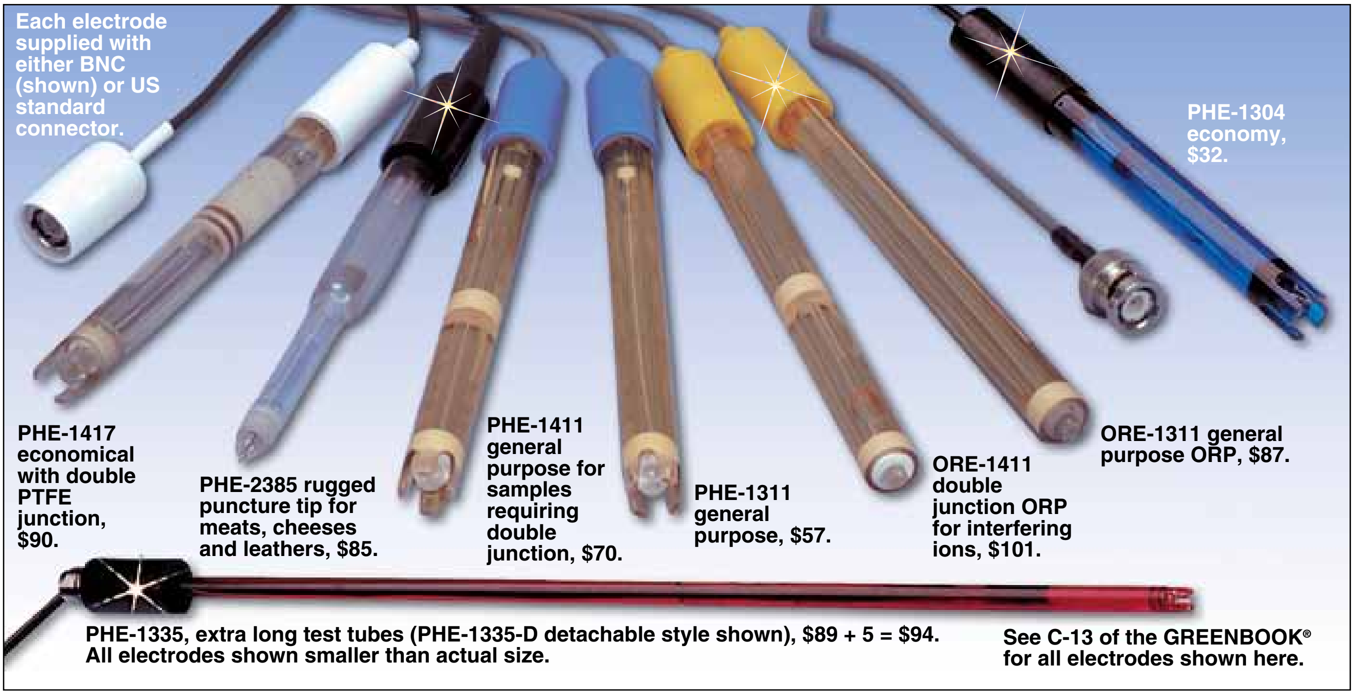
As pH values become more basic, the mV values become more negative; pH=9 corresponds to -120 mV. Dual calibration using buffers 4.0 or 10.0 provide greater system accuracy.

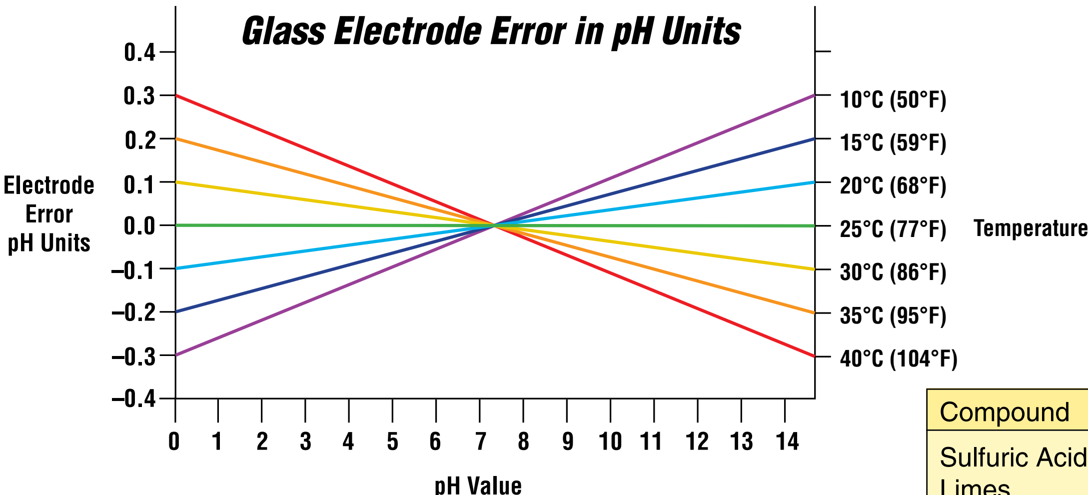
pH electrodes have junctions which allow the internal fill solution of the measuring electrode to leak out into the solution being measured. This junction can become clogged by particulates in the solution and can also facilitate poisoning by metal ions present in the solution. If a clogged junction is suspected, it is best to soak the electrode in some warm tap water to dissolve the material and clear the junction.

pH electrodes should always be stored in a moistened condition. When not in use, it is best to store the electrode in either buffer 4.0 or buffer 7.0. Never store an electrode in distilled or deionized water as this will cause migration of the fill solution from the electrode.

pH electrodes have a finite lifespan due to its inherent properties. How long a pH electrode will last will depend on how it is cared for and the solutions it is used to measure. Typically, a gel-filled combination pH electrode will last 6 months to 1 year depending on the care and application. Even if an electrode is not used it still ages. On the shelf, the electrode should last approximately a year if kept in a moistened condition. Electrode demise can usually be characterized by a sluggish response, erratic readings or a reading which will not change. When this occurs, an electrode can no longer be calibrated.

pH electrodes are fragile and have a limited lifespan. How long an electrode will last is determined by how well the probe is maintained and the pH application. The harsher the system, the shorter the lifespan. For this reason it is always a good idea to have a back-up electrode on hand to avoid any system down time. Calibration is also an important part of electrode maintenance. This assures not only that the electrode is behaving properly, but that the system is operating correctly. In summary these are the "electrode facts of life."





59 mV per decade at 25°C (77°F)
52 mV per decade at 0°C (32°F)
74 mV per decade at 100°C (212°F)

Automatic Temperature Compensation becomes more critical as the temperature changes from 25°C (77°F), or the pH from 7.0

Compound	pH Value
Sulfuric Acid	0.3
Limes	2.8-3.8
Wines	3.0
Oranges	3.0-4.0
Beer	4.0-5.0
Blood, Human	7.3-7.5
Egg whites	7.6-8.0
Sodium Bicarbonate	8.4
Ammonia	11.6
Sodium Hydroxide	14.0

	H^+ (Hydrogen Ions) Acid							Neutral	OH⁻ (Hydroxyl Ions) Alkaline						
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
mV @ 25°C (77°F)	+ 414	+ 355	+ 296	+ 237	+ 177	+ 118	+ 59	00	– 59	– 118	– 117	– 237	– 296	– 355	– 414

Temperature Compensation pH Measurement Error

The millivolt output of all pH electrodes varies with temperature in a manner predicted by theory. The magnitude of this variation is a function of temperature and of the pH value of the system being measured.

At a pH of 7 and a temperature of 25°C (77°F), temperature error is approximately zero. So, at any temperature when the pH is about 7, there is no temperature error. And, at any pH when the temperature is at 25°C (77°F), there is no error. When the temperature is other than 25°C (77°F) and the pH other than 7, the temperature error is:

0.03 pH error/pH unit/10°C (18°F).

The following table illustrates this combined effect:

pH TEMPERATURE ERROR TABLE

Temperature, °C	pH Value										
	2	3	4	5	6	7	8	9	10	11	12
5	–0.30	–0.24	–0.18	–0.12	–0.06	0	+0.06	+0.12	+0.18	+0.24	+0.30
15	–0.15	–0.12	–0.09	–0.06	–0.03	0	+0.03	+0.06	+0.09	+0.12	+0.15
25	0	0	0	0	0	0	0	0	0	0	0
35	+0.15	+0.12	+0.09	+0.06	+0.03	0	–0.03	–0.06	–0.09	–0.12	–0.15
45	+0.30	+0.24	+0.18	+0.12	+0.06	0	–0.06	–0.12	–0.18	–0.24	–0.30
55	+0.45	+0.36	+0.27	+0.18	+0.09	0	–0.09	–0.18	–0.27	–0.36	–0.45
65	+0.60	+0.48	+0.36	+0.24	+0.12	0	–0.12	–0.24	–0.36	–0.48	–0.60
75	+0.75	+0.60	+0.45	+0.30	+0.15	0	–0.15	–0.30	–0.45	–0.60	–0.75
85	+0.90	+0.72	+0.54	+0.36	+0.18	0	–0.18	–0.36	–0.54	–0.72	–0.90

NOTE: *Values in light blue are less than 0.1 error and may not require temperature compensation. Values in gray are temperature and pH in which there is no error in pH from temperature.*

Add the appropriate error factor to correct uncompensated readings. Correct uncompensated readings as follows (the factors from the table assume that the electrodes were calibrated in buffer at 25°C/77°F):

Effects of Temperature on pH

Temperatures Above 25°C: temperature compensation lowers high pH and raises low pH, resulting in value closer to neutral.

Temperatures Below 25°C: temperature compensation raises high pH (more basic) and lowers low pH (more acidic), resulting in values further away from neutral.

Whether or not temperature compensation need be used is a matter of the needed pH accuracy. For example, if the accuracy requirement is ±0.1 pH, at a pH of 6 and a temperature of 45°C (113°F), the error is 0.06, well within the accuracy requirements. On the other hand, with the same ±0.1 pH accuracy requirement, operating at pH 10 and 55°C (131°F) would give an error of 0.27 pH and compensation should be used.

When compensation is required, it can be done in one of two ways. If the temperature fluctuates, then an automatic compensator should be used. If the temperature is constant within several degrees C, then a manual compensator can be used. If no compensator is needed, a fixed resistor can be installed across the temperature compensator terminals.

Any of the above devices–automatic compensation, manual compensation or fixed resistor–operate as a function of the pH meter's electronic circuit. As such, information and parts should be obtained from the meter manufacturer.

If automatic compensators are used, they should always be at the same location as the pH electrode. When electrodes are calibrated in buffer, the temperature compensator also should be in the buffer. In a similar way, a manual temperature compensator should be adjusted to reflect the temperature to which the pH electrode is exposed during both calibration and operation.

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pH Measurement Tips

The measurement of pH is very important in many laboratories and industries. Below are a few guidelines to aid in making accurate and precise pH readings.

Meter Calibration

Frequency
For accurate results a pH meter should be calibrated at least once per 8-hour shift.

Buffers
Standard buffers should always be used for meter calibrations. Buffers can be purchased already prepared or in capsule form.

Standard buffers usually are available in three pH values—pH 4.00, pH 7.00, and pH 10.00.

Buffers should be stored away from heat and in tightly sealed containers.

Always use freshly poured buffers for meter calibration.

All buffers should be used at room temperature, 25°C (77°F).

PHB-600R, $570, with pH electrode, temperature probe, 2 buffer solutions and electrode holder (all included), shown smaller than actual size. See page B-25 for more information.

Types of Calibration

One-Point Calibration
Meter calibration using only one buffer. The value of buffer used should be that closest to value anticipated for sample.

Two-Point Calibration
Meter calibration using two buffers, one of which should always be 7.00. The second buffer used would depend on the application.

Method
Here is a general method for most pH meters. Some pH meters require slightly different techniques. Please read the instructions for their particular procedures.

1. The temperature setting on the meter must correspond to the temperature of the buffers used, or an automatic temperature compensator must be employed.
2. Turn pH meter to “pH” or “ATC” if automatic temperature compensation is used.
3. Place clean electrode into fresh, room temperature pH 7.00 buffer.
4. Adjust the pH reading to exactly 7.00 using the ZERO OFFSET, STANDARDIZED or SET knob.
5. Rinse the electrode with distilled or deionized water. (This would be the procedure for a one-point calibration. Continue through step 8 for a two-point calibration.)
6. Place electrode into the second buffer, either pH 4.00 or pH 10.00.
7. Adjust the pH reading to display the correct value using the SLOPE, CALIBRATE, or GAIN controls (coarse ajust).
8. Adjust the pH reading to read the correct value using the SLOPE knob (fine ajust).

The pH meter is now calibrated and ready to use.

Electrode Care
Over 80% of pH measurement difficulties are due to electrode problems. Proper storage, use, and maintenance increases accuracy.

Storage
Electrodes should be stored in an acidic solution with a low salt content. Commercial soaking solutions are available or you can make your own by mixing a 1M KCl solution adjusted to pH 4.0.

Use and Maintenance
Electrodes should be used in a vertical position.

Electrodes should be rinsed between samples with distilled or deionized water. NEVER wipe an electrode to remove excess water. Just blot the end of the electrode with a lint-free paper. Wiping the electrode can cause spurious readings due to static charges.

The level of filling solution in refillable electrodes should be kept at least 2/3 full. The filling hole should be open during use. pH electrodes are fragile. A proper electrode holder should be used to provide support and aid in raising and lowering the probe into solutions.