pH Reference
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 for negative logarithm, and “H,” the chemical symbol for Hydrogen. The formal definition of pH is: the negative logarithm of Hydrogen ion activity.

$$pH = -\log[H+]$$

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

The pH value of a substance is directly related to the ratio of hydrogen ion $[H^+]$ and hydroxyl ion $[OH^-]$ concentrations. If the H^+ concentration is greater than the OH^-, the material is acidic; *i.e.*, the pH value is less than 7. If the OH^- concentration is greater than its H^+, the material is basic, with a pH value greater than 7. If equal numbers of H^+ and 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 unit of pH represents a ten-fold change in hydrogen ion concentration. Table 1 shows the concentration of both hydrogen ions and hydroxyl ions at different pH values.

THE MOLAR CONCEPT

A mole of a compound is defined as Avogadro’s number of molecules (6.02×10^{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 (H^+) is one (1), there is one gram of hydrogen ions in a mole of hydrogen. A solution with a pH of 10 has 1×10^{-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 one or more electrons. The presence of ions in solution allows electrical energy to pass 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 (H^+) or hydroxyl (OH^-) ions in the solution.

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

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$NaOH \rightarrow Na^+ + OH^-$$

In an aqueous solution, hydrogen ions normally combine with the water solvent to form the hydronium ion (H_3O^+). 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 such 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:

$$H_2O + CH_3COOH \rightarrow H_3O^+ + CH_3COO^-$$

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

$$2H_2O \rightarrow H_3O^+ + OH^-$$

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:

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$
$$H_2O + NaOH \rightarrow Na^+ + H_2O + OH^-$$

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, next page, 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 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 using a pH meter. A pH measurement system consists of four components: a pH measuring electrode, a reference electrode, a high input impedance meter, and a sample of the material to be measured. 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 changes in the relative hydrogen ion concentration inside and outside the bulb.

Table 1 — HYDROGEN ION CONCENTRATION IN MOLES/LITER AT 25°C (77°F)

pH	H^+	OH^-
0	(10^{0}) 1	0.00000000000001 (10^{-14})
1	(10^{-1}) 0.1	0.0000000000001 (10^{-13})
2	(10^{-2}) 0.01	0.000000000001 (10^{-12})
3	(10^{-3}) 0.001	0.00000000001 (10^{-11})
4	(10^{-4}) 0.0001	0.0000000001 (10^{-10})
5	(10^{-5}) 0.00001	0.000000001 (10^{-9})
6	(10^{-6}) 0.000001	0.00000001 (10^{-8})
7	(10^{-7}) 0.0000001	0.0000001 (10^{-7})
8	(10^{-8}) 0.00000001	0.000001 (10^{-6})
9	(10^{-9}) 0.000000001	0.00001 (10^{-5})
10	(10^{-10}) 0.0000000001	0.0001 (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})

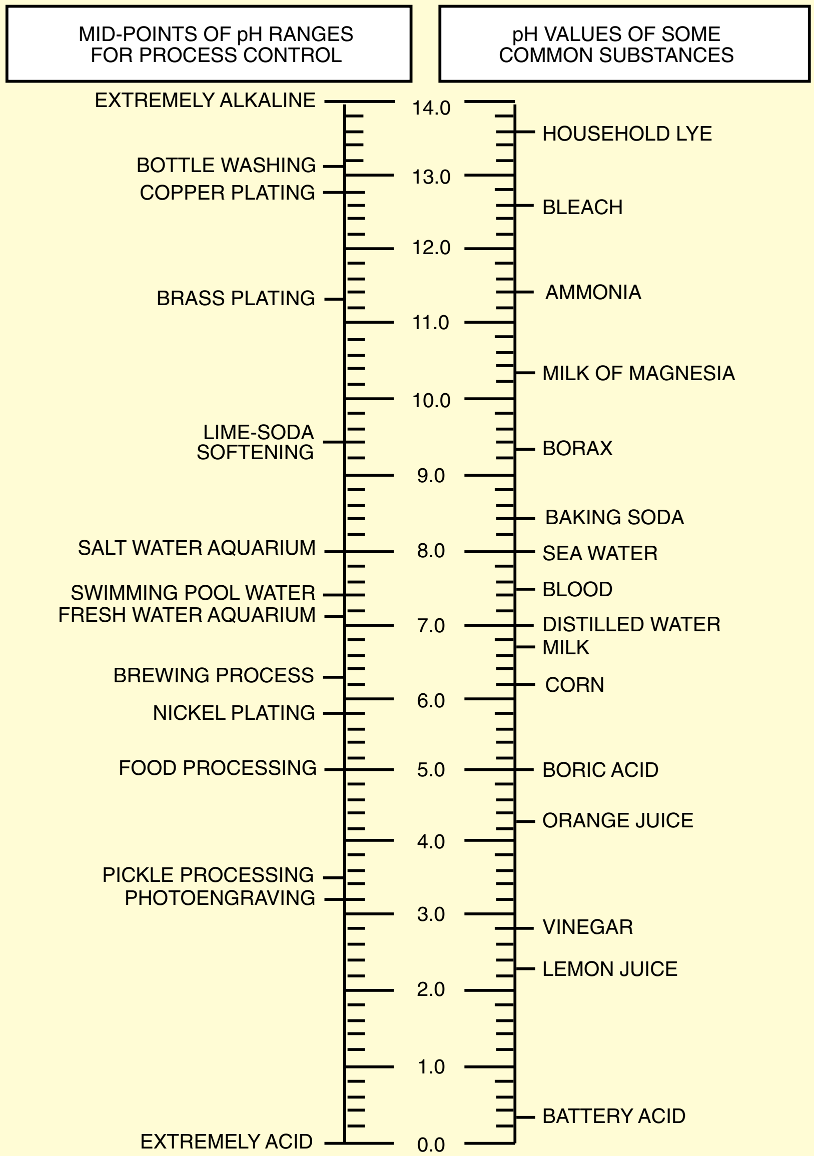


Figure 1

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 can be either manual or automatic. With manual compensation, a separate temperature measurement is required, and the pH meter's 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 the 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 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, each system must be calibrated periodically. Buffers are available with a wide range of pH values, and they come in both in 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°C/77°F), 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 H^+:

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

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

$$E = E_x - 1.98\ T_K pH$$

Changes in the temperature of a solution will alter the millivolt output of the glass pH electrode in accordance with the Nernst equation. Variation in electrode sensitivity with temperature is a linear function, and most pH meters have circuitry designed to compensate for this effect.

PHH-7011 pocket tester

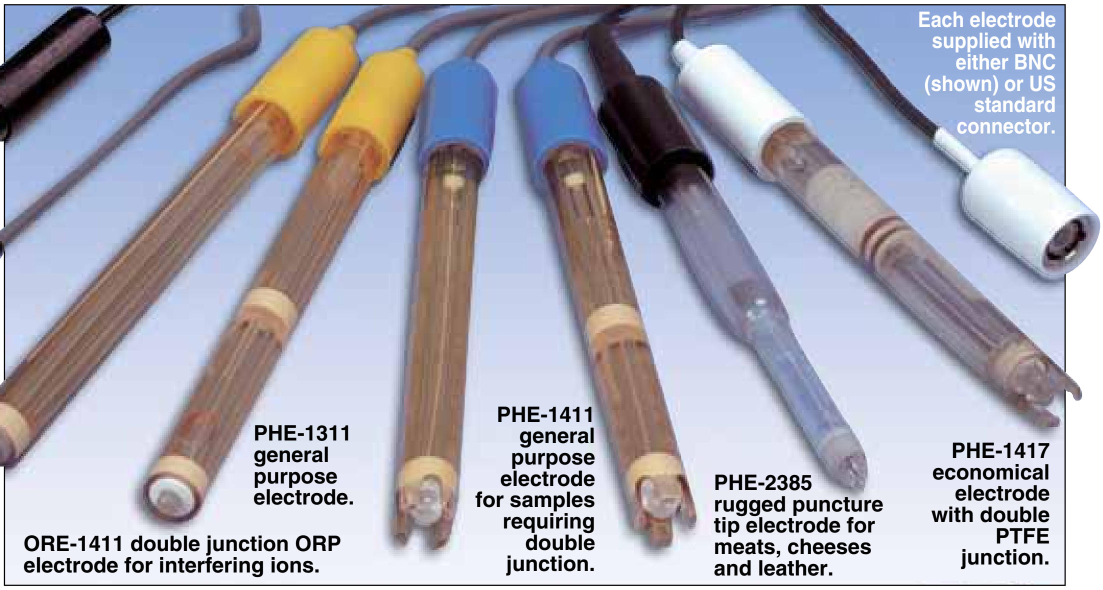
PHETX-600 1½ NPT pH transmitter.

PHETX-610 compression fitting pH electrode.

PHH-128

PHETX-620, hot tap pH transmitter with PHE-620-BVA, PVC hot tap ball valve.

PHE-6510, electrode with PHEH-65-10, mounting assembly and cable.



Each electrode supplied with either BNC (shown) or US standard connector.

PHE-1304 economy electrode.

BNC connector standard.

All models shown smaller than actual size.

ORE-1311 general purpose ORP electrode.

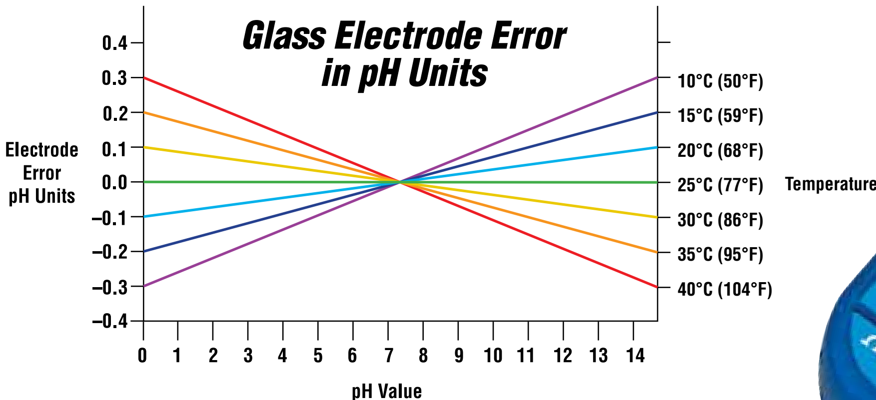
PHE-1311 general purpose electrode.

ORE-1411 double junction ORP electrode for interfering ions.

PHE-1411 general purpose electrode for samples requiring double junction.

PHE-2385 rugged puncture tip electrode for meats, cheeses and leather.

PHE-1417 economical electrode with double PTFE junction.



PHB21 benchtop meter.

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

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	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