HAMILTON®

pH Measurement Guide

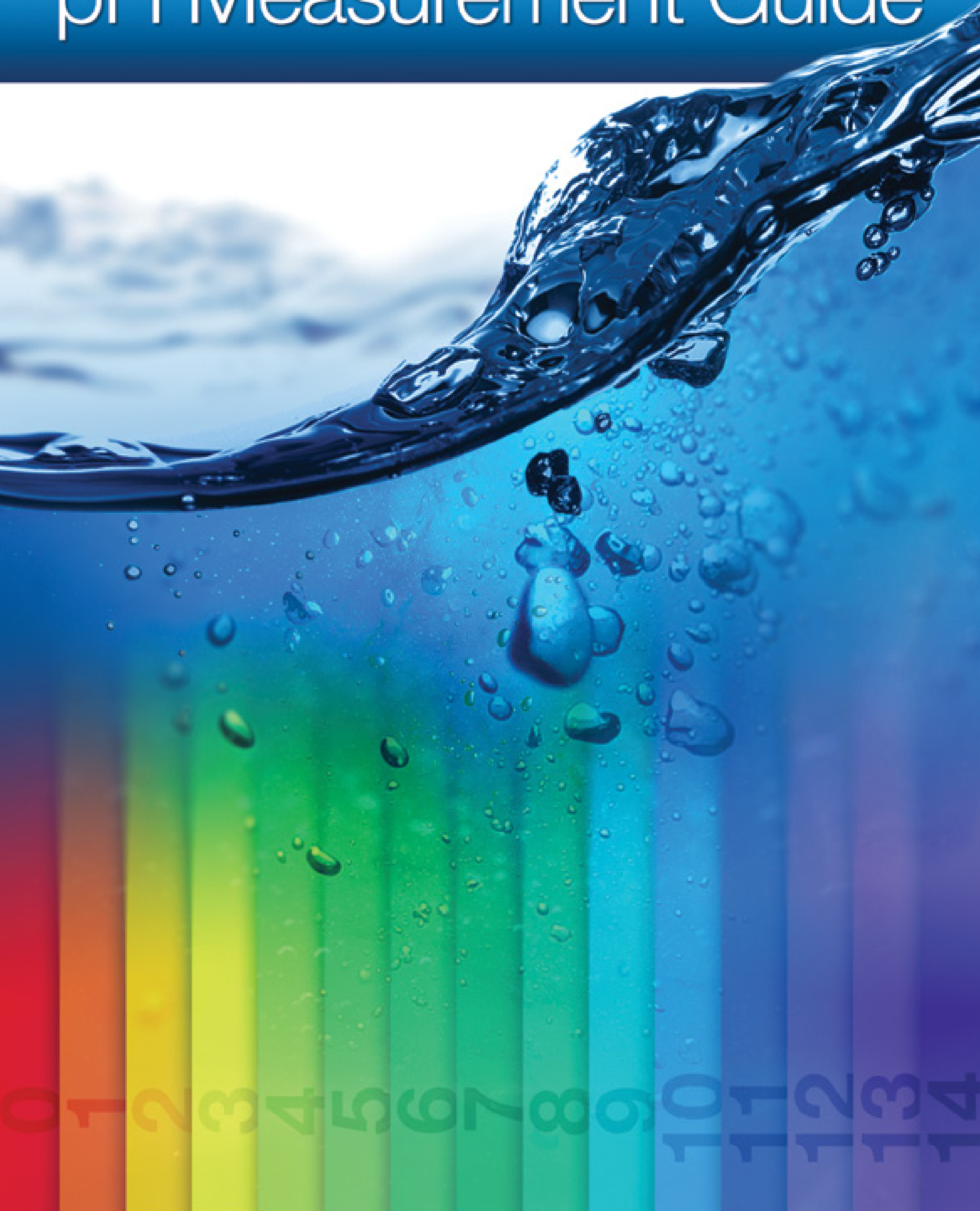


Table of Contents

1 Introduction

Since the creation of man, he could differentiate between sour and bitter when eating liquid or solid foods. We say that vinegar and lemon juice taste sour and that soap water tastes bitter. This characteristic of these liquids and the marked degree of sour or bitter is indicated by the pH value. The significance of the pH value is today known to a great portion of our population alone through the fact that it is accepted that the pH value of swimming pool water has to be kept within certain limits. The food we eat contains a lot of water and our drinks are nothing else than colored and flavored water, and this water can be either sour or bitter; or in other words, it will have a certain pH value.

In general we can say that water is the most important substance on earth. Without water there will be no life on our planet. People living in areas of severe drought have experienced the importance of water for their existence. Continuous droughts do not only affect the farmers, they are a disaster for the entire economy of a nation. It is therefore of utmost importance that we treat this precious liquid with care, use it responsibly and try to save every drop of it.

Water is everywhere! Three quarters of the surface of the earth is covered with water in the form of oceans, rivers, lakes and swamps. Brandy, whiskey, beer, wine, cool drinks, fruit juices, coffee and tea consist of water containing certain additives which change the property and the taste of the water. Blood, the vital liquid of our body is mainly water, in fact our entire body consists of approximately 65% water.

Water is used in industry as cooling water, wash water, boiler water, steam, condensate and solvent. Dirty water is usually disposed of as effluent. Notably the chemical industry especially makes use of this universal solvent, because most substances are somewhat soluble in water.

Through its usage water undergoes changes, the most substantial being the change of its hydrogen ion concentration. All the above mentioned liquids differ in their hydrogen ion concentrations, which makes them either acids or bases, sour or bitter. A measure for the hydrogen ion concentration of aqueous solutions is the pH value.

It can be said that the human tongue is the first pH measurement instrument, but only the potentiometric pH measurement provides an accurate and reproducible result, when the acidity or alkalinity of an aqueous solution has to be determined.

The pH measurement is therefore of vital significance in such diverse fields as biology, medicine, food technology, drinking water treatment, agriculture, mineralogy, surface treatment in metal processing, paper and textile manufacturing, chemical and petrochemical industry as well as waste water and sewage treatment for environmental protection.

On a daily basis the importance of measuring the pH value in industry becomes more significant and with it new problems in process control appear and have to be solved. Even in laboratories is the demand for a highly accurate and repeatable pH measurement a predominating factor.

The purpose of this booklet is to supply the basic knowledge of the pH measurement in a brief and understandable form. If it helps to eliminate the myths and mistakes arising from conceptual misunderstanding and if it leads to a successful application of pH measurement the author has fulfilled his task.

1.1 Booklet Overview

Without a basic knowledge of a few chemical principles as well as of potentiometry and the functionality of a pH electrode a successful pH measurement is practically impossible.

Therefore certain chemical and physical principles are described in the appendix of the booklet. These explanations will lead to the definition of the hydrogen ion concentration.

The book starts with the definition of the pH scale, explaining the NERNST equation and describing the fundamentals of the glass and reference electrode. pH related terminology will be dealt with in detail, the knowledge of this will lead to the successful application of the various Hamilton pH electrodes.

One cannot achieve a better measurement accuracy than the accuracy of the buffer solution one uses for calibration. Hamilton’s buffer solutions are described, after which the calibration of the pH measurement system is explained.

Connecting the pH electrode to the measurement instrument and the “dos and don’ts” of electrode handling will conclude the subject of pH measurement.

2 The pH scale

If we express the hydrogen ion concentration of an aqueous solution in relation to its molecular value we derive a scale of 1 (10^0) via 10^{-7} to 10^{-14} mole/liter.

This scale is impractical but if written as a function of its negative logarithm a real and simple scale of 0–14 has been created: the pH scale.

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

pH is the abbreviation of pondus hydrogenii and means the weight of hydrogen. This term was introduced in 1909 by the Danish biochemist S. P. L. Sørensen (1868 – 1939).

The pH scale covers the active concentration of the H^+ ions and OH^- ions and therefore the pH value is defined as the negative common logarithm of the active hydrogen ion concentration in an aqueous solution.

$$\text{pH} = \log \frac{1}{\text{hydrogen ion concentration (mole/liter)}}$$

If the H^+ ion concentration changes by a factor of ten, the pH value changes by one unit. This illustrates how important it is to be able to measure the pH value to a tenth of a unit or even a hundredth of a unit in special applications.

The pH definition refers to the active hydrogen ion concentration and not just to the hydrogen ion concentration. It is important to understand this difference. Only in dilute solutions are all anions and all cations so far apart that they are able to produce the maximum of the chemical energy, i.e. the H^+ ion concentration and the H^+ ion activity are identical. For instance 0.01 mole hydrochloric acid is still classified as a dilute solution which dissociates completely and therefore concentration equals activity.

0.01 mole HCl: concentration = activity

If the HCl concentration increases, the cation (H^+) and the anion (Cl^-) obstruct each other increasingly as the space between them gets smaller and smaller. In this case the ion activity is slowed down and does not correspond any longer with the ion concentration. With increasing concentration the ion activity differs to the ion concentration more and more.

1 mole HCl: concentration > activity

It is important to recognize the fact that a pH measurement determines only the concentration of active hydrogen ions in a solution, and not the total concentration of hydrogen ions. It is this factor that is responsible for the observed pH change in pure water with temperature.

If the temperature rises in pure water, the dissociation of hydrogen and hydroxyl ions increases. Since pH is related to the concentration of dissociated hydrogen ions alone, the pH value actually decreases although the water is still neutral. Therefore it is very important that we know the relationship between the dissociation constant and temperature, otherwise it is not possible to predict the pH value of a solution at a desired temperature from a known pH reading at some other temperature.

THE pH SCALE

The meaning of the pH scale is best explained if we compare the concentration of 1 mol/l pure hydrochloric acid (HCl) which has a pH value of 0, with a concentration of 1 mol/l pure sodium hydroxide (NaOH) which has a pH value of 14. When both solutions are mixed in same quantities, a neutralization reaction occurs as may be seen by the following equation:

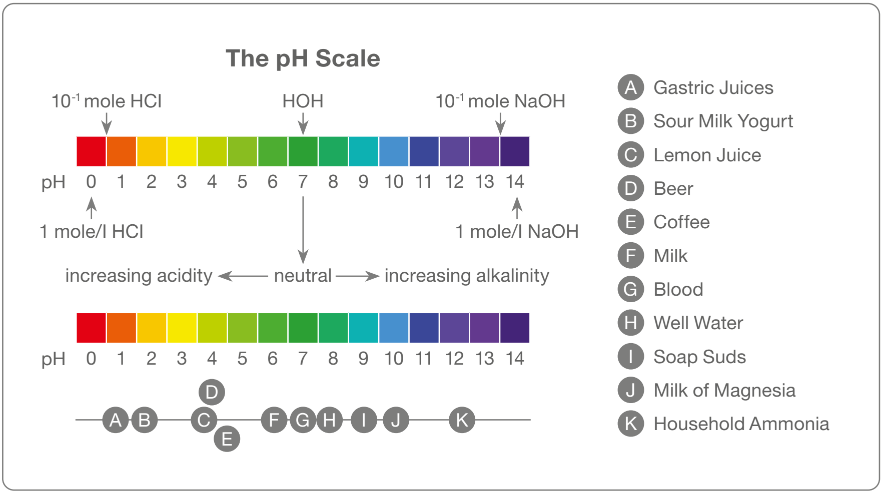
$HCl + NaOH$ > $HOH + NaCl$
> $H_2O + NaCl$

pH 0 + pH 14 > pH 7

The acidic and alkaline properties of the solutions are lost because of the union of the hydrogen and hydroxyl ions which form water. The newly formed sodium chloride (table salt) does not influence the pH value.

Generally the following can be stated:

- **If the concentration of active hydrogen and active hydroxyl ions in a solution is of the same quantity, the solution is neutral (pH value = 7).**
- **If the solution has a higher concentration of active hydrogen ions than that of hydroxyl ions, the solution is an acid (pH value below 7).**
- **If the solution has a higher concentration of active hydroxyl ions than that of hydrogen ions, the solution is a base (pH value above 7).**



3 The pH Measurement

3.1 The NERNST Equation

To determine the active hydrogen ion concentration, a pH measurement is necessary.

Three methods are generally used for the direct determination of the pH value in aqueous solutions:

1) **The visual method,** a color comparison with pH sensitive indicator paper (litmus) to a standard color scale.

2) **The photometric method**, using a spectrophotometer to measure the wave length of the pH sensitive colored solution.

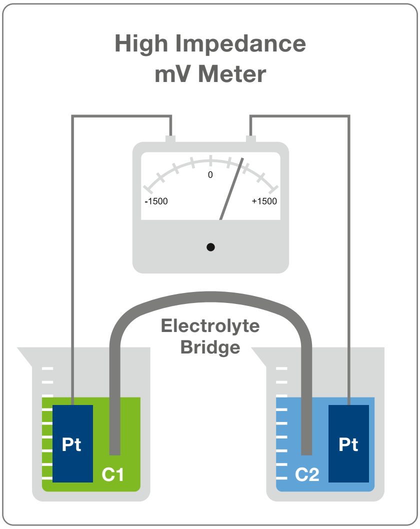
3) **The potentiometric method**, an electro chemical measurement, measuring the e.m.f. created by a chemical reaction, such as that which takes place between metals and dissolved salts.

The potentiometric method in determining the pH value of aqueous solutions is the only method which can be used in process control as a continuous in-line measurement and therefore this booklet will deal exclusively with this method of pH determination.

This pH measurement method is based on the NERNST equation which describes in a relatively simple form the relationship between the galvanic potential of a defined electrode assembly and the chemical activity of the ion concentration being measured.

An electrode assembly always consists of a measurement electrode which is sensitive to the ion activity to be measured and a reference electrode. The operation of an electrode assembly in its simplest form is demonstrated by the following example:

If two hydrogen electrodes (each a thin plate of polished platinum) are immersed in two solutions, having different hydrogen ion concentrations, each electrode will generate a potential which depends on the active hydrogen concentration of the solution in which the electrode is immersed. To be able to measure this potential, the two solutions are connected by a salt bridge (electrolyte bridge) and the two electrodes are connected to a high impedance voltmeter. Both solutions are saturated with pure hydrogen gas.



Since the current passing during such a measurement is negligible, the chemical composition of the sample solution is not altered. The bridge acts as a phase boundary between solution C_1 and solution C_2 and closes the electric circuit.

A potential difference will be generated between the two platinum electrodes by the different active hydrogen ion concentrations in the solutions. The relationship is expressed by the NERNST equation:

$$E = \frac{R \times T}{n \times F} \times \log \frac{C_1}{C_2}$$

where:
E = potential difference (mV)
R = gas constant ($8.31439\ J \times mol^{-1} \times K^{-1}$)
F = Faraday constant ($96495.7\ C \times mol^{-1}$)
T = absolute temperature in Kelvin (K)
n = charge number of the measured ion (in this case $n_H = 1$)
C_1 = active H-ion concentration in solution C_1
C_2 = active H-ion concentration in solution C_2

If we select between C_1 and C_2 a concentration ratio of 10:1, the equation may be written as:

$$E = \frac{R \times T}{n \times F} \times \log \frac{C_1}{C_2} \qquad E = \frac{R \times T}{n \times F} \times \log \frac{10}{1} \qquad E = \frac{R \times T}{n \times F} \times 2.303585$$

E is known as the NERNST's potential, given the symbol U_N. U_N corresponds to the change in potential with a ten fold change in activity.

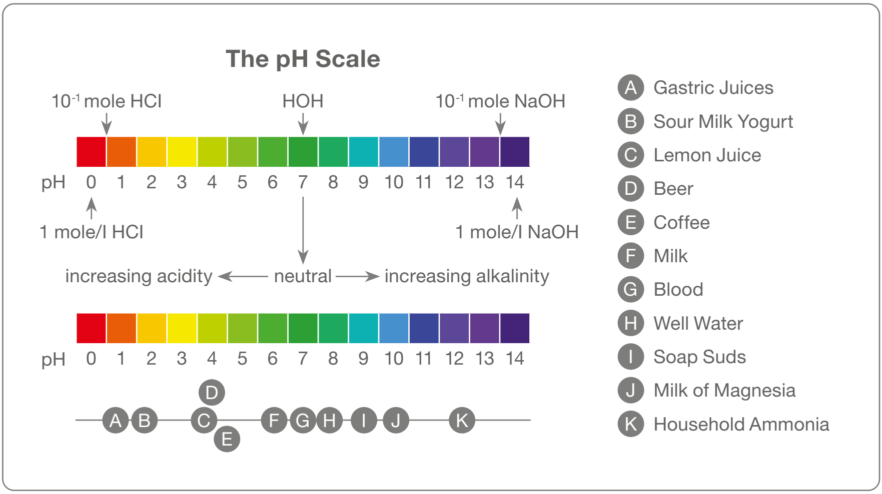
The values of R and F are constant. The charge number n is known for each kind of ion and the temperature T can be calculated from the measured value in °C.

If we assume the temperature of the solutions to be 25°C, then:

$T = 273.15 + 25 = 298.15$ Kelvin

This will give us a NERNST potential of:

$$U_N = 59.16\ mV$$



As the ion activity is temperature dependent, so is the NERNST potential (refer to the NERNST equation). The following table illustrates the temperature dependency:

T°C	U_N mV
0	54.20
5	55.19
10	56.18
15	57.17
20	58.16
25	59.16
30	60.15
35	61.14
40	62.13
45	63.12
50	64.12
55	65.11
60	66.10
65	67.09
70	68.08
75	69.08
80	70.07
85	71.06
90	72.05
95	73.04
100	74.04

Temperature Dependency of the NERNST Potential.

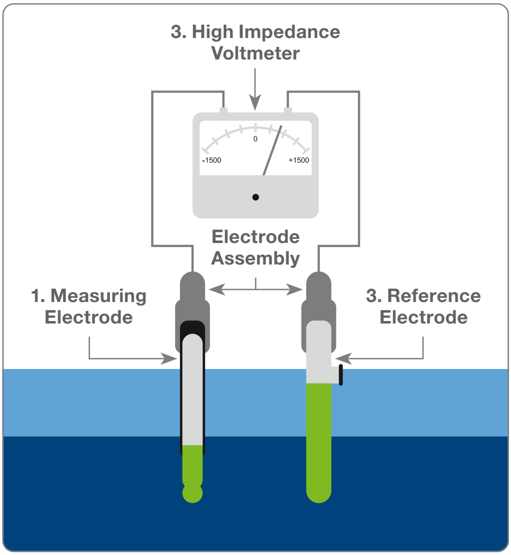
3.2 The pH Measurement System

A basic pH measurement system consists of:

1) The measurement electrode, a pH sensitive electrode.

2) The reference electrode.

3) A high impedance voltmeter.



3.2.1 The Measurement Electrode

The purpose of the measurement electrode is to determine the pH value of an aqueous solution.

The platinum/hydrogen electrode was originally used to measure the hydrogen ion concentration in aqueous solutions (since 1897) and today still serves as a reference standard for the electrometric pH determination. The hydrogen electrode consists of a platinized platinum plate or rod (coated with platinum black), subjected to a flow of gaseous hydrogen. A silver wire coated with silver chloride serves as a reference electrode.

The basic theory, when employing a hydrogen electrode, is as follows: If a metal rod (electrode) is immersed into an aqueous solution containing its own salt (silver electrode in silver nitrate), the atoms on the surface of that metal rod will ionize. The water molecules will attract the positively charged metal ions from the surface of the rod, which leaves the metal rod negatively charged. This charge exchange develops a potential difference at the phase boundary metal/solution. The potential depends on the ion concentration in the solution and is known as the galvanic potential.

Today the hydrogen electrode still serves as a reference standard especially as its measuring results are extremely accurate. However, for practical reasons the hydrogen electrode has lost its importance because of its difficult and complicated handling.

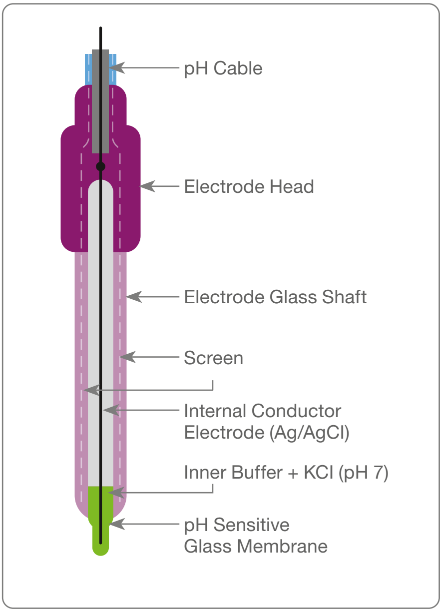
Only the antimony electrode has survived out of various metal electrodes. Antimony is resistant to hydrofluoric acid which is well know to etch glass. Unfortunately the accuracy and measurement range is limited. Antimony requires special handling as it is a known carcinogenic material for humans.

The Glass Electrode

It was not until the development of the glass electrode that pH measurement became a simple and reliable tool for all kinds of applications. In recent years the glass electrode has outgrown all other types of indicator electrodes for pH measurements. The pH determination of an aqueous solution is today as common as temperature and pressure measurements, thanks to the reliability and accuracy of the glass electrode in combination with extreme stable electronic amplification. However, the successful application of the glass electrode requires some knowledge about its functionality and its maintenance, which this booklet will provide.

A glass electrode consists of a shaft made from glass which should be highly resistant to hot alkaline solutions and its electrical resistance must be several times greater than that of the membrane glass. The pH sensitive part of the glass electrode is the hemispherically shaped electrode tip, the glass membrane.
The membrane is made from special hydrogen ion sensitive glass and is fused to the electrode shaft. The glass electrode is partly filled with a buffer solution, normally having a pH value of 7.

A defined amount of Potassium Chloride (KCl) is added to this internal buffer. A silver wire, coated with silver chloride (Ag/AgCl) is inserted into the glass electrode right down into the internal buffer and serves as a conducting electrode. Via the core of the coaxial pH cable, the Ag/AgCl wire is connected to one terminal of a pH meter.



The Construction of a Glass Electrode.

The Glass Membrane

All types of glasses possess the property of producing a potential difference relative to the hydrogen ion concentration in aqueous solutions. However, only special types, such as the conventional Mc-Innes glass (Corning 015) produce galvanic potentials which satisfy the NERNST equation over a wide range of the pH scale.

Every manufacturer of pH electrodes is constantly researching for better pH sensitive glasses. Through constant development Hamilton has achieved results which have not previously been available without unsatisfactory compromises.

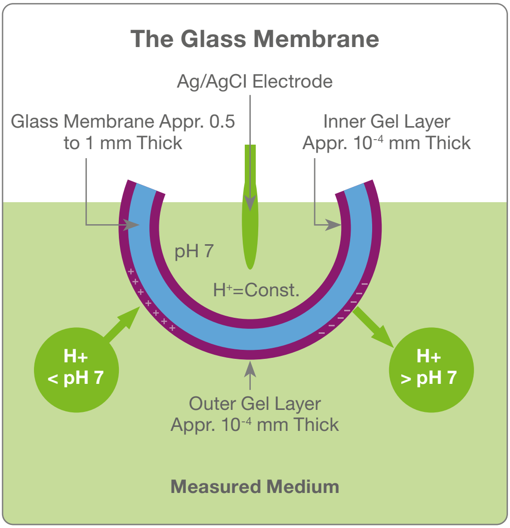
When the membrane glass of a measurement electrode comes into contact with an aqueous solution, it forms a thin gel layer of approximately 10^{-4} mm thickness between the glass surface and the solution. The thickness of the gel layer depends on the quality and composition of the membrane glass, the temperature and the pH value of the measured solution. As the internal side of the glass membrane is in contact with the inner buffer (an aqueous solution of pH 7) a gel layer is also formed on the inside of the glass membrane.

A continuous exchange of H^+ ions in the gel layers and H^+ ions of the solutions takes place on both sides of the membrane. This ion exchange is controlled by the H^+ ion concentration of both solutions.

If the hydrogen ion concentration of each solution is identical on both sides of the glass membrane, the ion exchange stops after an equilibrium has been reached between the H^+ ions in the solutions and the H^+ ions in the gel layers. Therefore, both sides of the membrane glass have the same potential and the potential difference is 0 mV.

If a difference of a hydrogen ion concentration exists between the inner buffer and the outer solution, a potential difference develops between the inner and outer sides of the membrane glass which is proportional to the difference in pH between the inner buffer and the outer solution. To be able to measure the membrane potential, the membrane itself has to be conductive. This is achieved by the mobility of the alkaline ions in the membrane glass (Li^+ ions in most glasses today or Na^+ ions in older membrane glasses).

The thickness and composition of the gel layer determine the response time and the characteristic slope of the glass electrode. Therefore the gel layer is of critical importance to the electrode performance.


The Glass Membrane

Without the gel layer there can be no pH measurement. Unfortunately it takes approximately one to two days until a gel layer is fully developed. Therefore a measurement electrode needs to be hydrated (immersed into normal clean tap water) for at least 24 hours prior to use. Most manufacturers deliver their electrodes already hydrated (the membrane is kept wet with a KCl solution in a plastic cap) which renders the electrode ready for immediate use.

3.2.2 The Reference Electrode

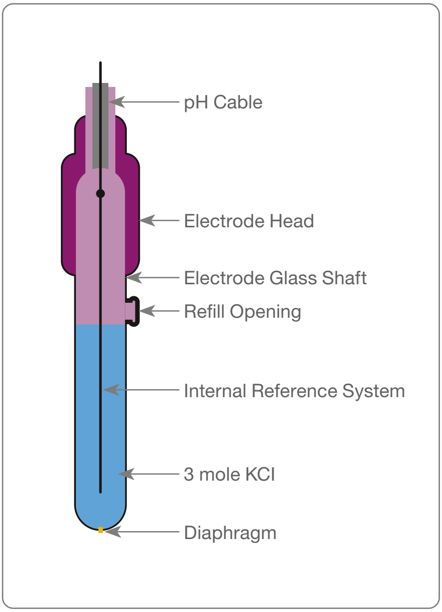
The reference electrode represents a defined electrical connection between the measured liquid medium and the pH meter. The accuracy of the pH measurement is often determined by the reference electrode and therefore the choice of the reference electrode is of significant importance. An ideal reference electrode should produce a predictable potential, which should respond only in accordance with the NERNST equation. A good and stable reference electrode should also have a low temperature coefficient and possess no temperature hysteresis.

A reference electrode consists of an internal electrode (similar to the measurement electrode) which is immersed into a defined electrolyte. This electrolyte must be in contact with the measured medium. Over the years various reference systems have been employed, but only two systems, the mercury mercurous chloride (calomel) and the silver/silver chloride reference electrodes were found reliable with respect to an accurate and stable potential. Hamilton applies exclusively the silver/silver chloride reference system (refer also to “The Everef reference system” on in chapter 3.4.2).

At low and stable temperatures (max. 80°C) the calomel electrode has a high potential stability and a high accuracy down to a hundredth of a millivolt. But today the silver/silver chloride electrode has gained practical acceptance and is by far the most frequently employed reference system. It is easy to manufacture, its potential rapidly attains equilibrium between -30°C and 135°C, and is very reproducible. The Ag/AgCl reference electrode remains stable and accurate especially with wide temperature fluctuations and at high temperatures up to 135°C.

The internal electrode of an Ag/AgCl reference electrode consists of a silver chloride coated silver wire which is immersed into potassium chloride of 3M concentration situated in a large chamber formed by the glass body of the reference electrode.

A liquid junction or “diaphragm” (normally a small porous ceramic rod) is fitted at the bottom of this chamber to permit the potassium chloride to diffuse or leak into the measured medium. To complete the electric circuit the silver/silver chloride wire is connected via a coaxial cable to the pH meter.

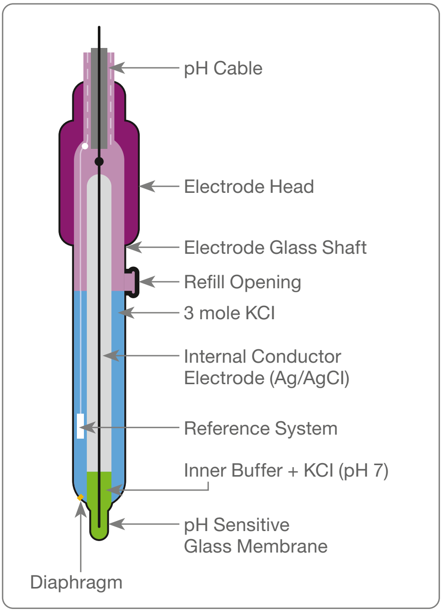


The Construction of a Reference Electrode.

3.2.3 The Combination Electrode

Since 1947 electrode manufacturers have combined the measurement electrode and the reference electrode into one unit, hence the name combination electrode. Today, the combination electrode is almost exclusively employed in laboratories and industrial plants. Only when the life expectancy is significantly different for the measurement and the reference electrode, is the use of a pH measurement system consisting of two separate electrodes recommended.

In a combination electrode the concentric space surrounding the measurement electrode is filled with the reference electrolyte and contains the internal reference system. A diaphragm near the bottom of the electrolyte chamber serves as the junction between the KCl solution and the measured medium. As the reference electrolyte is a conductive medium, it acts as a screen to the measurement electrode.

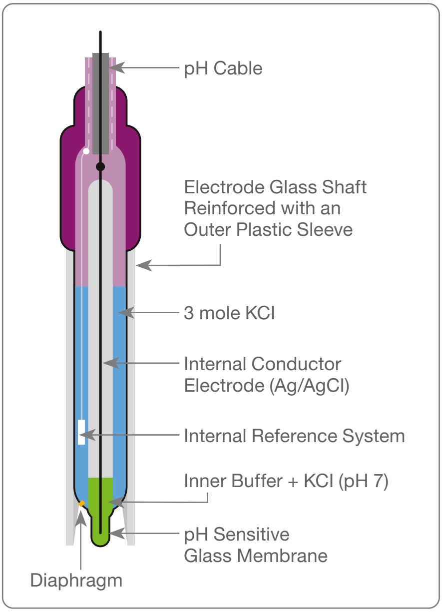


The Construction of a Combination Electrode.

3.2.4 Combination Electrode filled with KCl Gel as a Reference Electrolyte

Reference electrodes incorporating a liquid reference electrolyte are maintenance intensive as their electrolyte level has to be controlled and regularly refilled. The search for a maintenance free electrode assembly led to the development of the gel reference electrode.

The gel electrode is a low maintenance electrode. The reference electrolyte chamber is filled with 3M KCl electrolyte in viscous gel form. The diaphragm is normally made from ceramic. The glass shaft is often reinforced with an outer plastic sleeve or the electrode shaft is made completely out of plastic (Epoxy).



The gel electrode is mostly used for simple measuring applications, e.g. municipal water treatment or portable laboratory electrode applications. This electrode does not need to be topped up with reference electrolyte – which reduces maintenance time. However, it has to be taken into account that the gel electrode has a reduced accuracy and a shorter life span than its counterpart with a liquid reference electrolyte.

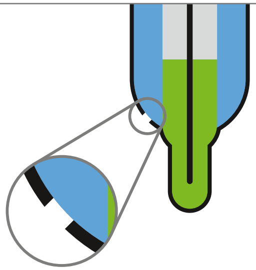
The response time of a gel electrode is somewhat slower than an electrode filled with a liquid electrolyte.

3.2.5 Reference Electrode with Polisolve Plus Electrolyte (Polymer)

In the early 1980s electrode manufacturers introduced the polymer reference electrode. The polymer electrode relies on a reference electrolyte chamber that is completely filled with a semi solid polymerized plastic material into which the KCl is embedded. No diaphragm junction is required. Therefore the KCl saturated polymer has direct contact with the measured solution. The contact is established through a small aperture, which could either be one or more holes near the bottom of the reference electrolyte chamber or a fissure separating the bottom electrolyte chamber from the measurement electrode.

Since its inception polymer electrodes have had specialized use. Initially, pH values below 2 pH could not be measured, the temperature limit was 90°C, and measurements in media containing organic solvents were not possible.

What does not exist can not clog up!



Hole in Electrolyte Chamber

With Hamilton's new developed Polisolve Plus polymer (protected by patent law) these limitations are a thing of the past. The Polisolve Plus polymer reference system allows pH measurements down to pH 0, and it is resistant to organic solvents. pH measurements in the laboratory or at industrial plants utilizing the Polisolve Plus reference system are reliable and accurate. The Polisolve Plus polymer can be applied to almost every measurement problem, including very dirty, fatty, oily, ion weak or protein media. Suspended solids do not create diaphragm problems any more.

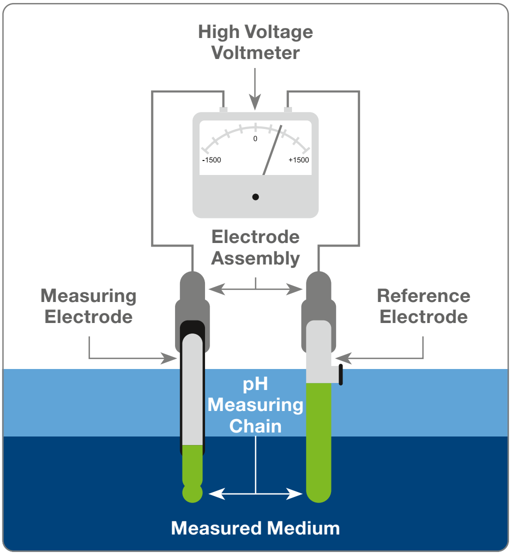
Since the KCl saturated polymer is free of AgCl, there is no possibility of silver sulfide contamination in processes that contain hydrogen sulfide or other sulfide compounds.

The high pressure rating of 10 bar (145 PSIG), its extended temperature rating of up to 130°C, and its maintenance free operation should make the Polisolve Plus reference system always a first choice in difficult applications.

Electrodes, utilizing the Polisolve Plus polymer electrolyte, are even suitable for steam sterilization in biotechnology applications.

3.2.6 The Measurement of the Potential Difference

The pH measurement electrode and the pH reference electrode form a so called pH measurement chain within the measured medium. This chain can be compared to a battery of which the voltage produced depends on the liquid medium.



The difference in voltage potential between the measurement electrode and the reference electrode is a function of the pH value of the measured medium. In theory the voltage changes by 59.16 mV per pH unit at 25°C according to the NERNST equation. The voltage produced by the pH measurement chain is large enough not to present any problem for a measurement. But the measurement chain is a voltage source from which no current can be drawn, not even the low current which a moving coil of a DC voltmeter draws. The potential difference of the measurement chain has to be measured without drawing any current from the voltage source, otherwise the voltage would be reduced and the pH measurement would be drastically falsified. The reason is the high electrical resistance of the glass electrode which is mainly determined by the resistance of the glass membrane.

The resistance values of a glass membrane vary between 10 MΩ and 1000 MΩ at 25°C and increase 10 times at a temperature decrease of 25°C. The lowest possible operating temperature of a pH electrode is often determined by the increased resistance of the glass membrane at low temperatures, the internal resistance of the measuring instrument, the required accuracy of the pH measurement and the freezing point of the electrolyte.

Special electrodes are manufactured for pH measurements at very low temperatures, having especially low resistance due to a particular glass composition and reduced membrane thickness. In order to still achieve an accuracy of +/- 0.1 pH the resistance of the measurement electrode should not be higher than a hundredth of the internal resistance of the measuring instrument. The upper limit of the membrane resistance lies at 5000 MΩ (5×10^9). Membrane resistance that is too high causes faults and disturbances in the electronic measuring instrument. This is often referred to a as pH measurement “noise.” Refer to section 3.7.1 for more information on Hamilton membrane glass formulations.

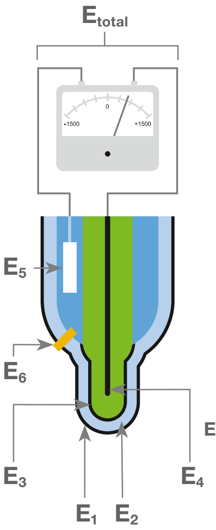
The e.m.f. (electromotive force) produced by the high resistance measurement chain can only be measured by an instrument having such a high internal resistance that it does not draw a current from the chain. For practical purposes the pH meter or pH transmitter should therefore have an internal resistance of at least 10^{12} ohms.

3.3 The Characteristics of a pH Measurement Chain

The characteristics of a pH measurement chain are the result of the individual properties of the measurement and the reference electrode. Most of the electrode assemblies in use today are combination electrodes. For this reason we will refer to the combination electrode when examining the different properties of a measurement chain. However, everything that is said about the properties of a combination electrode may be applied to the individual measurement and reference electrode as well.

3.3.1 The Different Potentials of a Combination Electrode

When a combination electrode is immersed into an aqueous solution, a potential develops at the outer gel layer of the glass membrane which forms a phase boundary between the glass membrane and the measured solution. This potential is dependent on the pH value of the measured solution and is therefore of primary interest. Unfortunately this potential cannot be measured individually as there are more phase boundaries in a pH measurement chain which all produce their individual potentials. Only the resultant e.m.f. of all single potentials added together is measurable and forms the mV value used to determine the pH measurement.



E_1: Potential Developing on the Outer Gel Layer

E_2: Asymmetry Potential of the Glass Membrane

E_3: Potential Developing on the Inner Gel Layer

E_4: Potential Developing on the Internal Conductor Electrode

E_5: Potential Developing on the Reference Electrode

E_6: Diffusion Potential of the Diaphragm

E_{total}: The Total Potential Measured by a pH Electrode Assembly is the Sum of Potentials E_1 to E_6

As can be seen from the picture above there are six potentials which develop on a pH measurement chain, but only one potential – E_1 – is dependent on the pH value of the solution being measured. Ideally the potentials E_2 to E_6 should stay constant during the measuring time in order to enable the measurement of the variable potential of E_1.

E_2 is the asymmetry potential of the glass membrane. If the measurement and the reference electrode possess the same internal conducting system and if the measurement chain is immersed into a buffer solution having the same pH value as the internal buffer solution, the potential difference between the inside and the outside of the glass membrane should theoretically be 0 mV. However, in reality even a new and perfect electrode assembly will show an asymmetry potential of a few millivolts. The asymmetry potential depends mainly on the different thickness of the gel layers and on the thickness of the glass membrane.

E_3 is the potential which develops on the inner gel layer of the glass membrane and is dependent on the hydrogen ion concentration of the inner buffer solution. Since this buffer solution is sealed within the measurement electrode it does not change in value, therefore the potential E_3 should be constant at all times.

E_4 and E_5 are potentials which develop on the phase boundaries metal/buffer solution (measurement electrode) and metal/electrolyte (reference electrode). If both conductor systems are identical and buffer solution and electrolyte have the same chloride ion activity the E_4 and E_5 neutralize each other and do not contribute to the total potential determined by the pH measurement device.

E_6 is the diffusion potential of the diaphragm. This potential occurs at the boundary between two electrolytes, when both differ in concentration and composition. It is determined by the diffusion of ions having different polarity and different ionic mobility.

As stated earlier, potentials E_2 to E_6 should ideally be constant in order to determine E_1. Since the individual potentials E_2 to E_6 are subject to certain errors, there is a resultant zero point error of the electrode assembly. This is why a zero point calibration is required before a pH measurement can commence and be repeated in regular time intervals during the measurement duration.

3.3.2 The Zero point of an Electrode Assembly

The zero point of an electrode assembly is the pH value at which the entire electrode assembly potential E_{total} is equal to 0 mV. Theoretically the zero point of a pH measurement chain is determined by the internal buffer solution of the measurement electrode, which under normal circumstances has the value of pH 7. If the pH value of the measured medium also equals pH 7, then the potential difference of the pH measurement chain should be 0 mV.

In practice, however, this is seldom the case, because E_{total} is the resultant of the sum potentials E_1 to E_6. Each potential reacts differently to temperature changes and to the composition of the measured liquid solution. Therefore it is difficult, if not impossible, to produce a pH electrode assembly with an accurately defined and reproducible zero point.

The zero point tolerance, as stipulated by the German Industrial Standard (DIN), may vary within –30 mV and +30 mV. Many manufacturers of pH electrodes deliberately set their electrode assembly zero point (pH 7 = 0 mV) slightly lower (approximately pH 6.8) since the zero point tends to drift upwards during the ageing process of the electrode assembly.

The repeatability of a pH electrode assembly (the uncertainty factor) is seldom stated by electrode manufacturers. Experience has shown that the repeatability of a pH electrode assembly seldom exceeds +/- 0.02 pH (≈1.16 mV).

The exact zero point deviation of a pH electrode assembly has to be established by the user, prior to a pH measurement, and must then be compensated for by a zero adjustment at the pH meter/transmitter. Microprocessor based pH meters adjust the zero point of an electrode assembly automatically during the calibration procedure.

The zero point check and adjustment should be repeated at specific time intervals during the measurement process, as the zero point tends to drift due to the following reasons:

a) Penetration of the measured solution into the reference electrolyte via the diaphragm. The ingress of liquid will either poison or dilute the reference electrolyte. Both will change the chloride ion activity of the electrolyte, resulting in a change of the reference potential.

b) A change of the measurement electrode buffer solution. Exposure of the glass membrane to high temperature will cause the release of alkali hydroxide into the inner solution which gradually increases its pH value.

c) Increase in electrical resistance due to corrosion of the contact metals used in the sensor electrical connector or related mating cable.

3.3.3 The Asymmetry Potential

In theory the potential difference across the glass membrane of a measurement electrode should be 0 mV if both the inner buffer solution and the measured solution possess an equal pH value (normally pH 7). In practice, however, a potential difference of a few millivolts, the asymmetry potential, is measured across the membrane.

The difference in age of the inner and outer gel layer is partly responsible for the asymmetry potential. The inner gel layer starts developing from the first day after the glass electrode is filled with the inner buffer solution (following manufacture) and will hardly change afterwards. The outer gel layer is continuously attacked through chemical reaction with the measured liquid solution and in certain cases even by abrasion from particulates in the process.

The asymmetry potential can also be attributed to small imperfections in the manufacture of the glass membrane. During normal use, exposure of the glass membrane to strong acids or strong alkaline solutions alters the external surface of the glass membrane to the extent that the response of the membrane to the presence of hydrogen ions gradually changes.

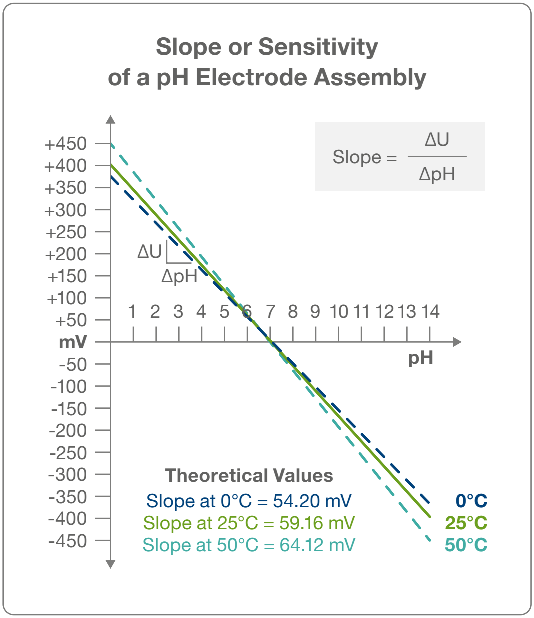
The asymmetry potential should not be larger than +/- 47 mV (≈+/- pH 0.8) at pH 7 and can be compensated for during the calibration process.

3.3.4 The Slope or Sensitivity of a pH Electrode Assembly

The slope of a pH electrode assembly is defined as the quotient of the potential difference developed per pH unit:

$$\text{Slope} = \frac{\Delta U}{\Delta \text{pH}}$$

In theory a pH electrode assembly should develop a potential difference of +59.16 mV per pH unit between pH 7 and pH 0, and correspondingly –59.16 mV between pH 7 and pH 14.


Slope or Sensitivity of a pH Electrode Assembly

In practice, however, a new and well hydrated electrode assembly reaches at best 99.8% of the theoretical value. With time the slope decreases, initially slowly and later more rapidly. It is essential that a slope compensation be carried out during the calibration procedure, using the slope calculation of the pH meter/ transmitter. As with the zero point adjustment, the slope adjustment has to be performed at regular intervals to maintain best accuracy.

The slope of a pH electrode assembly is temperature dependent in accordance with the NERNST equation. The slope increases with the rise in temperature of the measured solution, as can be seen from the diagram above. In theory, all temperature dependent slope lines intersect the theoretical zero point (pH 7).

In order to produce a response as near as possible to the NERNST equation an electrode assembly must fulfill certain criteria:

a) The inner and outer gel layers of the glass membrane must produce potentials having identical slopes.

b) The internal buffer solution must maintain a constant pH value.

c) The asymmetry potential should be as small and as constant as possible.

d) The electrode assembly must be symmetrical, i.e. measurement and reference electrode must have identical conducting systems in order to neutralize their galvanic potentials.

e) The diffusion potential of the diaphragm should be as small and as constant as possible.

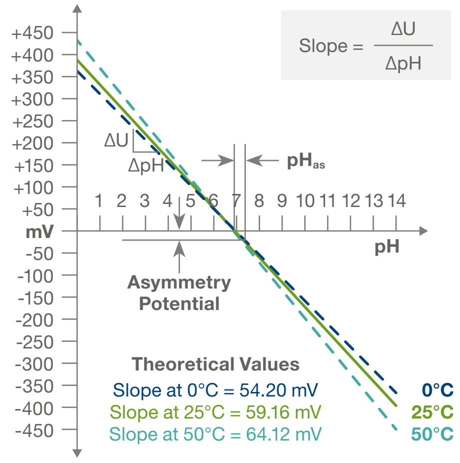
3.3.5 The Isopotential Point

Again we have a disagreement between theory and practice. In theory all temperature dependent slope lines intersect the theoretical zero point (0 mV/pH 7). When an asymmetry potential is present – and that is always the case – this intersection shifts either to the right or to the left of the zero point, as can be seen from the bottom right diagram.

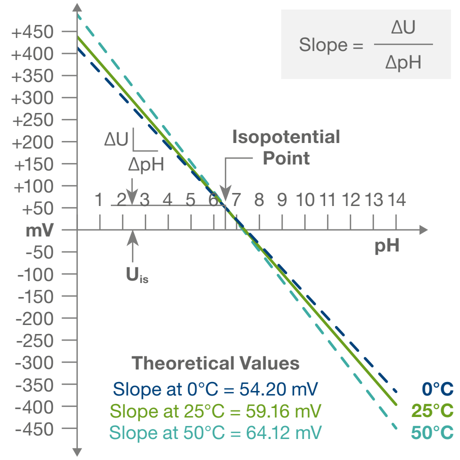
All potentials of a pH electrode assembly vary with temperature. The temperature dependency of each individual potential cannot be accurately defined, but it will shift the resultant intersection point of all temperature slope lines away from the theoretical zero point and away from the asymmetry potential. This intersection point is then known as the isopotential point (U_{is} = isotherm potential).

In order to perform an accurate pH measurement, the position of the isopotential point has to be established. Two buffer solutions are required. The position of the isopotential point can then be determined by measuring the potential difference of the pH

Slope and Asymmetry Potential of a pH Electrode Assembly



Slope and Isopotential Point of a pH Electrode Assembly



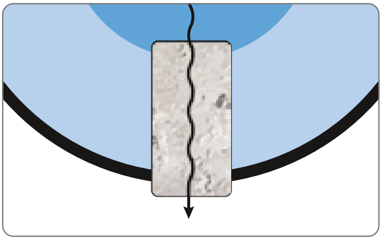
electrode assembly against various temperatures (heated buffer solutions). The mV outputs of the electrode assembly are then plotted against their pH value on graph paper and thereby the position of the isopotential point is established. Modern, microprocessor based pH meters/ transmitters have the capacity to compensate for the U_{is} potential.

New electrodes from Hamilton show a maximum compensation error of 0.1 pH when calibrated at 25°C and thereafter measuring in a solution having 60°C.

3.4 The Diaphragm

The diaphragm or liquid junction as it is frequently called, is a very important and critical part of the reference electrode. It provides an electrolytic interface between the silver/silver chloride conducting system and the measured solution. In most cases the diaphragm consists of a porous ceramic plug fused into the glass wall at the lower end of a reference electrode (porous ceramic diaphragm).

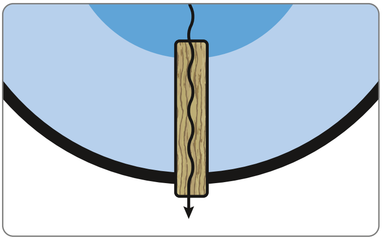
Various diaphragm types (differing in construction and shape) are available, each type has its advantages and limitations. It is normally the measurement application which determines the use of a specific diaphragm.



a) Porous Ceramic (Coatramic) Diaphragm

The porous ceramic diaphragm is probably the most frequently used today. It possess a high chemical resistance and it is easy to manufacture.

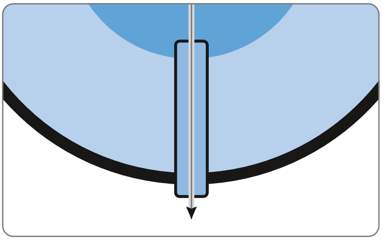
This junction provides a reproducible electrolyte flow but because of its large surface it is very vulnerable to contamination. Coatramic and HP-Contramic are the Hamilton trade names that refer to this style of diaphragm.



b) Platinum Fiber Diaphragm

Platinum fiber diaphragms consist of very fine platinum wires which are spun loosely together and fused into the glass.

This type of junction resist contamination to a certain extent but their electrolyte flow is less reproducible than ceramic diaphragms.

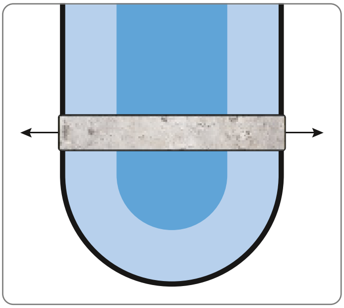


c) Single Pore™ Diaphragm

The Single Pore diaphragm is strictly speaking not a diaphragm at all. It is a very small glass aperture which allows a larger leakage rate than a ceramic or platinum diaphragm. A constant and very reproducible electrolyte flow is assured. Due to the size of the hole, clogging or contamination is difficult. It gives the most accurate and repeatable results.

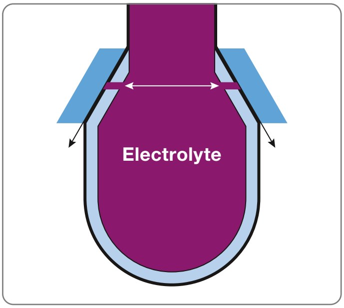
In combination with polymer electrolyte the Single Pore principle is well suited for industrial electrodes. Due to the lack of contamination and maintenance it has a lot of advantages.

The German Federal Physical Technical Institute (PTB) decided during a traceability test in 1997 that the Single Pore pH electrode is the most accurate laboratory electrode. (“Traceability of pH measurement” by Petra Spitzer; ISBN 3-89429-877-4 or ISSN 0947-7063.)



d) Annular Ceramic Diaphragm

The annular ceramic diaphragm is formed by a porous ceramic layer between two glass tubes. The direction of the measured medium is not critical due to the annular shape of this junction. The electrolyte flow is not reproducible. Hence it is mainly applied in gel type electrodes.



e) Ground Sleeve Diaphragm

Ground sleeve diaphragms are ideally suited for applications in suspensions and emulsions, as these diaphragms can be cleaned easily by moving or twisting the glass sleeve. Another successful application of this diaphragm is the pH measurement in low ionic solutions or in non aqueous media. The electrolyte flowrate depends on the roughness of the ground glass surface of the sleeve and the tightness of the sleeve fit. However, this diaphragm is not suitable for applications where the pH electrode assembly is subjected to vibration as this might loosen the diaphragm sleeve.

The selection of the right diaphragm for a measurement application is of utmost importance but not always easy. Very often only the experimental “trial and error” method will lead to a successful application of a certain diaphragm type. For detailed information one has to consult the technical data sheets of the electrode manufacturers.

A diaphragm provides a deliberate leak of the electrolyte solution into the measured medium whilst preventing unrestricted mixing of both solutions within the reference electrode. Penetration of the measured solution into the reference electrolyte, and thus poisoning of the reference conducting system occurs frequently during pH measurements, especially when the measured solution is pressurized.

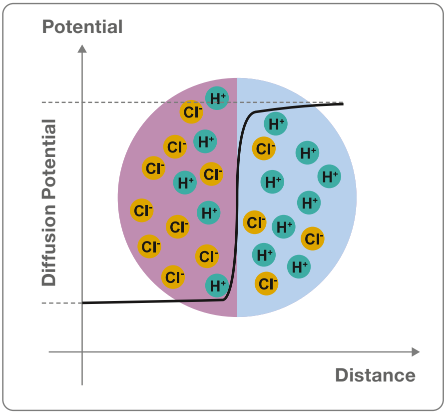
pH electrodes such as Hamilton’s EasyFerm Plus and ChemoTrode allow the electrolyte storage vessel to be pressurized in order to counteract the penetration of the measured solution through the diaphragm. As a rule of thumb a pressure of 1 bar (14.5 PSIG) above the pressure of the measured solution will normally suffice. As a result a small amount of electrolyte solution will penetrate into the measured solution which is generally of no significance to the process. However, this decreases the resistance of the reference electrode to between 0.1 kΩ and 2 kΩ, improves the reproducibility of the measurement, and prevents the diaphragm from clogging up.

Before the electrode assembly is immersed into the measured medium periodic inspection of the electrolyte level should be part of the electrode maintenance program.

3.4.1 The Diffusion Potential

Another disturbing factor of the diaphragm is its diffusion potential (E_6). This potential always develops at the phase boundary between the internal KCl electrolyte and the process liquid. The diffusion potential is attributed to the different migration velocities of ions, which again depends on the polarity and size of the ion type.

The illustration to the right explains the diffusion potential between two HCl solutions of different concentration.



The H^+ ions diffuse nearly five times faster to the right than the Cl^- ions. This creates a potential across the boundary of the two solutions.
In order to keep the diffusion potential at the diaphragm of a reference electrode as small as possible, the different ions in the reference electrolyte should have identical ionic mobility. With a 3M KCl solution this ideal condition is nearly reached.

In general it can be said:

1) The higher the KCl concentration of the reference electrolyte, the lower the diffusion potential.

2) The larger the flowrate of the reference electrolyte through the diaphragm, the smaller the diffusion potential.

The more the pH value of the measured solution differs from pH 7, the larger the diffusion potential.

Diffusion Potentials which Develop Between Various Solutions and a Saturated KCl Electrolyte

1.0	mole HCl	=	14.1 mV
0.1	mole HCl	=	4.6 mV
0.01	mole HCl	=	3.0 mV
0.1	mole HCl	=	1.8 mV
Buffer pH	1.68	=	3.3 mV
Buffer pH	4.01	=	2.6 mV
Buffer pH	4.65	=	3.1 mV
Buffer pH	7.00	=	1.9 mV
Buffer pH	10.01	=	1.8 mV
0.01	mole NaOH	=	2.3 mV
0.1	mole NaOH	=	-0.4 mV
1.0	mole NaOH	=	-8.6 mV

From the above examples it can be seen that different measured solutions will create different diffusion potentials at the diaphragm of a reference electrode.

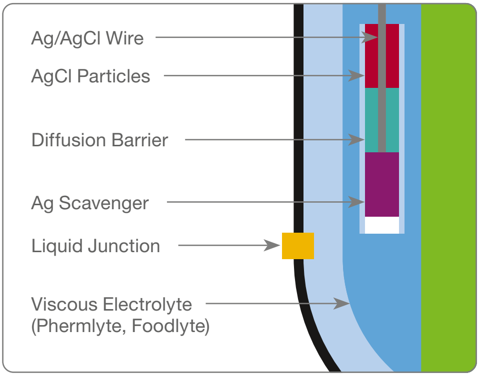
3.4.2 Diaphragm Contamination through Chemical Reaction

Chemical reaction at the diaphragm between the reference electrolyte and the measured solution must be avoided at all costs. This reaction will lead to diaphragm contamination, increase of resistance across the diaphragm and pH measurement errors. The reference electrolyte contains silver chloride which is prone to chemical reactions, especially with sulfides and proteins.

Silver sulfide contamination can easily be identified by a blackened diaphragm. As a result, the response time of an electrode assembly increases substantially, the diaphragm resistance increases radically and calibration may become impossible due to changes in the potential voltage.

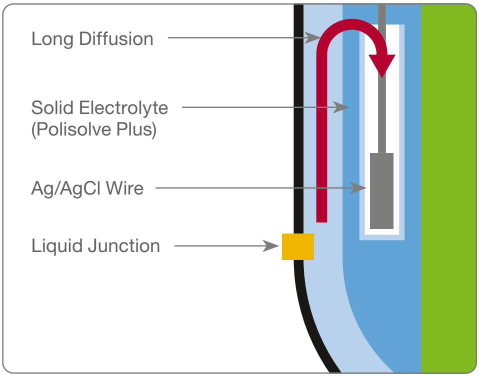
Proteins are also well known to react with Ag^+ ions that may be present in the reference electrolyte. The reaction forms a solid particulate that can clog the porous liquid junction causing loss of electrolyte flow and possible loss of measurement. Often these proteins can be removed through a proper cleaning process, however, it is better to prevent the initial precipitation through the reference design.

The Everef-F Reference System



In order to counteract silver sulfide contamination and protein precipitation at the diaphragm Hamilton has invented the Everef-F reference system. The goal of the system is to isolate the Ag/AgCl element from the KCl reference electrolyte. This system consists of a silver chloride reservoir from which the silver reference wire leads to the sensor's electrical connector. The reservoir is separated from the reference electrolyte by a diffusion barrier consisting of densely packed cotton wool in a glass tube. The barrier prevents the loss of silver chloride into the reference electrolyte induced by temperature variations. In front of the diffusion barrier is a Ag^+ scavenger. The scavenger uses the principles of ion exchange resins to capture the Ag^+ ions before they can escape into the reference electrolyte. The Everef-F reference system enhances the stability of the reference potential and extends the life of the combination electrode considerably. It is commonly used in Hamilton pre-pressurized pH sensors.

The Everef-L Reference System

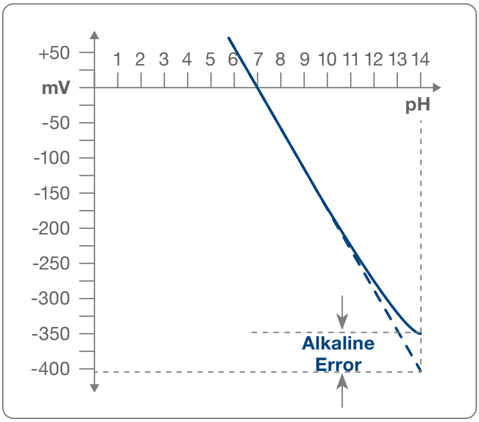


In applications where a chemical reaction at the liquid junction is unavoidable, then lengthening the diffusion path through the reference electrolyte provides a solution. The Everef-L labyrinth liquid junction system from Hamilton addresses the long diffusion path idea.

The Ag/AgCl element is extended the full length of the pH sensor. The element is enclosed in its own glass sheath with only a small opening near the top of the sensor where the reference electrolyte enters the sheath. The Everef-L design creates an extremely long diffusion path. Any ingress of sulfides into the electrolyte must travel this long distance before they can react with the AgCl and impact the potential voltage generated by the reference electrode. The Everef-L design is highly successful in industrial applications and commonly used with Hamilton’s polymer pH sensors.

3.5 Alkaline and Acid Error

3.5.1 Alkaline Error



At a value above pH 10 the gel layer structure at the membrane of a measurement electrode is subject to certain changes which lead to a measuring inaccuracy, the alkaline error. This alkaline error is caused by the presence of a high concentration of alkaline ions, especially sodium ions (Na^+). These ions replace, partly or completely, the hydrogen ions in the outer gel layer of the glass membrane, and by doing so, contribute to the potential at the outer phase boundary.

As a result a lower pH value will be measured than the actual pH value of the measured solution.

In earlier days the alkaline error of glass electrodes occurred starting between pH 9 and pH 10. Today, where the glass membranes contain lithium instead of sodium, the alkaline error is only noticeable from between pH 12 and pH 13.

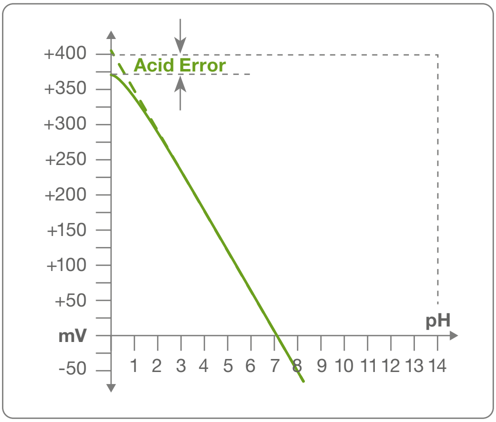
The alkaline error increases with increasing pH value, with higher alkaline concentration and with rising temperature.

In order to counteract the alkaline error, electrode manufacturers use special membrane glasses with low alkaline errors for electrodes which are used to measure high pH values.

3.5.2 Acid Error

At low pH values (< pH 2) the potential difference between measurement and reference electrode will not conform exactly to the NERNST equation. Through experiments it has been proven that the gel layer of the membrane will absorb acid molecules at very low pH values.

This absorption decreases the activity of the H^+ ions and results in a lower potential at the outer membrane phase boundary. The pH measurement shows a higher pH value than the actual pH value of the measured solution. This effect is known as the acid error.



As with the alkaline error, manufacturers supply measurement electrodes with membrane glasses having specially low acid errors.

Hamilton membrane glasses show no acid error above pH 1.

3.6 Temperature Influence and Temperature Compensation

The pH measurement is temperature dependent. Three temperature factors have to be considered in order to perform a nearly perfect pH measurement:

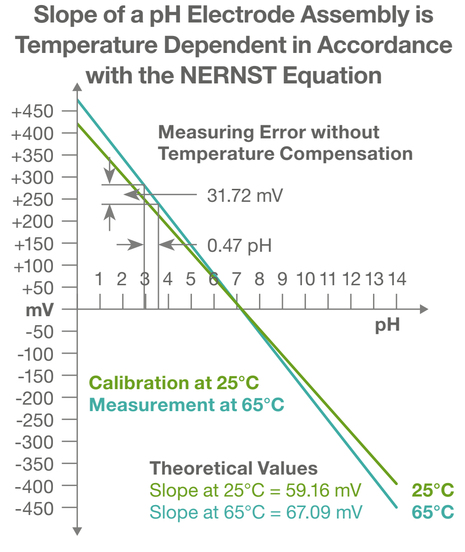
1) **The temperature dependency of the NERNST equation.**

2) **The position of the isotherm intersection point.**

3) **The pH/temperature dependency of the measured solution.**

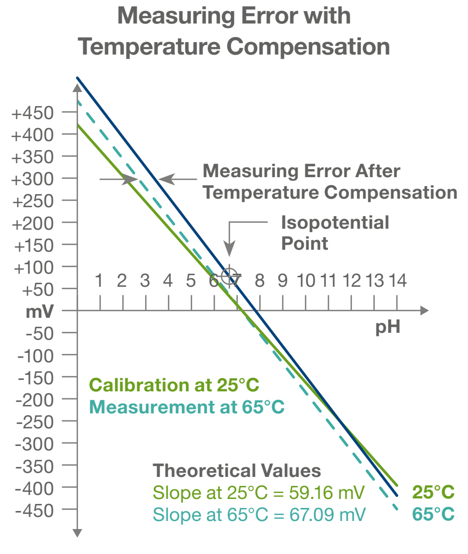
The temperature dependency of the NERNST equation and with it the temperature dependency of the theoretical slope of a pH electrode assembly has already been discussed in paragraph 3.1.

The temperature dependency of the NERNST equation is easily calculated, and as a rule, only this temperature influence is considered by instrument manufacturers when they incorporate conventional manual or automatic temperature compensation in their pH measurement products. The adjacent graph illustrates the theoretical error which is compensated for by conventional temperature compensation.



The position of the isopotential point has to be taken into consideration as well. The reason for the existence of the isopotential point and the determination of its position has been explained in paragraph 3.3.5.

Today electrode manufacturers try to produce pH measurement electrodes which have the isopotential point positioned as near as possible to the theoretical zero point (pH 7). This will reduce the residual error of conventional temperature compensation. Nowadays only microprocessor based pH meters/ transmitters have the capacity to correct the position of the isopotential point (U_{is}).



The third factor is the pH/temperature dependency of the measured solution which is referred to as the temperature coefficient of that solution. The dissociation of molecules is highly temperature dependent. Any change in temperature of the measured solution results in a change in the hydrogen ion concentration of that solution and therefore in its pH value. This pH change is a reality that is specific to the measured liquid media and cannot be described as a measurement error due to the sensor itself.

The pH/temperature dependency of all acids and bases is not known and it is therefore of utmost importance to state the related temperature when giving a pH value of a solution, otherwise the pH measurement is meaningless.

3.7 Various Electrode Shapes

It is not possible to use one electrode shape for every application. More often in the laboratory and in process measurements different electrode shapes are required as there are numerous pH measurement applications. Electrode manufacturers try to cover most of these applications by offering varying electrode constructions.

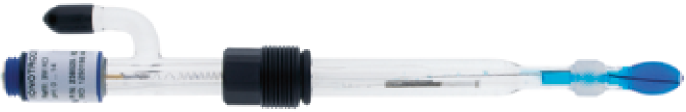
Form a)

This is the most common electrode shape and a wide field of applications can be covered with this type of electrode, both in the laboratory and in process control. Measurement, reference and combination electrodes are manufactured using this construction. It uses a 12 mm body and PG13.5 mounting thread.

Form b)

A standard combination electrode construction with a ground sleeve diaphragm. This electrode is mainly used in the laboratory where dirty or strongly contaminated solutions have to be measured. Its application includes non aqueous media as well. The diaphragm can easily be cleaned by pushing the sleeve upwards. There is a limited use for this construction in process control (be aware of vibration).

Form c)



This design example includes two electrode features: a ground sleeve diaphragm and a side arm filling tube. In order to minimize maintenance time and to pressurize the reference electrolyte an external electrolyte reservoir is connected to the electrode via the pipe connector. This electrode construction can be used in the laboratory and in process control, especially for high purity water control found in boilers and power plants.

Form d)

This refillable electrode design is mainly used in the chemical industry and in biotechnological processes. The electrode features a large electrolyte vessel which is sometimes combined with an intermediate electrolyte vessel. The electrolyte can be pressurized and also steam sterilized. A special electrode holder is required for this electrode thus it is not suitable for laboratory applications.

Form e)

The above electrode design is used in the laboratory where small samples are measured. It is commonly used with test tubes, NMR tubes, and microtiter plates.

Form f)

The main feature of this design is the flat membrane which enables the operator to measure the pH of surfaces, such as skin, leather, paper etc. Hamilton supplies this electrode with an unbreakable plastic shaft, as it will often be carried around and used with a portable pH meter.

Form g)

This construction is used exclusively for combination electrodes featuring a gel or polymer reference electrolyte. The shaft is made completely from plastic. This design makes the shaft unbreakable as it is often used with a portable pH meter.

Form h)

The above design uses a pointed electrode. It is normally applied in the food and dairy industry measurements. The spear shaped electrodes are ideal for use with meats and cheeses.

3.7.1 Membrane Glass Formulations

All pH sensor manufacturers will alter the design of the membrane glass to provide advantages in specific processes. For example, the requirements to survive in a process with strong chemicals or high temperatures may be different than those of pure water. Changing the glass membrane includes altering the type and concentration of alkaline ions embedded within the glass as well as the glass membrane thickness. The desired results of these changes include longer sensor life, measurement stability, and improved accuracy.

Abbreviations to each Hamilton glass formulation along with the glass impedance and suggested applications are listed below.

Hamilton Glass Formulations	Glass Impedance	Suggested Applications
PHI	Moderate	Best lifespan in frequent SIP and autoclavation applications with very low drift. Very little shift after cleaning. Good general chemical robustness. The PHI glass is our recommended membrane glass for bioreactor installations found in R&D, upstream and downstream pharmaceutical applications.
HB	Moderate	Best lifespan in frequent CIP and autoclavation applications. A good choice in high pH applications. Fastest response time. The HB Glass is our recommended membrane glass for food, beverage, and brewing applications.
HF	Moderate	The HF membrane glass formulation is specifically recommended for use in media containing hydrofluoric acid. This glass membrane is also good for flat / flush electrodes that may be exposed to abrasive processes.
F	Low	Low conductivity pure water applications. Low temperature applications. Not for use with strong acids or bases. The F membrane glass is well suited for Ultrapure water and boiler water applications.
H	Moderate	Provides stable readings in anhydrous or partially aqueous solutions. Low alkali error with good accuracy at high pH or elevated temperature. The H membrane glass works well for most general industrial applications.
V	Low	General purpose glass. Low temperature applications. Not for use with strong acids or bases.

3.8 Ageing

3.8.1 The Ageing of a Measurement Electrode

Every glass measurement electrode undergoes an ageing process, even if it is not in use. The ageing process is continuous and starts immediately after manufacture.

Primary reasons for ageing are:

1) The chemical composition of the membrane glass.

2) The steady growth of the internal gel layer of the membrane.

3) The chemical and mechanical attacks to the outer gel layer of the membrane during measuring and cleaning.

Ageing is significantly accelerated by:

1) Measurements in hot solutions above 60°C.

2) Measurements in high acidity and especially in high alkalinity solutions.

3) Incorrect handling of electrode assemblies when not in use, i.e. cleaning and storage.

Typical symptoms of an aged measurement electrode are:

a) An increased response time.

b) An increased membrane resistance.

c) A declining slope, especially in the alkaline region.

d) A shift of the asymmetry potential.

It is of course impossible to state the lifetime of a glass measurement electrode, especially as a combination of the above listed reasons for ageing may cause the deterioration of the electrode performance. For example, a pH electrode, used continuously in an aqueous solution of 4 to 8 pH at ambient temperature and good handling may have an operating life of 18 months. The same sensor could last only 2 months if operated above at 90°C. Furthermore, the same electrode may stop performing after 2 to 3 weeks if it is subjected to high alkalinity > 13 pH and simultaneously at high temperature above 90°C.

The increasing membrane resistance, the declining slope and the zero point drift (shift of the asymmetry potential) may all be compensated for, within limits, by modern pH meters/ transmitters during the calibration process.

After proper pH calibration, a deteriorating response time is a certain indication of ageing. New pH sensors typically have a response time of 20 to 30 seconds when checked in pH buffers with a difference of 3 pH units or more. If the response time is unacceptable to the user, then there is no other alternative, but to replace the electrode assembly with a new one.

3.8.2 The Ageing of the Reference Electrode

Reference electrodes do not age in principle, but their life may be considerable shortened by incorrect handling, during usage and storage.

If the reference electrode is a refillable design then it should always be topped-up with an identical electrolyte used originally by the manufacturer. Electrolytes with different KCl molarity may cause the reference potential to become unstable, the response time of the pH electrode assembly gets sluggish, and in extreme circumstances the entire conducting system may be destroyed.

The diaphragm, being the most critical part of the reference electrode, has to be kept clean at all times. No process liquid must enter the electrolyte vessel through the diaphragm and all chemical reactions at the diaphragm must be avoided (see paragraph 3.4 The Diaphragm).

Reference electrodes utilizing a gel electrolyte reduce maintenance cost as they don’t have to be topped up with liquid electrolyte. Although this reference design is pressure resistant (up to 200 kPa), diffusion over the diaphragm does take place in both direction and will gradually reach the Ag/AgCl reference system, resulting in electrode poisoning. In addition the KCl concentration in the gel electrolyte will be diluted over time by the measured media. Both of these factors result in a limited life of the reference electrode. High temperature or rapid temperature changes will also shorten the life of a gel electrode. A combination sensor with gel electrolyte should never be used continuously in media having a temperature higher than 60°C. A reasonable life span of a gel electrode is approximately 6 months if used under normal condition (pH 2 to 12 at temperatures of 25°C).

Hamilton reference electrodes utilizing the Polisolve Plus electrolyte can be used in high acidic media down to pH 0. This reference electrode is absolutely maintenance free. Although the temperature limit is raised to 130°C, it must be understood that if the electrode is continuously exposed to this high temperature the life span is drastically reduced. Under normal conditions an electrode with Polisolve Plus electrolyte may easily be used up to 12 months.

3.9 Calibration

No pH electrode assembly can measure more accurately than its calibration accuracy! In order to perform a relatively accurate pH measurement, special care has to be taken when calibrating a pH measurement system.

3.9.1 pH Standard and Technical Buffer Solutions

A prerequisite for an accurate pH calibration is the availability of a suitable buffer solution.

pH buffer solutions are mixtures of weak acids and the salt of these acids with a strong base, or mixtures of weak bases and the salt of these bases with a strong acid. Buffer solutions are notable by the fact that they resist change to their pH value regardless of additions of small quantities of acids or bases. Their hydrogen ion activity is stable over a wide range of dilution or concentration.

The National Institute of Standards and Technology (NIST) recommends nine different buffer solutions for the exact calibration of pH measurement systems. These buffer solutions also serve as reference points for the pH scale, as it is impossible to prove the activity of single hydrogen ions by measurement.

All buffer solutions which are produced according to the NIST formulas are called Standard Buffer Solutions.

As the activity of the hydrogen ions is temperature dependent, so is the pH value of any buffer solution. The temperature dependency of the NIST standard buffer solutions is given in the table on the following page.

Standard buffer solutions have an accuracy better than +/- 0.005 pH units between 0°C and 60°C. Between 60°C and 95°C their accuracies are not worse than +/- 0.008 pH units. NIST buffer solutions are exclusively used in laboratories. For industrial use, where the demand on absolute accuracy is normally not as high as in the analytical laboratory, manufacturers offer so called Technical Buffer Solutions.

Technical buffer solutions are more stable than standard buffer solutions and easier to manufacture. Their accuracies are given as +/- 0.02 pH units in best cases, but may differ from manufacturer to manufacturer. The temperature dependency of technical buffer solutions is normally printed on their container by the manufacturer. Conventional technical buffer solutions have a limited shelf life, most of them only one year in sealed bottles. Once opened, their shelf life is reduced to a few months. Alkaline buffer solutions are especially affected by CO_2 contamination from the atmosphere.

DuraCal pH buffer solutions from Hamilton are different. These patented technical buffer solutions provide a pH stability never achieved before; their high accuracies are guaranteed for 5 years after date of manufacture. The pH 9.21 and pH 10.01 buffer solutions are stable even in open air.

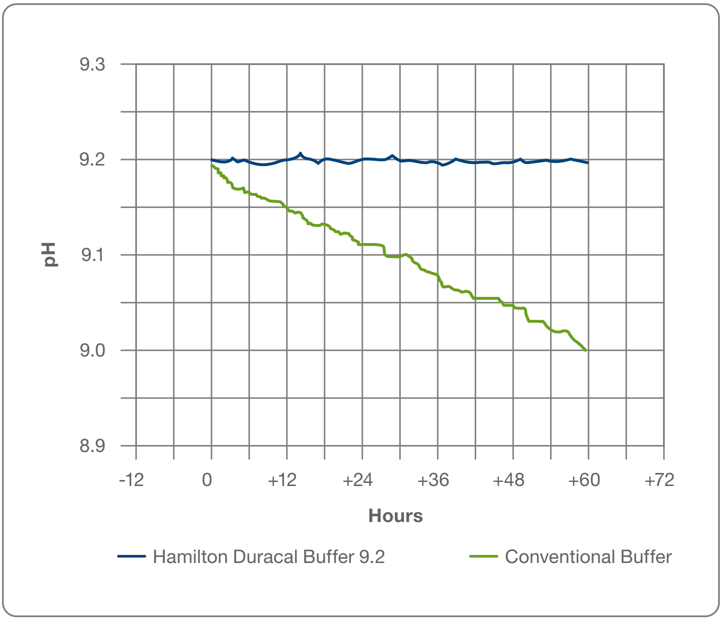
Each bottle of Hamilton buffer solutions is certified, including the actual pH value and expiration date. The certification is traceable to primary standards from NIST and PTB.

pH Values of Standard Buffer Solutions According to NIST

NBS	A	B	H	C	D	E	F	I	G
Temp. C	Potassium tetra-oxalate	Potassium hydrogen tartrate	Potassium dihydrogen citrate	Potassium hydrogen phthalate	Phosphate	Phosphate	Borax	Sodium carbonate/ sodium hydrogen carbonate	Calcium hydroxide
0	–	–	3.863	4.010	6.984	7.534	9.464	10.137	13.423
5	1.668	–	3.840	4.004	6.951	7.500	9.395	10.245	13.207
10	1.670	–	3.820	4.000	6.923	7.472	9.332	10.179	13.003
15	1.672	–	3.802	3.999	6.900	7.448	9.276	10.118	12.810
20	1.675	–	3.788	4.001	6.881	7.429	9.225	10.062	12.627
25	1.679	3.557	3.776	4.006	6.865	7.413	9.180	10.012	12.454
30	1.683	3.552	3.766	4.012	6.853	7.400	9.139	9.966	12.289
35	1.688	3.549	3.759	4.021	6.844	7.389	9.102	9.925	12.133
38	1.691	3.548	3.755	4.027	6.840	7.384	9.081	9.903	12.043
40	1.694	3.547	3.753	4.031	6.838	7.380	9.068	9.889	11.984
45	1.700	3.547	3.750	4.043	6,834	7.373	9.038	9.856	11.841
50	1.707	3.549	3.749	4.057	6.833	7.367	9.011	9.828	11.705
55	1.715	3.554	3.750	4.071	6.834	–	8.985	–	11.574
60	1.723	3.560	3.753	4.087	6.836	–	8.962	–	11.449
70	1.743	3.580	3.763	4.126	6.845	–	8.921	–	–
80	1.766	3,609	3,780	4.164	6.859	–	8.885	–	–
90	1.792	3.650	3.802	4.205	6.877	–	8.850	–	–
95	1.806	3.674	3.815	4.227	6.886	–	8.833	–	–

Stability Comparison of Hamilton Alkaline Buffer to Conventional Alkaline Buffer

Both buffer solutions have been exposed to blowing air.



Used buffer solutions should always be discarded and never be returned to their original storage bottle. For this reason Hamilton has developed a unique storage bottle which includes a calibration compartment with a non return valve at the bottom, preventing the used buffer solution to be returned into the storage bottle. This Calpack bottle is practical and no additional calibration container is required. It's also economical and only the required amount of buffer solution is used.

The Practicality of the Hamilton Calpack Calibration Bottle

Values and Accuracies of Hamilton Buffer Solutions

Buffer Solution	pH Value	Accuracy	Stability in Months
Hamilton DuraCal	1.09	+/- 0.02 pH	60
Hamilton DuraCal	1.68	+/- 0.02 pH	60
Hamilton DuraCal	2.00	+/- 0.02 pH	60
Hamilton DuraCal	3.06	+/- 0.02 pH	60
Hamilton DuraCal	4.01	+/- 0.01 pH	60
Hamilton DuraCal	5.00	+/- 0.02 pH	60
Hamilton DuraCal	6.00	+/- 0.02 pH	60
Hamilton DuraCal	7.00	+/- 0.01 pH	60
Hamilton DuraCal	8.00	+/- 0.02 pH	60
Hamilton DuraCal	9.21	+/- 0.02 pH	60
Hamilton DuraCal	10.01	+/- 0.02 pH	60
Hamilton	11.00	+/- 0.05 pH	24
Hamilton	12.00	+/- 0.05 pH	24

It must always be remembered: one cannot achieve a better measurement accuracy than the accuracy of the buffer solution one uses for calibration.

3.9.2 The Calibration Procedure

It has been said and explained before that no pH electrode assembly responds ideally to the NERNST potential. The reason lies in the behavior of the various potential sources of the electrode assembly as well as their response to temperature change and the changes of these parameters with time.

In order to use a single electrode assembly (separate measurement electrode and reference electrode) or a combined electrode assembly effectively and to perform an accurate and repeatable pH measurement, the pH meter/transmitter has to be adapted to the characteristics of the applied electrode assembly.

Consider that it is not the electrode assembly that is calibrated, it is the mV measuring instrument which is adjusted in order to compensate for the imperfection of any utilized electrode assembly. The performance properties of an electrode assembly cannot be changed at will.

The adaptation of the pH measuring instrument to the performance characteristics of the electrode assembly is done by calibrating the pH measurement system (pH electrode assembly plus instrument) against buffer solutions having definite pH values.

In principle, the calibration procedure should be outlined in the operating instructions supplied with the pH meter/transmitter. With this in mind, Hamilton has provided some general guidelines that can be used for most devices.

Calibration of Microprocessor-based pH Meters

Microprocessor-based pH meters have largely replaced traditional analog pH meters in laboratories and as on-line instruments in industrial plants. Even portable pH meters are nowadays microprocessor controlled. Their handling is relatively simple as there are no potentiometers to adjust. Normally the operator is menu-guided through the procedure of his task. These instruments give less reasons for wrong handling and therefore less measuring errors.

The calibration procedure uses two buffer solutions that should have a difference of at least 2 pH units or greater. It is not necessary to calibrate the zero point with buffer 7. The two buffer solutions required should approximate the start and the end of the selected measuring span for the process. The zero point, the slope and even the isopotential point are all calculated by the microprocessor during the different stages of calibration.

In general the two point pH calibration is performed as follows:

1) Two buffer solutions of different pH values are selected. The pH value of one buffer solution should lie somewhere in the region of the beginning of the desired measurement span and the pH value of the second buffer solution should lie somewhere near the end of the measurement span. Hamilton Buffer Solutions can be found here.

2) Rinse the pH sensor in deionized water prior to immersing in the first buffer solution. This removes any residual liquids that could influence the calibration accuracy. After the calibration mode of the pH meter is activated, the calibration menu guides the operator through the calibration procedure. It is typical that the sensor has to stay in the buffer solution for a short time (normally one to three minutes) until the meter can settle on the actual pH value. Sometimes the buffer values still have to be entered manually, however, very often the microprocessor identifies the buffer values automatically from a preset table stored in the device memory.

3) After the first buffer calibration, the sensor should be rinsed again with deionized water and dried with tissue paper. When drying the sensor, care must be taken not to rub the membrane, i.e. only dab the electrode with tissue paper. Under no circumstances must an electrode be rubbed. This could introduce static electricity into the glass shaft of the sensor which could upset the accuracy of the pH calibration for hours.

Additional notes on this procedure:

The temperature of the buffer solutions must be measured; either with the integral temperature element within the pH sensor or separately with a dedicated RTD. The temperature values are either entered manually into the meter or, detected automatically with the incorporated temperature element.

In order to keep the temperature error as low as possible, especially errors due to the diffusion potential and the isopotential point, it is recommended that the calibration be executed at the temperature at which the actual pH measurement will be performed.

After the successful calibration the used buffer solution should be discarded. Never reuse a buffer solution and never return it to its original storage container.

3.9.3 Recalibration

As the pH sensor experiences ageing over time, the pH calibration has to be periodically repeated. The time interval between calibrations cannot be specified. This depends on various factors:

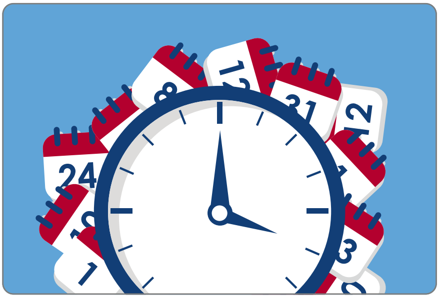
a) The measured pH value.

b) The measured solution.

c) The temperature of the measured solution.

d) The age of the electrode assembly.

e) The accuracy required.



The frequency of re-calibration has to be established experimentally.

The calibration interval can vary between hours, days, weeks or even months, and has to be established individually for each application. When working with unknown process liquids, it is advisable to initially recalibrate as often as possible and to keep records of the results. Often changes in values such as the slope may indicate that a sensor requires more frequent calibration. If no significant change of the calibration values is noticed, the frequency of the calibration may be progressively extended.

3.9.4 Response Time

If a pH electrode assembly is immersed into a buffer solution, it does not show the pH value of that buffer solution instantaneously. A response time of approximately 30 seconds is normal in order to reach the buffer value with a tolerance of 0.01 pH units (0.6 mV). For this reason it is very important to wait long enough during the calibration cycle for the indication of the pH meter to become stable. Only then can the indicated value be adjusted to the buffer value. A premature interruption of the electrode adaptation to the buffer value is often a major source for incorrect pH measurements. Patience is a virtue in pH calibration.

The response time of an electrode assembly is especially slow if the electrode temperature and the temperature of the buffer solution differ by more than 10°C. In cases where buffer solutions have to be heated, one has to delay the calibration procedure until the electrode reaches the temperature of the heated buffer solution. This ensures that proper heat transfer through the electrode body occurs and the internal temperature element can output the correct value.

A further point to consider is the storage medium used for electrode assemblies. When not in use avoid storing the pH electrode in distilled water, as this will slow down the response time of that electrode assembly considerably. It has been found that a 3M KCl solution is the best storage medium for glass electrode assemblies.

Modern microprocessor based pH meters/transmitters include menu-based software for early detection of a stable pH calibration value (auto-cal). Hamilton verification measurements of many manufacturers have shown that the auto-cal values do not differ more than 0.01 pH units from the actual value found between new electrodes and tested buffer solutions and, thus, are highly reliable.

3.9.5 Reasons for calibration problems

Three common problems might be encountered when calibrating a pH measurement system. These are:

1) Difficulty in achieving a zero point calibration.

2) No success in obtaining a slope calibration.

3) A very long response time (longer than 3 minutes).

There could be various reasons for the above mentioned problems. The most frequent ones are listed below:

a) The utilized buffer solutions are either contaminated or expired. It could be that the buffer solution used is incorrect – therefore never store buffer solutions in unmarked bottles or an open beaker.

b) The reference electrode electrolyte is contaminated and/or the diaphragm is blocked. This may be apparent through discoloration of the ceramic junction or a color change of the KCl electrolyte.

c) An older sensor is used which no longer generates the proper mV output.

d) The pH sensor has dried out or has not been hydrated long enough (after dry storage or after cleaning with an acid solution).

e) Hairline cracks are present in the glass membrane of the measurement electrode.

f) An electrostatic charge has developed due to rubbing the electrode shaft with a cloth instead of gently dabbing it with tissue paper.

g) A temperature difference between electrode assembly and buffer solution of more than 10°C during calibration.

h) The zero point of the pH electrode assembly and the pH meter differ. (Note - This is seldom the case as normally both sensor and electronics have pH 7 as their zero potential. In exceptional cases a poorly manufactured pH sensor could have a zero point which differs from pH 7).

i) The connection between electrode assembly and measurement transmitter could also cause problems. This is normally recognized as either an open circuit in the cable or a short circuit in the cable and / or the connection plug (usually due to moisture ingress).

Note: Hamilton Arc Intelligent sensors allow for diagnostics checks of many of the error messages described above. These sensors convert electrical measurements into either digital protocol (Modbus RTU) or Bluetooth wireless communication. The resulting diagnostic error messages can be displayed on a PC, mobile phone or tablet using ArcAir Software. Consult Hamilton Support for more information.

3.10 The Accuracy to be Expected

The accuracy of a pH measurement depends on many factors of which may or may not be controllable. In order that the non-controlled factors do not influence the pH measurement, the controllable factors must be monitored and kept as small as possible.

The calibration of the pH sensor is one of the most important factors. To ensure high measurement accuracy the user must follow correct calibration procedures, use new and accurate buffer solutions, and wait long enough for stable pH values to accept the calibration. The time interval between re-calibration should be as short as practically possible. Remember: no pH measurement can be more accurate than its calibrated accuracy.

It has been stated repeatedly that temperature influences the result of the pH measurement. In order to achieve high measurement accuracy the temperature difference between the pH buffer solutions used for calibration and the measured liquid medium must be kept as low as possible. The temperature of the measured medium must be determined accurately or, if possible, controlled at a constant value in order to perform an effective temperature compensation.

Ideally, the reference electrode must be kept pressurized by approximately 100 kPa (1 bar) above the process pressure to keep the reference electrolyte flowing and prevent the ingress of measured solution into the reference electrode body. The liquid junction must be kept clean at all times. The correct matching of the liquid junction to the application can drastically improve the pH measurement accuracy.

The glass membrane of the measurement electrode must also be kept clean at all times. Coating on the glass membrane will reduce the surface area directly impacting measurement accuracy and in extreme cases make a pH measurement impossible.

Accuracy expectations should not exceed practical achievable results. Realistic accuracies of between +/- 0.03 pH units and +/- 0.05 pH units can be achieved with a well hydrated and intact pH sensor connected to a properly grounded, microprocessor based pH transmitter or meter with a high impedance input circuit of at least 10^{12} ohms. In the laboratory under controlled conditions, accuracies of +/- 0.02 pH units are achievable.

3.11 Installation Considerations

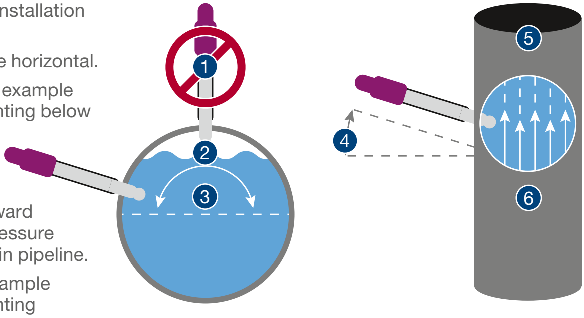
pH electrodes get installed in a variety of liquid processes. The mounting and installation of these sensors in vessels and pipelines often raises questions. This chapter discusses some basic installation tips to consider when installing sensors.

Orientation

Since pH sensors are liquid filled, they should be mounted at an angle of at least 15 degrees above horizontal. Polymer-based and specified upside-down sensors are the exception to this rule as their electrolyte is solid. If mounted in a vertical position then avoid applications where a partially full vessel or pipeline could expose the sensor to air causing loss of measurement.

In-Line Mounting

1) If air is present, avoid vertical installation (okay if pipe is full).
2) Optimum installation 15° above horizontal.
3) Horizontal pipeline installation example (consult factory if sensor mounting below horizontal is required).
4) Optimum installation 15° above horizontal.
5) Process liquid should flow upward (if downward flow then backpressure should be present to avoid air in pipeline.
6) Vertical pipeline installation example (consult factory if sensor mounting below horizontal is required).



Flow Velocity

pH sensors do not require flow velocity for measurement; however, some flow past the sensor helps avoid potential coating and build up from occurring. A flow velocity of at least 1 m/s (3 ft/s) is often adequate to prevent coating from occurring. Flow velocities higher than 3 m/s (10 ft/s) should also be avoided if particulates are present. These higher velocity flowrates may abrade the glass membrane of the sensor causing shortened lifespan. Sensors with flat glass electrodes may be an option in these installations.

Insertion depth

The glass bulb at the tip of the sensor should be fully exposed to the process by protruding out into the liquid roughly 8-10 mm. This insertion depth helps avoid air pockets and ensures that the pH sensitive glass membrane and liquid junction is past any laminar flow area near the inner wall of the process vessel / pipeline. Good mixing with turbulent flow allows for quick response and helps prevent any potential process related coating that could occur. Avoid excessive insertion depth that could put mechanical stress on the sensor and increase potential for breakage of the glass shaft.

Sensor Mounting

pH sensors need to be removed for cleaning, calibration, and eventual replacement. In batch processes, removal between each run for maintenance can easily be accomplished during shut down. In continuous processes the sensor must be isolated from the process prior to removal to avoid shutdown.

Retractable housings such as shown to the right mount directly to the process and allow the sensor to be isolated prior to removal. The sensor is removed from the process and o-ring seals are used to avoid any leakage. There are multiple retractable holder options for either manual or pneumatic sensor exaction. Retractable holders such as the Hamilton Retractex shown to the right also offer additional ports for flushing of the sensor and any residual liquid prior to removal from the process.

4 Electrode Handling

pH measurement systems are by nature maintenance intensive. Most of the maintenance activities are mainly concentrated towards the pH electrode assembly, e.g. calibration and cleaning. The correct handling of the electrode assembly during the maintenance period is of utmost importance to the ideal functioning of the entire pH measurement system.

Incorrect handling might shorten the life of the electrode assembly considerably or cause an unreliable measurement result. Correct handling of the pH electrode assembly does not only improve the measurement result, it can also save the plant owner a substantial amount of money.

4.1 Storage

When considering the storage of a pH electrode assembly, one should evaluate each portion of the electrode assembly: measurement electrode, reference electrode, or combination electrode. The storage time must also be taken into account, i.e. long term storage for weeks or months, or short storage intervals between measurements.

4.1.1 The Storage of Measurement Electrodes

Measurement electrodes can be stored dry for long periods. However, before using the measurement electrode it has to be hydrated for at least 48 hours in normal tap water or a slightly acidic solution in order to establish an outer gel layer at the pH sensitive membrane.

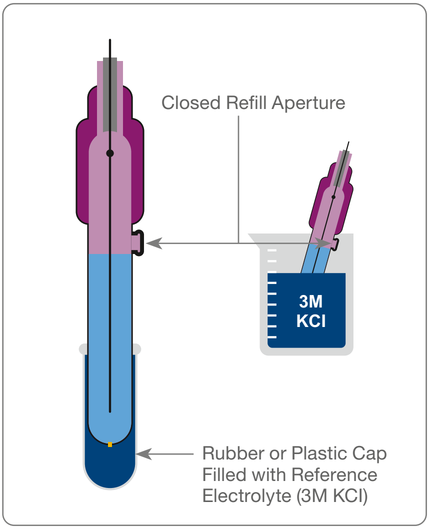
Nevertheless, in order that the electrode is ready for immediate use, most manufacturers supply their measurement electrodes hydrated, i.e. a plastic or rubber cap filled with a liquid solution is placed over the membrane. It is essential that this cap is kept filled at all times. The filling liquid is either tap water or a weak acidic solution. This will keep the membrane hydrated and therefore the outer gel layer well developed.

If a measurement electrode has to be stored for short periods between measurements it should be immersed in a container filled with tap water or be fitted with a watertight plastic cap filled with tap water. Therefore one should not throw the supplied plastic caps away. They should be kept for reuse.

4.1.2 The Storage of Reference Electrodes

Reference electrodes should always be stored wet, i.e. the diaphragm should be covered with the same reference electrolyte with which the reference electrode has been filled. Wet storage must also be applied when the electrode is stored for a long time.

It is not advisable to store reference electrodes dry as the reference electrolyte will slowly penetrate through the diaphragm and crystallize on the outside of the electrode. The salt crystals do not inherently cause a problem but the reference electrode might dry out completely resulting in a substantial increase in the diaphragm resistance. Even when the reference electrode is refilled with its respective electrolyte, the high diaphragm resistance will not disappear immediately and will result in large measurement errors or even make a measurement totally impossible.



For short or long time periods it is essential to store reference electrodes in their respective reference electrolyte. If the sensor is refillable, then the filling port should be closed with a suitable stopper.

Storage in tap water or in distilled water should be avoided. Any penetration of these liquids through the diaphragm will increase the diaphragm potential considerably, dilute the electrolyte concentration, and significantly alter the subsequent pH measurement.

4.1.3 The Storage of Combination Electrodes

A combination electrode consists of a measurement electrode and a reference electrode combined into one single sensor. The storage conditions must therefore be suitable for a measurement and for a reference electrode. Since every reference electrolyte is an aqueous solution it has been found that the optimum storage liquid is a 3M KCl electrolyte of similar formation to what is used in that combination electrode. If the sensor is a refillable design then the refill aperture has to be closed during storage time.

All that has been stated about the storage of a reference electrode applies equally to the storage of a combination electrode. Gel-filled combination pH sensors are an exception to the rule. These electrodes have no refill aperture and the drying-out of their diaphragm has to be avoided at all costs. Therefore gel-filled combination electrodes must be stored wet in a 3M KCl solution.

This statement applies to polymer electrodes as well.

4.2 Cleaning of Electrode Assemblies

Industrial pH electrode assemblies are often immersed into process solutions which tend to contaminate the membrane of the measurement electrode or the diaphragm of the reference electrode or both. The result is one, or a combination of the following:

a) A zero point shift.

b) A reduced slope.

c) A long response time.

Ideally the pH sensor should be clean at all times in order to guarantee an ideal pH measurement. Periodic cleaning of the pH probe should be part of any regular plant maintenance schedule. Since the cleaning frequency depends solely on the goals of the application, a cleaning cycle time has to be established individually for each pH measurement. The cleaning interval could vary between hours and weeks.

The pH cleaning procedure also depends on the kind of contamination. The following procedures have been found practical and effective:

- Initially always try to remove any deposits from the membrane or from the diaphragm by rinsing the electrode with a mild detergent.
- Hard, scale-type calcium deposits may be removed by soaking the electrode for several minutes in a solution of 0.1M HCl acid.
- To remove oil and fat deposits the use of a strong household solvent is recommended. If this is unsuccessful a brief rinsing in ethyl alcohol is advisable.
- Applications containing proteins tend to contaminate the glass membrane and diaphragm of the electrode assembly. Soaking the electrode assembly for several hours in a solution of 1% pepsin in 0.1M HCl is normally a remedy. Pepsin is an enzyme that is effective at softening protein deposits.
- Inorganic coatings such as hydrocarbons can be removed using commercially available glass cleaning solutions.
- Process liquids containing sulfides will react with the silver chloride present in most reference electrolytes. This reaction will lead to the contamination of the diaphragm with silver sulfide deposits which discolor the porous ceramic material. To remove the silver sulfide precipitation the electrode has to be soaked in a thiourea/HCl solution until the diaphragm is totally bleached.
- Hard, scale-type coatings may be removed with hydrogen peroxide or sodium hypochloride.
- Coatings that are acid or alkaline soluble may be removed by either rinsing the electrodes in 0.1M HCl or in 0.1M NaOH for 5 to 10 minutes.

It is very important that after each above cleaning process the sensor should be soaked in 3M KCl electrolyte for approximately 12 hours, or preferably a day for rehydration. Since the cleaning solution may penetrate the diaphragm during cleaning the diffusion potential can be affected. After the cleaning and soaking process, it is absolutely necessary to perform a recalibration before a new pH measurement takes place (see paragraph 3.8).

During the cleaning process the electrode should only be rinsed or soaked. Under no circumstances must an electrode be cleaned mechanically, i.e. with a knife, screwdriver or any other sharp tool as this might destroy the electrode. Rubbing with a cloth must also be avoided as this will introduce static electricity into the glass shaft of the electrode and prolong the response time considerably (see paragraph 3.9.2).

4.3 Refilling or Replacing the Reference Electrolyte

A reference electrode or a combination electrode utilizing a liquid reference electrolyte has to be inspected at regular time intervals to check its electrolyte level. The electrolyte has to be replenished when the internal reference system is no longer fully covered by the electrolyte. The topping up is done by injecting a corresponding reference electrolyte through the refill aperture. This can easily be done by using a pipette or syringe.

If the reference electrolyte is contaminated by the ingress of the measured medium or if the concentration of the reference electrolyte has been increased through the evaporation of water, the reference electrolyte should be replaced completely.

Hamilton supplies a brief operating and maintenance instruction for each of their electrodes. Please observe these instructions – they could save you a great amount of trouble, frustration and a lot of money.

5 The Connection of the pH Electrodes to the pH Measurement Instrument

5.1 Measurement Electrode Connection Cable

The pH measurement electrode has inherently a high internal resistance (up to 5×10^9 ohms in some cases) due to the fact that the potential voltage must pass through the membrane glass which adds resistance. Therefore the electrical connection to a pH meter or transmitter is prone to all kinds of electro-magnetic interference. For this reason specialized cable and connectors become important for the success of the pH measurement.

The measurement electrode is always connected with a low noise screened coaxial cable to the measurement instrument. This cable must have a very high insulation resistance, always higher than the input impedance of the measurement instrument (normally $10^{12}\ \Omega$). The market offers coaxial cables having an insulation resistance of $10^{14}\ \Omega$ to $10^{17}\ \Omega$ per meter cable length.

Another specification to observe is the cable capacitance. This should be as low as possible in order not to increase the time constant of the signal transmission. Experience has shown that the capacitance of a pH connection cable should not be higher than 150 pF/m. A 200 pF/m cable capacitance on a 50 m long cable would add approximately 50 seconds time delay to the response time of the electrode assembly. Coaxial cables available for pH measurements have a capacitance of between 64 pF/m to 102 pF/m.

The temperature rating of the pH connection cable also has to be considered. For normal measurement applications below 70°C, standard pH connection cables have a temperature rating of -30°C to +80°C. Special high temperature cables are available having a maximum temperature rating of 130°C.

5.2 Reference Electrode Connection Cable

The connection of a separate reference electrode to the measurement instrument is not challenging, as long as the cable is protected from any electromagnetic interference. Normally a standard single core, screened cable suffices. Temperature ratings of the cable must be observed.

5.3 Combination Electrode Connection Cable

What has been said about the cable requirements for a separate measurement electrode must also be observed for the connection of a combination electrode. It is advisable to use a double screened coaxial cable (triax cable). To save costs it is normal practice to connect the inner screen of the coaxial cable to the reference electrode part of the combination electrode.

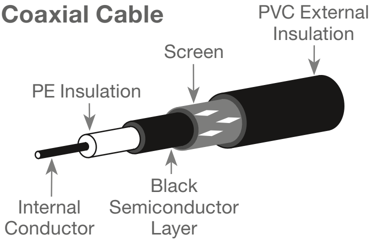
5.4 Cable Preparation and Cable Routing

The insulation of the internal conductor of a pH connection cable is not only screened with copper wire mesh but also with an additional black semiconductive layer. This layer suppresses voltages which might be created when moving the coaxial cable. This phenomenon is known as triboelectric noise. It is also critical that this black layer must be carefully removed when preparing the cable ends for connection to the electrical connector and/or to the measurement instrument. If the black layer is not fully removed, it will cause a short circuit between the internal conductor and the copper screen. When stripping the coaxial cable, tools and hands of the technician should be dry and clean to prevent contamination. After stripping, the cable ends should be cleaned with alcohol, using a cloth or a brush, both of which should be absolutely clean. Testing has shown that touching the stripped cable ends with wet or oily fingers will reduce the insulation resistance down to, or below, 10^7 ohms, which will result in a short circuit of the high resistance measuring chain – a pH measurement now becomes impossible.

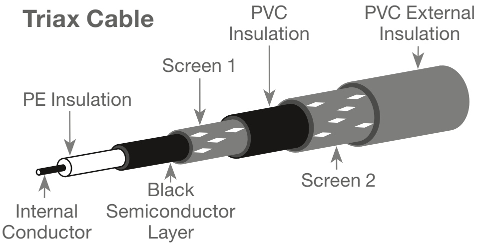
When routing the pH connection cable from the sensor to the transmitter, care must be taken not to route the cable parallel to power cables. Parallel power cables in the vicinity of the pH connection cables can lead to electro-magnetic interference (induction), which must be avoided at all cost. The outer screen of the triax cable (combination electrode) should always be earthed (grounded) on one side only. In principle, every pH connection cable should be as short as possible, but should under no circumstance be longer than 50 meters.

pH connection cables cannot be buried straight into the ground. If this has to be done these cables must be installed in a metal or plastic conduit.

Coaxial Cable



Triax Cable



5.5 Plug or Cable?

Sensor manufacturers supply their pH probes in two configurations: either with an integrally installed cable (normally 1 to 3 m in length), or with a plug-style electrical connector. Both configurations have their advantages and disadvantages.

If the cable is integral to the pH sensor, the customer can be assured that the cable connection is water tight and measuring faults attributed normally to the electrode/ cable connection (short circuit, moisture ingress) can be ruled out. On the other hand, however, when the pH electrode assembly has to be replaced (remember: a pH electrode is a consumable item with a certain life expectancy), the cable also has to be re-purchased.

A plug connection eases the electrode removal or replacement during the maintenance period and is more economical in the long run (saving of cable cost). However, care must be taken to always mate the connection socket firmly to the cable plug, otherwise moisture, the biggest enemy to the electrode/cable connection, might penetrate the socket/plug coupling. Once moisture has entered this joint, a reliable pH measurement is no longer possible.

Electrode Head with Integrated Cable and Different Instrument Plugs

Electrode Socket – Cable Plug Connection

6 Appendix: The Hydrogen Ion Concentration

Before the term pH can be defined, certain chemical and physical principles have to be described, central of which will be the water molecule with its two hydrogen atoms (H_2) and its one oxygen atom (O).

6.1 The Atom Structure

In ancient Greek philosophy the word atom was used to describe the smallest bit of matter that could be conceived. This fundamental particle, to use the present day term for this concept, was thought of as indestructible; in fact, the Greek word for atom “atomos” means “not divisible”. Knowledge about the size and nature of the atom grew very slowly throughout the centuries as people were content merely to speculate about it.

With the advent of experimental science in the sixteenth and seventeenth centuries, progress in atomic theory accelerated. Chemists soon recognized that all liquids, gases and solids could be analyzed into their ultimate components, or elements. For example, salt was found to be composed of two distinct and different elements: sodium and chlorine, which are joined together in an intimate bond known as a chemical compound.

The atoms are the building blocks of an element. All atoms of any given element behave chemically in the same way. Thus, from a chemical viewpoint, the atom is the smallest entity to be considered. The chemical properties of the various elements are quite different; their atoms combine in many different ways to form a multitude of different chemical compounds. There are as many different atoms as there are elements. Today we know of 112 different elements.

In 1911 the British physicist Ernest Rutherford (1871 – 1937) formulated a theory of atomic structure that was the first visualization of the atom as a dense nucleus surrounded by a cloud of electrons. Rutherford established that the mass of the atom is concentrated in its nucleus. The nucleus has a positive charge of electricity; the electrons each have a negative charge. The charges carried by the electrons add up to the same amount of electricity as resides in the nucleus, and thus the normal electrical state of the atom is neutral. Rutherford called the particles, forming the nucleus, protons. Rutherford’s vision of an atom was revised in 1913 by Niels Bohr (1885 – 1962) (see next section “The Bohr Atom”).

In 1932, another British physicist James Chadwick (1891 – 1974), discovered another particle in the nucleus of an atom, known as the neutron, having the same mass as the proton but without an electric charge. It was then realized that the nucleus is made up of protons and neutrons. In any given atom, the number of protons is equal to the number of electrons and hence to the atomic number of the atom (its position in the “Periodic Table of the Elements”).

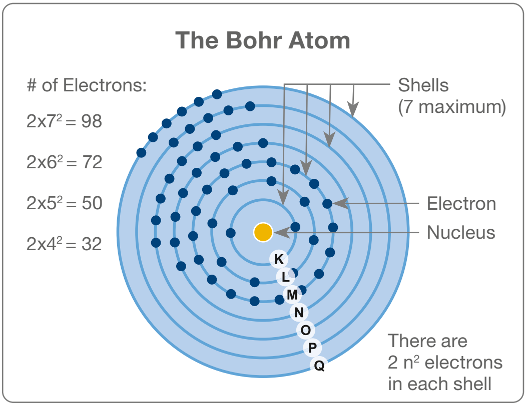
6.2 The Bohr Atom

To explain the structure of the atom, The Danish physicist Niels Hendrik David Bohr developed in 1913 a hypothesis known as “The Bohr Theory of the Atom”. He assumed that electrons are arranged in definite shells, or quantum levels, at a considerable distance from the nucleus. The arrangement of these electrons is called the electron configuration.

The Bohr Atom

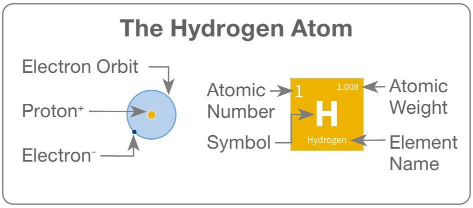
The number of such electrons equals the atomic number of the atom: hydrogen has a single orbital electron, oxygen has 8, and uranium has 92.

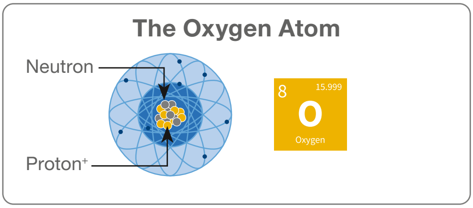
The electron shells are built up in a regular fashion from a first shell to a total of seven shells, each of which has an upper limit of the number of electrons that it can accommodate. The shells are named from inner shell to outer shell: K-shell, L-shell … to Q-shell. The K-shell is complete with two electrons, the L-shell can hold up to eight electrons, the M-shell 18 electrons and in general the nth shell 2n^2 electrons. Only the electrons in the outer shell determine the chemical behavior of the atom.


The Bohr Atom

Atomic shells do not necessarily fill up with electrons in consecutive order. The electrons of the first 18 elements in the periodic table are added in a regular manner, each shell being filled to a designated limit before a new shell is started.

Starting with the 19th element, the outermost electron starts a new shell before the previous shell is completely filled. A regularity is still maintained, however, as electrons fill successive shells in a repetitive back and forth pattern. The result is the regular repetition of chemical properties for atoms of increasing atomic weight that corresponds to the arrangement of the elements in the periodic table.


The Hydrogen Atom


The Oxygen Atom

6.3 The Periodic Table of Elements

In 1869 the Russian chemist Dmitri Ivanovich Mendeleyev (1834 – 1907) arranged all elements known at the time in a table according to their atomic mass. By doing so, he discovered that certain properties of the elements repeat themselves periodically. Therefore Mendeleyev grouped the elements with similar chemical activities in the same columns underneath each other. This element arrangement is called the periodic table.

Over the years more and more elements were discovered and the periodic table had to be rearranged a few times. The table, as we know it today, is illustrated on page 57. The elements are arranged by their ascending atomic number (number of protons in the nucleus) horizontally in seven rows. Each row represents one of the seven electron shells of the atom. Hydrogen in position 1 in row 1 is the lightest element. The last element in the table is, for the time being, the artificial element "ununbium", taking the 112th position with an atomic mass of 277. The table provides for a total of 118 elements. The 18 vertical columns group the elements according to their chemical activities, i.e. the numbers of electrons in their outer shell.

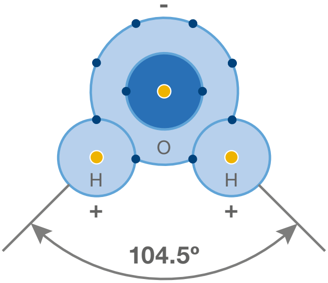
6.4 The Molecule

The molecule is the smallest unit of a chemical compound having the same chemical properties of that compound. The water molecule consists of a single atom of oxygen and two atoms of hydrogen joined by an electrical force called a chemical bond.

It was the French chemist Antoine Laurent Lavoisier (1743 – 1794) who proved that water was not a basic element, as the ancient philosophers thought, but a compound of oxygen and hydrogen – as expressed by the present day formula H_2O.

Molecules are held together by sharing two electrons (covalent bonds). In order to maximize these bonds, the atoms adopt specific positions relative to each other, i.e. each molecule has its own definite structure. For instance in the water molecule two hydrogen atoms are bonded to the oxygen atom at an angle of 104.5°. Therefore water has a dipole moment as the hydrogen electrons are attracted slightly towards the nucleus of the larger oxygen atom. In contrast the structure of CO_2 is linear and has therefore no dipole moment.

The Water Molecule H_2O



Certain elements do not combine with other elements. These are the group of noble gases. Their atoms contain either 2 electrons (He) or 8 electrons (Ne; Ar; Kr; Xe and Rn) in their outer shell. Any other element having less than 8 electrons in its outer shell will form a bond with other “non noble” elements.

The stated theory of noble gases does not hold good any more – at least not for the three heaviest noble gases: krypton, xenon and radon. Since 1962 scientists have succeeded in producing certain compounds involving Kr, Xe and Rn. But with the aid of this theory the phenomenon of the chemical bond can be explained.

The number of bonds that an atom can form is called its valence. Oxygen has a valence of two as it has 6 electrons in its outer shell and needs another 2 electrons in order to reach the magic number of 8. Hydrogen has only 1 electron in its single shell, the outer shell, and has therefore a valence of one; it requires another electron to fill its shell or it can give an electron to an atom which is short of 1. As oxygen requires 2 electrons, two hydrogen atom fulfil its needs and together they form a molecule of water.

Electron Configuration of Noble Gases

Helium

K	L	M	N	O	P	Q
2						

Neon

K	L	M	N	O	P	Q
2	8					

Argon

K	L	M	N	O	P	Q
2	8	8				

Krypton

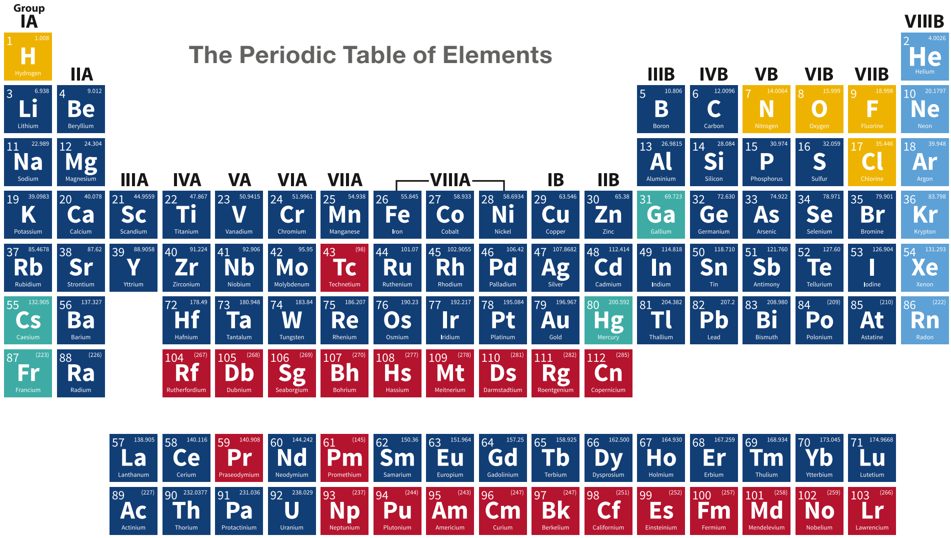
K	L	M	N	O	P	Q
2	8	18	8			

Xenon

K	L	M	N	O	P	Q
2	8	18	18	8		

Radon

K	L	M	N	O	P	Q
2	8	18	32	18	8	



The Periodic Table of Elements

Group IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
1 1.008 H Hydrogen																	2 4.0026 He Helium
3 6.938 Li Lithium	4 9.012 Be Beryllium											5 10.806 B Boron	6 12.0096 C Carbon	7 14.0064 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Fluorine	10 20.1797 Ne Neon
11 22.989 Na Sodium	12 24.304 Mg Magnesium											13 26.9815 Al Aluminium	14 28.084 Si Silicon	15 30.974 P Phosphorus	16 32.059 S Sulfur	17 35.446 Cl Chlorine	18 39.948 Ar Argon
19 39.0983 K Potassium	20 40.078 Ca Calcium	21 44.9559 Sc Scandium	22 47.867 Ti Titanium	23 50.9415 V Vanadium	24 51.9961 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.6934 Ni Nickel	29 63.546 Cu Copper	30 65.38 Zn Zinc	31 69.723 Ga Gallium	32 72.630 Ge Germanium	33 74.922 As Arsenic	34 78.971 Se Selenium	35 79.901 Br Bromine	36 83.798 Kr Krypton
37 85.4678 Rb Rubidium	38 87.62 Sr Strontium	39 88.9058 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.95 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.9055 Rh Rhodium	46 106.42 Pd Palladium	47 107.8682 Ag Silver	48 112.414 Cd Cadmium	49 114.818 In Indium	50 118.710 Sn Tin	51 121.760 Sb Antimony	52 127.60 Te Tellurium	53 126.904 I Iodine	54 131.293 Xe Xenon
55 132.905 Cs Caesium	56 137.327 Ba Barium		72 178.49 Hf Hafnium	73 180.948 Ta Tantalum	74 183.84 W Tungsten	75 186.207 Re Rhenium	76 190.23 Os Osmium	77 192.217 Ir Iridium	78 195.084 Pt Platinum	79 196.967 Au Gold	80 200.592 Hg Mercury	81 204.382 Tl Thallium	82 207.2 Pb Lead	83 208.980 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon
87 (223) Fr Francium	88 (226) Ra Radium		104 (267) Rf Rutherfordium	105 (268) Db Dubnium	106 (269) Sg Seaborgium	107 (270) Bh Bohrium	108 (277) Hs Hassium	109 (278) Mt Meitnerium	110 (281) Ds Darmstadtium	111 (282) Rg Roentgenium	112 (285) Cn Copernicium						

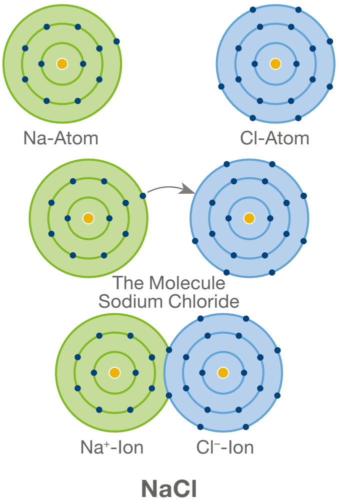
57 138.905 La Lanthanum	58 140.116 Ce Cerium	59 140.908 Pr Praseodymium	60 144.242 Nd Neodymium	61 (145) Pm Promethium	62 150.36 Sm Samarium	63 151.964 Eu Europium	64 157.25 Gd Gadolinium	65 158.925 Tb Terbium	66 162.500 Dy Dysprosium	67 164.930 Ho Holmium	68 167.259 Er Erbium	69 168.934 Tm Thulium	70 173.045 Yb Ytterbium	71 174.9668 Lu Lutetium
89 (227) Ac Actinium	90 232.0377 Th Thorium	91 231.036 Pa Protactinium	92 238.029 U Uranium	93 (237) Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (258) Md Mendelevium	102 (259) No Nobelium	103 (266) Lr Lawrencium

Gas **Noble Gases** **Liquid** **Solid** **Synthetically Prepared**

When the elements sodium (Na) and chlorine (Cl) combine to form the molecule sodium chloride (NaCl) which we know as table salt, they form an ionic bond. The neutral sodium atom, having a single electron in its outer shell, will share this electron with the chlorine atom which has 7 electrons in its outer shell. Again the outer shell is, by this bonding, filled with 8 electrons.

This changing of an electron will throw both atoms out of their electrical equilibrium. The sodium atom will become a positively charged (loss of one electron) sodium ion (Na$^+$) and the chlorine atom will become a negatively charged (gain of one electron) chlorine ion (Cl$^-$). The new shell structure of the sodium ion resembles that of a neon atom and the new shell structure of the chlorine ion is similar to an argon atom. Both ions are held together by their electrostatic attraction.

The Ionic Bond of Sodium and Chlorine



6.5 The Ion

An ion is a particle formed when a neutral atom gains or loses one or more electrons. An atom that loses an electron forms a positively charged ion called a cation; an atom that gains an electron forms a negatively charged ion, called an anion. The word “ion” derives from the Greek language and means “the traveller.” Under the influence of an electric field ions will migrate (travel) to their opposite pole, and thereby they create conductivity in gases and liquids.

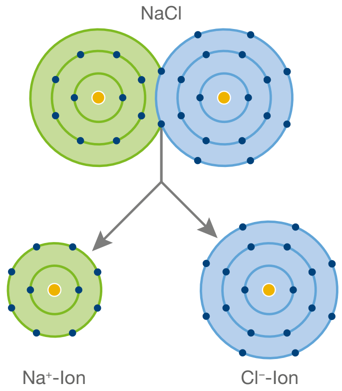
If the ionic bond of a NaCl molecule is broken either through high temperature or through solution in water, the chlorine atom will keep its gained electron, and stays a negatively charged ion. The sodium atom will stay a positively charged ion.

6.6 Dissociation

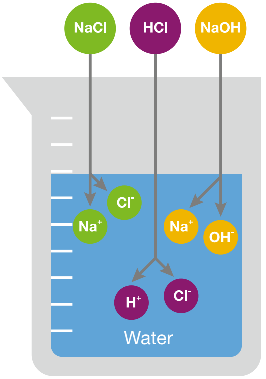
Water is an excellent solvent for three groups of chemical compounds: salts, acids and bases. When introduced to water, these chemical compounds separate into their ions – they dissociate. When sodium chloride is placed into water, the polar forces of the water molecules will reduce the electrostatic attraction between the negatively and positively charged ions and pull the ions apart. The ions are then surrounded by water molecules (they become hydrated) which prevents the recombining of the ions. Hydrochloric acid will dissociate in the same way into H$^+$ and Cl$^-$ ions and sodium hydroxide (caustic soda) will dissociate into Na$^+$ and OH$^-$ ions.

The dissociation of salts, acids and bases in water causes the water to become an excellent conductor. The resulting solutions are therefore called electrolytes.

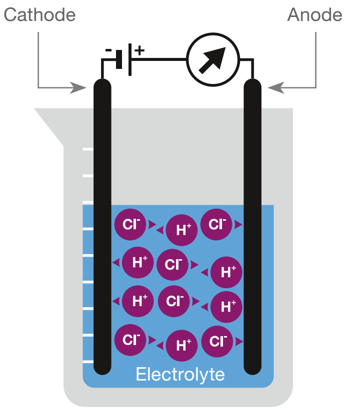
The Dissociation of Sodium Chloride



Electrolytes



If two electrodes are immersed into an electrolyte and a potential difference is applied to these electrodes, the negatively charged ions will be attracted by the positively charged electrode (anode) and by reaching the anode will lose their charge (lose electrons). Hence the name anion. Similarly the positively charged ions will move towards the negatively charged electrode (cathode) and lose their charge by gaining electrons (cation).



6.7 Acids – Bases – Salts

In chemistry we differentiate between three electrolytes: acids, bases and salts.

Acids are chemical compounds which, when dissolved in water, produce a concentration of hydrogen ions, H^+ (protons), greater than that of pure water. An acid is therefore a proton donor (proton = positively charged hydrogen ion H^+).

Acids taste sour and turn litmus red. Litmus is the oldest and most often used indicator of whether a solution is an acid or a base. It is a pink dye derived from licheus, a plant organism composed of a fungus and an alga in symbiotic association.

The most common acids are:

Hydrochloric Acid	HCl	Component of Gastric Juices
Nitric Acid	HNO_3	Used to Manufacture Dyes and Explosives
Acetic Acid	CH_3COOH	Vinegar
Formic Acid	$HCOOH$	Used for Dyeing and Tanning
Sulfuric Acid	H_2SO_4	Batteries
Phosphoric Acid	H_3PO_4	Dental Cement, Fertilizer

Bases are chemical compounds which, when dissolved in water, produce an excess of hydroxyl ions, OH^- or accept protons – a base is a proton acceptor. Bases taste bitter and turn litmus blue. A base feels slimy. The most common bases are:

Sodium Hydroxide (Caustic Soda)	$NaOH$	Drain and Oven Cleaner
Calcium Hydroxide	$Ca(OH)_2$	Slated Lime (used in mortar for construction)
Aluminium Hydroxide	$Al(OH)_3$	Raw material for Aluminium Compounds
Potassium Hydroxide (potash lye)	KOH	Soft Soap
Magnesium Hydroxide	$Mg(OH)_2$	Milk of Magnesia
Ammonia	NH_3	Household Cleaners

Salts: When aqueous solutions of an acid and a base are combined, a neutralization reaction occurs. This reaction takes place very rapidly and generally produces water and a salt. For example, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), yield water and sodium sulfate (Na_2SO_4).

$$H_2SO_4 + 2NaOH = 2H_2O + Na_2SO_4$$

Salts are produced by substituting the H^+ ion with a base part or by substituting the OH^- ion with an acid part. Cations and anions combine to form an electrically neutral compound.

Examples:

Sodium nitrate	$NaNO_3 = Na^+ + NO_3^-$
Aluminium sulfate	$Al_2(SO_4)_3 = 2Al^{3+} + 3SO_4^{2-}$
Calcium phosphate	$Ca_3(PO_4)_2 = 3Ca^{2+} + 2PO_4^{3-}$

6.8 The Mole

"The mole is the SI unit of an amount of substance equal to the quantity containing as many elementary units as there are atoms in 0.012 kg (12g) of carbon-12. The elementary entities must be specified and may be atoms, molecules, ions, electrons or other particles. The unit was established in 1971 for international use."

(The Oxford Dictionary)

The number of elementary particles contained in 12 g of carbon-12 (the atom against which other substances are measured) is 6.0221367×10^{23}. This number is known as the Avogadro's number in honor of the Italian physicist Amedeo Avogadro (1776 – 1856). Avogadro postulated in 1811 that equal volumes of gases, at equivalent temperatures and pressures, contain the same number of molecules.

A mole, then, is an amount of any substance that weighs, in grams, as much as the numerically equivalent atomic weight of that substance.

1 mole	H_2	=	2 g
1 mole	H_2O	=	18 g
1 mole	Cl_2	=	71 g
1 mole	Rn	=	222 g
1 mole	HCl	=	36.5 g
1 mole	NaOH	=	40 g

6.9 The Hydrogen Ion Concentration in Aqueous Solutions

Not only does water dissolve electrolytes and further their dissociation, but a small amount of water molecules dissociate as well into positively charged hydrogen ions (H^+) and negatively charged hydroxyl ions (OH^-).

$$H_2O = H^+ + OH^-$$

H^+ = Positive electrically charged hydrogen ion with acidity action

OH^- = Negative electrically charged hydroxyl ion with alkalinity action

If the amount of hydrogen ions equals the amount of hydroxyl ions, the water is called neutral. In clean, neutral water only one out of 10,000,000 (10^7) water molecules will dissociate.

The hydrogen ion is in reality a proton and the union of a hydrogen ion with an electron to form hydrogen may, in the generalized theory of acids and bases, be viewed as the simplest acid base neutralization:

$$2H^+ + 2e^- = H_2$$

Hydrogen ions, or protons, do not exist freely in solution but are associated with water molecules. The ionization of water should thus be written more correctly as:

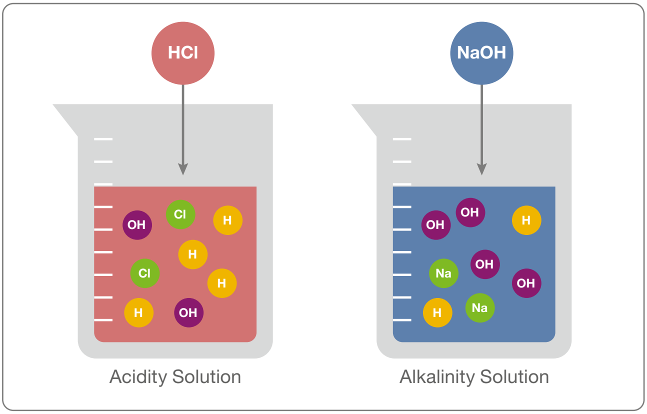
$$2HOH = H_3O^+ + OH^-$$

H_3O^+ is called the hydronium ion and is, in aqueous solutions, the ion responsible for acidic properties. For simplicity, equations are normally written using H^+.

By dissolving an acid in neutral water the H^+ ion concentration is increased by the H^+ ions which are produced by dissociation of that acid. The water changes its characteristic, i.e. it tastes sour like vinegar or lemon juice, it becomes corrosive and dissolves metals.

By dissolving a base in neutral water the OH^- ion concentration is increased by the OH^- ions which are produced by the dissociation of that base. There, the relative amount of the H^+ ions will be reduced. The water changes its characteristic, i.e. it tastes bitter and feels slimy like wet soap.

In both cases we cannot call the solution water any more, we have to speak of an aqueous solution.



All aqueous solutions of acid and bases owe their chemical activity to their relative hydrogen ion (H+) and hydroxyl ion (OH^-) concentration.

The hydrogen ion concentration in an aqueous solution is expressed by the amount of non dissociated water molecules in relation to one hydrogen ion, i.e.

- If one H^+ ion is found in 100 water molecules we write 1:100 or $1/10^2$ or 10^{-2}.
- If one H^+ ion is found in 10,000,000 water molecules we write 1: 10,000,000 or $1/10^7$ or 10^{-7}.
- And if one H^+ ion is found in 1,000,000,000 water molecules we write 1:1,000,000,000 or $1/10^9$ or 10^{-9}.

The ion product of dissociated H+ ions and dissociated OH^- ions in water has been found to be a constant of 10^{-14} (mole/liter) at 22°C. Thus, when the concentration of H^+ ions and OH^- ions in pure water are equal, the H^+ ion concentration must be 10^{-7} and, of course, the OH^- ion concentration must be 10^{-7} as well.

This automatically leads to the pH definition which is expressed as

the negative common logarithm of the active hydrogen ion concentration in an aqueous solution

or in mathematical terms:

$$\text{pH} = \log \frac{1}{\text{hydrogen ion concentration (mole/litre)}}$$

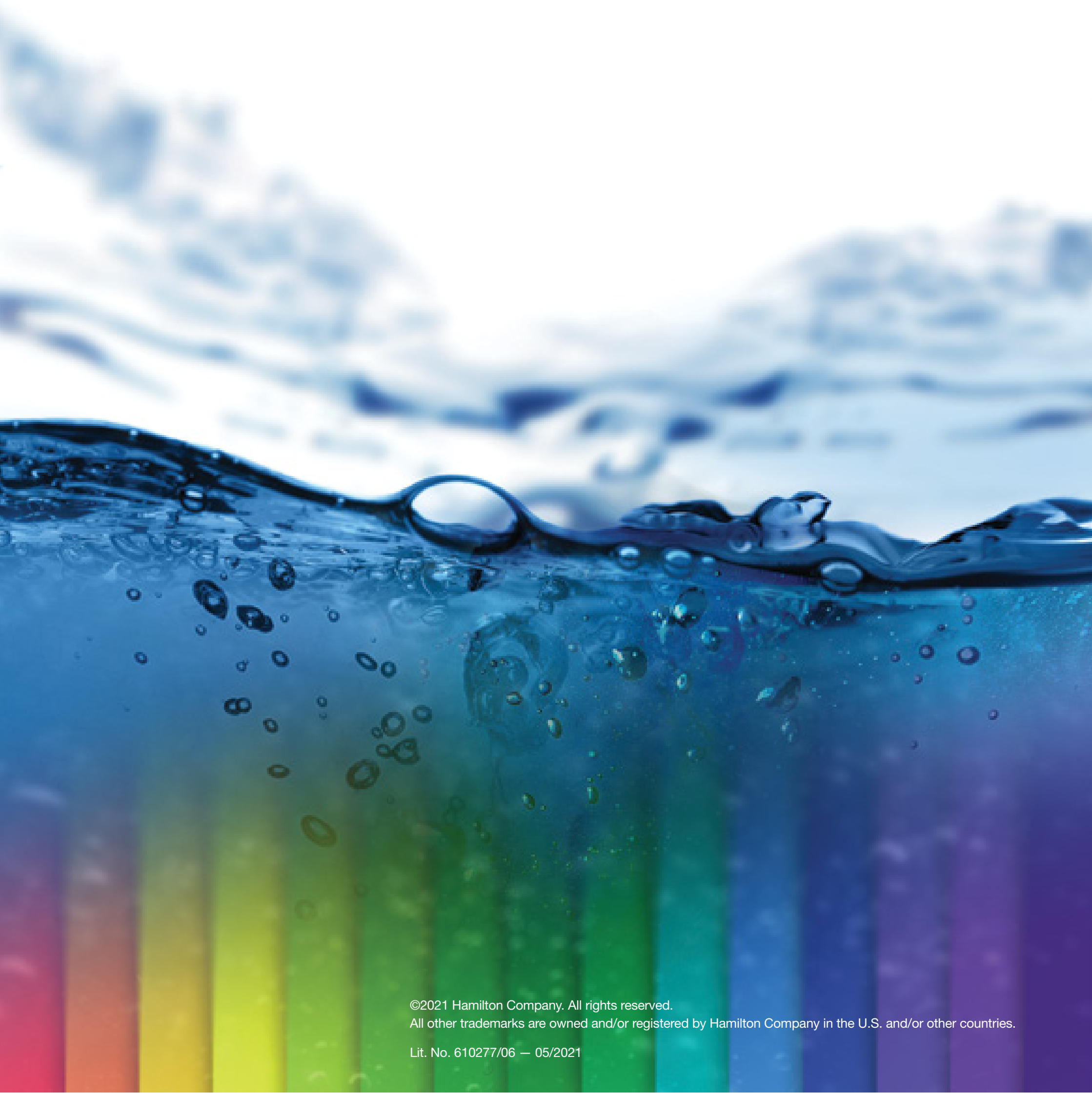
(please refer to page 6 of this publication).

For detailed technical specifications and application notes on Hamilton’s pH electrodes please visit Hamilton’s website at www.hamiltoncompany.com or contact your local dealer.

Theory is necessary –
Experience is essential

Good luck with your
pH measurement!

NOTES



Lit. No. 610277/06 — 05/2021

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