pH MEASUREMENT GUIDE

By Erich K. Springer

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pH Measurement
utilising
Glass Electrodes
Theory and Practice
by Erich K. Springer

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 coloured and flavoured water, and this water can be either sour or bitter; or in other words, it will have a certain pH value.
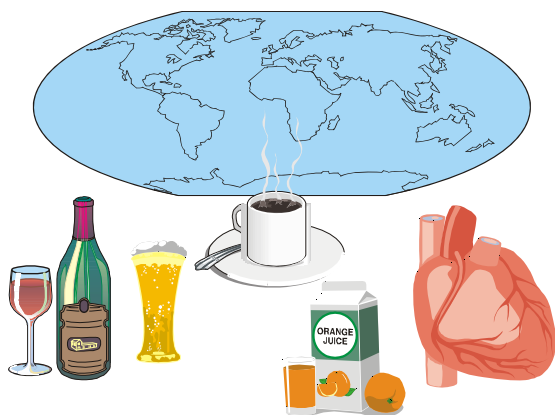
In general we can say that water is the most important substance on earth. Without water there will be no life on our planet. People living in areas of severe drought have experienced the importance of water for their existence. Continuous droughts do not only affect the farmers, they are a disaster 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.
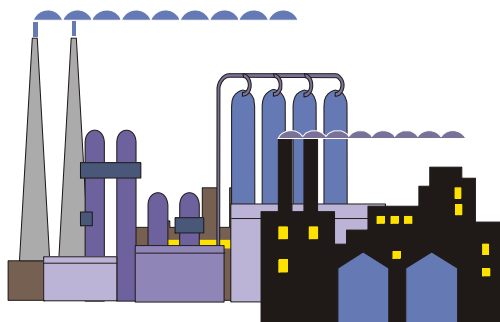
Water is used in industry as cooling water, wash water, boiler water, steam, condensate and solvent. Dirty water is usually disposed of as effluent. Notably the chemical industry especially makes use of this **universal solvent**, because most substances are somewhat soluble in water.

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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 measuring 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 measuring accuracy than the accuracy of the buffer solution one uses for calibration. HAMILTONS buffer solutions are described, after which the calibration of the pH measuring system is explained.

Connecting the pH electrode to the measuring instrument and the "do's and don'ts" of electrode handling will conclude the subject of pH measurement.

Acknowledgements

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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/litre.

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/litre)	OH- concentration (mole/litre)	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.***

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

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

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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.

<div style="border:1px solid black; padding:8px; text-align:center;">

1 mole HCl: concentration > activity

</div>

It is important to recognise 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 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 neutralisation reaction occurs as may be seen by the following equation:

$$HCl \ + \ NaOH \ \rightarrow \ \ HOH + NaCl$$
$$\rightarrow \ \ H_2O \ + \ NaCl$$

$$pH \ 0 + \ pH \ 14 \ \rightarrow \ \ pH \ 7$$
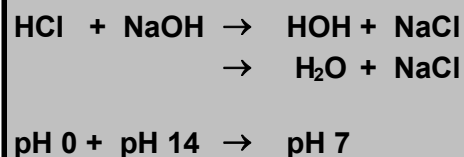
The acidic and alkaline properties of the solutions are lost because of the union of the hydrogen and hydroxyl ions which form water. The newly formed sodium chloride (table salt) does not influence the pH value.

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)

The pH Scale

increasing acidity ← neutral → increasing alkalinity

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 colour comparison with pH sensitive indicator paper
   (litmus) to a standard colour scale.

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2) **The photometric method**, using a spectrophotometer to measure the wave-length of the pH sensitive coloured 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 **measuring 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.
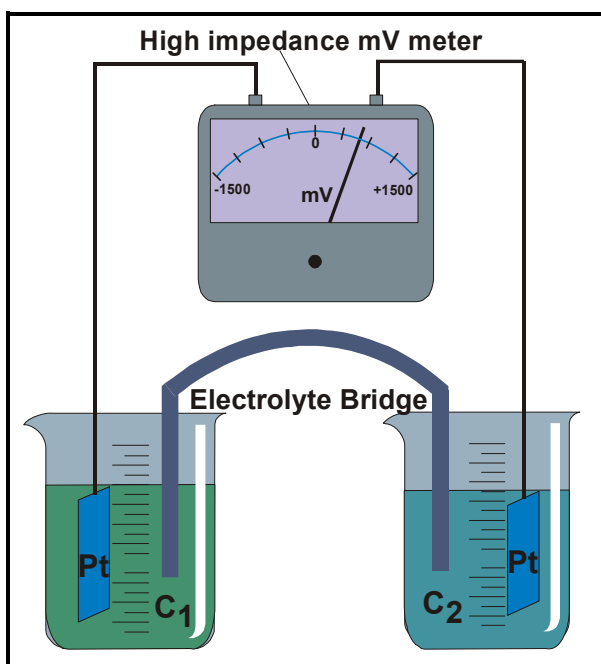
Since the current passing during such a measurement is negligible, the chemical composition of the sample solution is not altered. The bridge acts as a phase boundary between solution C_1 and solution C_2 and closes the electric circuit.

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 x mol^{-1} x K^{-1})

F = Faraday constant (96495,7 C x mol^{-1})

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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:

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

$$E = \frac{R \times T}{n \times F} \times \log \frac{10}{1}$$

$$E = \frac{R \times T}{n \times F} \times 2{,}303585$$

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.

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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 20 °C, then:

$$T = 273,15 + 20 = 293,15 \text{ Kelvin}$$

This will give us a **NERNST potential of**

$$U_N = 58,16 \text{ mV}$$

The pH Scale and the Related NERNST Potential
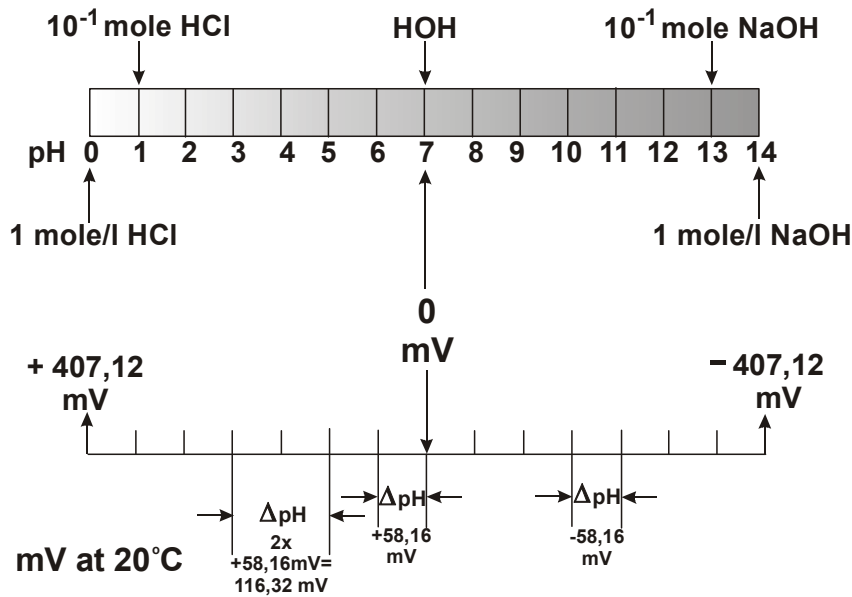
As the ion activity is temperature dependent, so is the NERNST potential* (refer to the NERNST equation). The following table illustrates the temperature dependency:

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

Temperature Dependency of the NERNST Potential

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3.2 The pH Measuring System
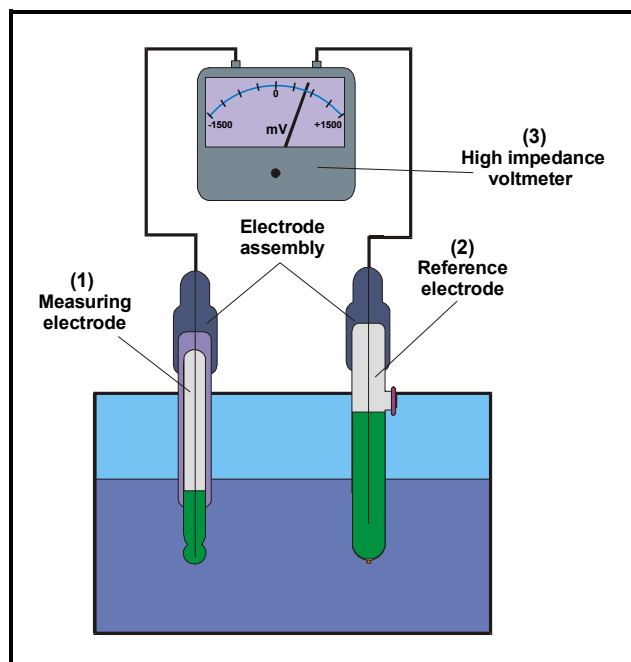
A basic pH measuring system consists of

(1) the measuring electrode,
a pH sensitive electrode,

(2) the reference electrode

and **(3)** a high impedance voltmeter.

3.2.1 The Measuring Electrode

The purpose of the measuring 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 platinised 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 ionise. 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 chemically resistant to hydrofluoric acid and can therefore be used for the pH measurement in solutions containing hydrofluoric acid. However, the accuracy and reproducibility of the measuring result incorporates large tolerances.

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3.2.1.1 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.

The Construction of a Glass Electrode

- pH cable
- Electrode head
- Electrode glass shaft
- Screen
- Internal conductor electrode (Ag/AgCl)
- Inner buffer + KCl (pH 7)
- pH sensitive glass membrane
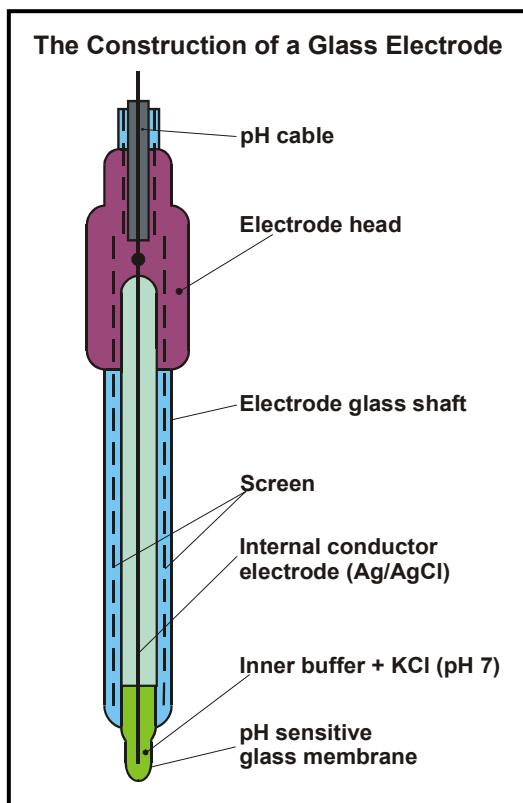
A glass electrode consists of a shaft made from glass which should be highly resistant to hot alkaline solutions and its electrical resistance must be several times greater than that of the membrane glass. The pH sensitive part of the glass electrode is the normally cylindrically shaped electrode tip, 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.

3.2.1.2 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 measuring 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.

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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.

The Glass Membrane

Ag/AgCl electrode

Glass membrane appr. 0,5 to 1mm thick

Inner gel layer approx. 10^{-4} mm thick

pH 7
H^+ = const.
Li^+

H^+ < pH 7

H^+ > pH 7

Outer gel layer approx. 10^{-4} mm thick

Measured medium
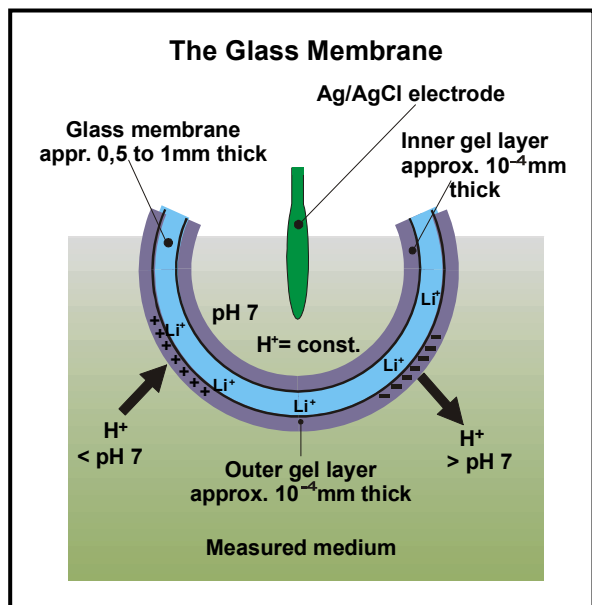
If a difference of a hydrogen ion con-centration exists between the inner buffer and the outer solution, a potential difference develops between the inner and outer sides of the membrane glass which is proportional to the difference in pH between the inner buffer and the outer solution. To be able to 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**.

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 measuring 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 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 measuring 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 page 25).

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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.

The Construction of a Reference Electrode

- pH cable
- Electrode head
- Electrode glass shaft
- Refill opening
- Internal reference system
- 3 mole KCl
- Diaphragm
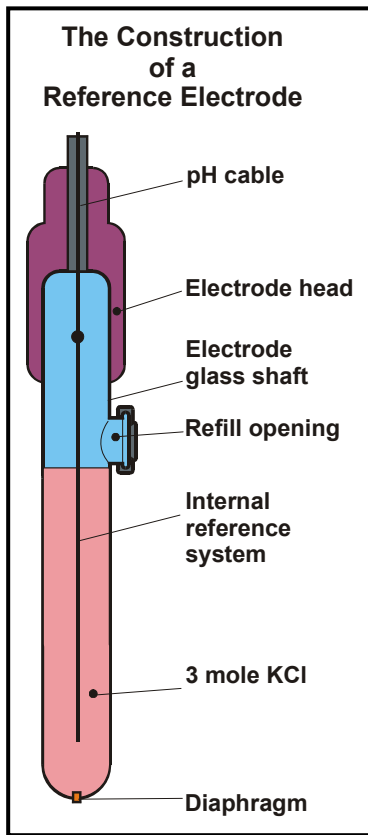
But today the silver/silver chloride electrode has gained practical acceptance and is by far the most frequently employed reference system. It is easy to manufacture, its potential rapidly attains equilibrium between –30 °C and 135 °C, and is very reproducible. The Ag-AgCl reference electrode remains 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 3 mole concentration situated in a large chamber formed by the glass body of the reference electrode.

A 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 Combination Electrode

- pH cable
- Electrode head
- Electrode glass shaft
- Refill opening
- 3 mole KCl
- Reference system
- Internal conductor electrode (Ag/AgCl)
- Inner Buffer + KCl (pH 7)
- pH sensitive glass membrane
- Diaphragm

3.2.3 The Combination (Single Rod) Electrode

Since 1947 electrode manufacturers have combined the measuring 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 measuring and the reference electrode, is the use of a pH measuring system consisting of two separate electrodes recommended.

In a combination electrode the concentric space surrounding the measuring 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 measuring electrode.
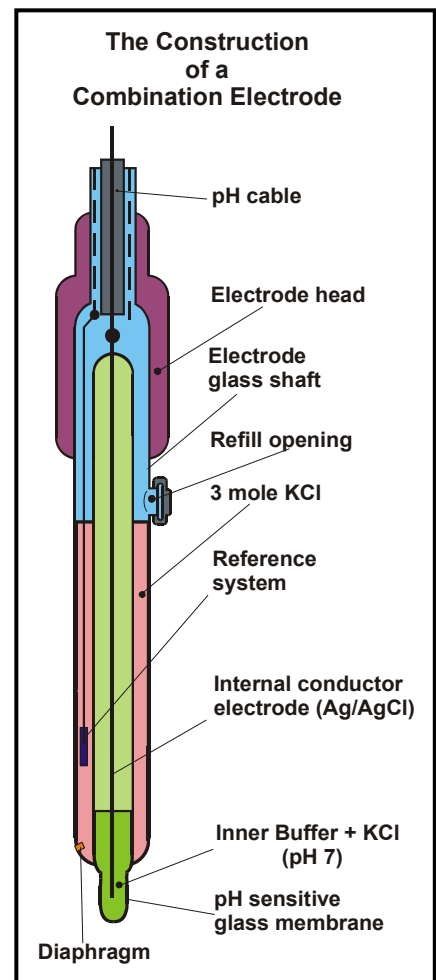
3.2.4   Combination Electrode filled with KCl-Gel as a Reference Electrolyte

pH cable

Electrode glass shaft reinforced with an outer plastic sleeve

3 mole KCl saturated electrolyte in gel form

Internal reference system

Internal conductor electrode (Ag/AgCl)

Inner buffer + KCl (pH 7)

Diaphragm

pH sensitive glass membrane
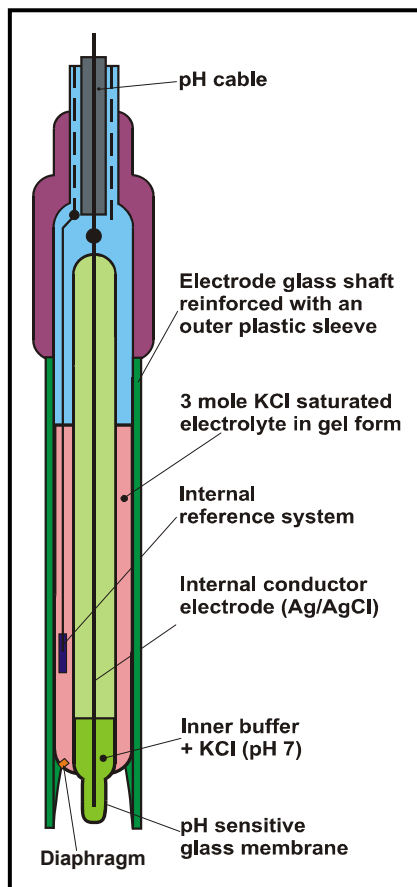
Reference electrodes incorporating a liquid reference electrolyte are maintenance intensive as their electrolyte level has to be controlled and regularly topped up. The search for a maintenance-free electrode assembly led to the development of the *gel reference electrode*.

The gel electrode is a low-maintenance electrode. *The reference electrolyte chamber is filled with 3 mol/l KCl electrolyte in 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 in combination with portable pH meters or laboratory pH meters for simple measuring applications, e.g. public swimming pools. 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 Electrolyte (Polymer)

In the early 1980s electrode manufacturers created the *polymer electrode*. The polymer electrode is either a standard combination glass electrode or a separate reference electrode. In both cases *the reference electrolyte chamber is completely filled with a semi-solid polymerised 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 an 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 measuring electrode.

- What does not exist can not clog up! –

Hole in electrolyte chamber

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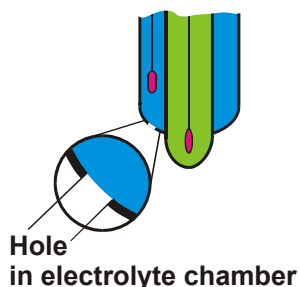
Since its inception polymer electrodes had a limited use. pH values below 2 pH could not be measured, the temperature limit was 90 °C, and measurements in media containing organic solvents were not possible.

With HAMILTON's new developed **POLISOLVE** polymer (protected by patent law) these limitations are a thing of the past. The **POLISOLVE** 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** reference system are reliable and accurate. The **POLISOLVE** polymer can be applied to almost every measuring problem, including very dirty, fatty, oily, ion weak or protein media. Suspended solids do not create diaphragm problems any more.

As the KCl saturated polymer is free of AgCl, there is no possibility of silver sulphide contamination when measuring the pH value of solutions containing sulphides.

The high pressure rating of 600 kPa, its extended temperature rating of up to 130°C and its main-tenance-free operation should make the **POLISOLVE** reference system always a first choice.

Electrodes, utilizing the **POLISOLVE** polymer electrolyte, are even suitable for steam sterilisation in biotechnology applications.

3.2.6 The Measurement of the Potential Difference

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

The difference in potential between the measuring electrode and the reference electrode is a function of the pH value of the measured medium. ***In theory the voltage changes by 58,16 mV per pH unit at 20 °C according to the NERNST equation***. The voltage produced by the pH measuring chain is large enough not to present any problem for a measurement. But the measuring 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 measuring 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 1 000 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 resistance increase 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.
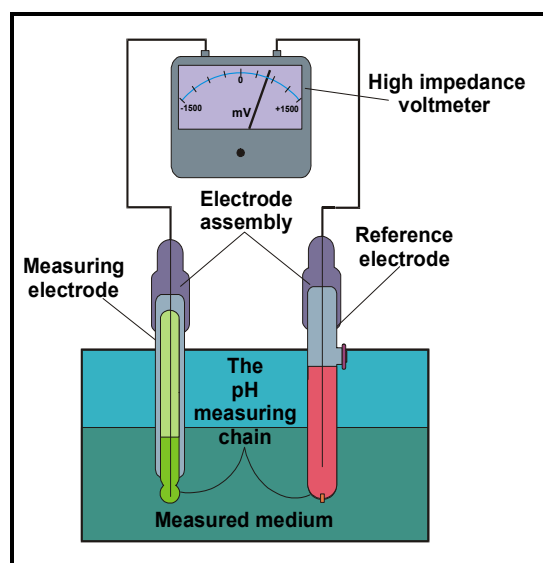
Special electrodes are manufactured for pH measurements at very low temperatures, having especially low resistance due to a particular glass composition and reduced membrane thickness. In order to still achieve an accuracy of +/- 0,1 pH the resistance of the measuring electrode should not be higher than a hundredth of the internal resistance of the measuring instrument. The upper limit of the membrane resistance lies at 5 000 MΩ (5×10^9). Membrane resistance that is too high causes faults and disturbances in the electronic measuring instrument.

The e.m.f. produced by the high resistance measuring 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 Measuring Chain

The characteristics of a pH measuring chain are the result of the individual properties of the measuring 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 measuring chain. However everything that is said about the properties of a combination electrode may be applied to the individual measuring and reference electrode as well.

3.3.1 The Different Potentials of a Combination Electrode

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.

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When a combination electrode is immersed into a solution to be measured, 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 measuring 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 of the pH determination.

As can be seen from the picture above there are six potentials which develop on a pH measuring chain, but only one potential – E_1 – is dependent on the pH value of the solution under test. 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 measuring and the reference electrode possess the same internal conducting system and if the measuring 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. As this buffer solution does not change in value, 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 (measuring 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 neutralise each other and do not contribute to the total potential measured by the pH measuring 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 electrode assembly potential E_{total} is equal to 0 mV. Theoretically the zero point of a pH measuring chain is determined by the internal buffer solution of the measuring 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 measuring chain should be 0 mV.

In practice however this is seldom the case, because E_{total} is the resultant of the chain potentials E_1 to E_6. Each potential reacts differently to temperature changes and to the composition of a

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measuring 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 ($\approx$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 the zero adjustment potentiometer 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 has to 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. This 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 internal buffer solution. Due to the exposure to high temperature the glass membrane of the measuring electrode releases alkali hydroxide into the inner buffer solution which gradually increases its pH value.

c) Increase in electrode plug and cable contact resistance due to corrosion of the contact metals.

3.3.3 The Asymmetry Potential

In theory the potential difference across the glass membrane of a measuring 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 alter thereafter. The outer gel layer is continuously attacked through chemical reaction with the measured solution and in certain cases even by abrasion.

The asymmetry potential can also be ascribed to small imperfections in the manufacture of the glass membrane. 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 ($\approx$+/- pH 0,8) at pH 7 and can be compensated for by the zero potentiometer of the pH meter/transmitter during the calibration process of the electrode assembly.

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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:

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

In theory a pH electrode assembly should develop a potential difference of +58,16 mV per pH unit between pH 7 and pH 0, and correspondingly –58,16 mV between pH 7 and pH 14.

In practise 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 potentiometer of the pH meter/transmitter. As with the zero point adjustment, the slope adjustment has to be performed at regular intervals.

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 below. In theory, all temperature dependent slope lines intersect the theoretical zero point (pH 7).

The Slope or Sensitivity of a pH Electrode Assembly

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

Theoretical Values

Slope at 0 °C = 54,20 mV

Slope at 20 °C = 58,16 mV

Slope at 50 °C = 64,12 mV
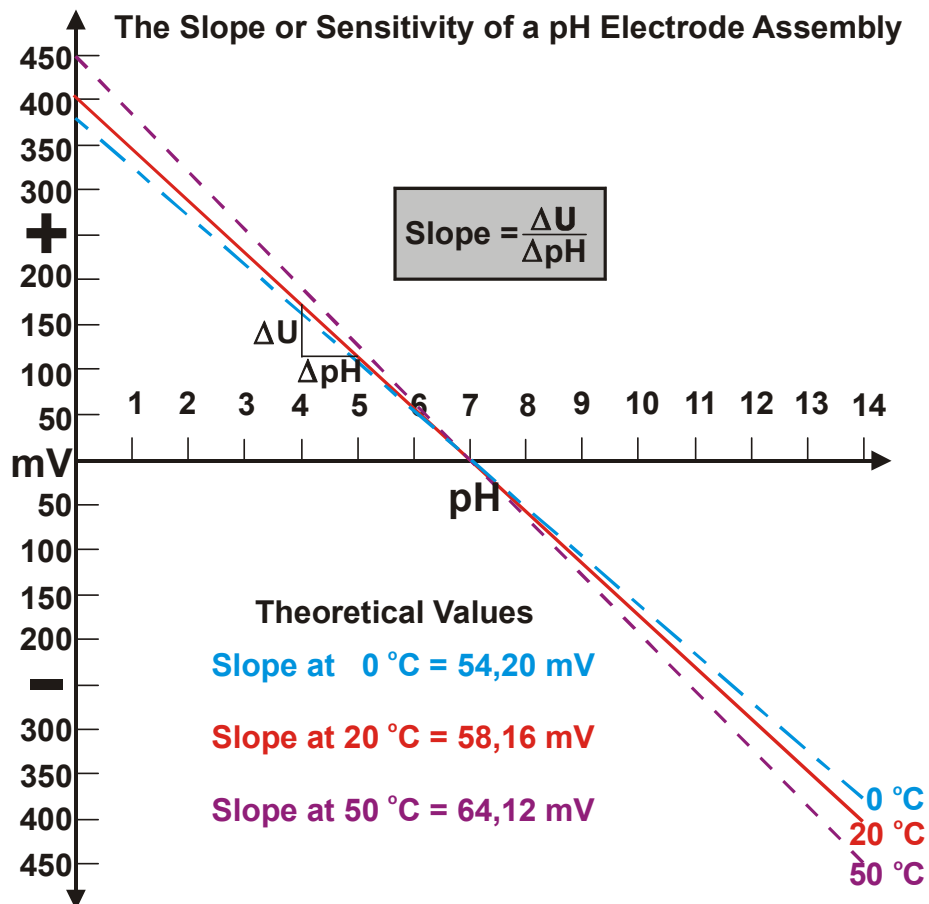
In order to produce a response as near as possible to the NERNST equation an electrode assembly must fulfil certain criteria:

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. measuring and reference electrode must have identical conducting systems in order to neutralise their galvanic potentials.

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

Slope and Asymmetry Potential of a pH Electrode Assembly

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

Asymmetry Potential

Theoretical Values

Slope at 0 °C = 54,20 mV

Slope at 20 °C = 58,16 mV

Slope at 50 °C = 64,12 mV
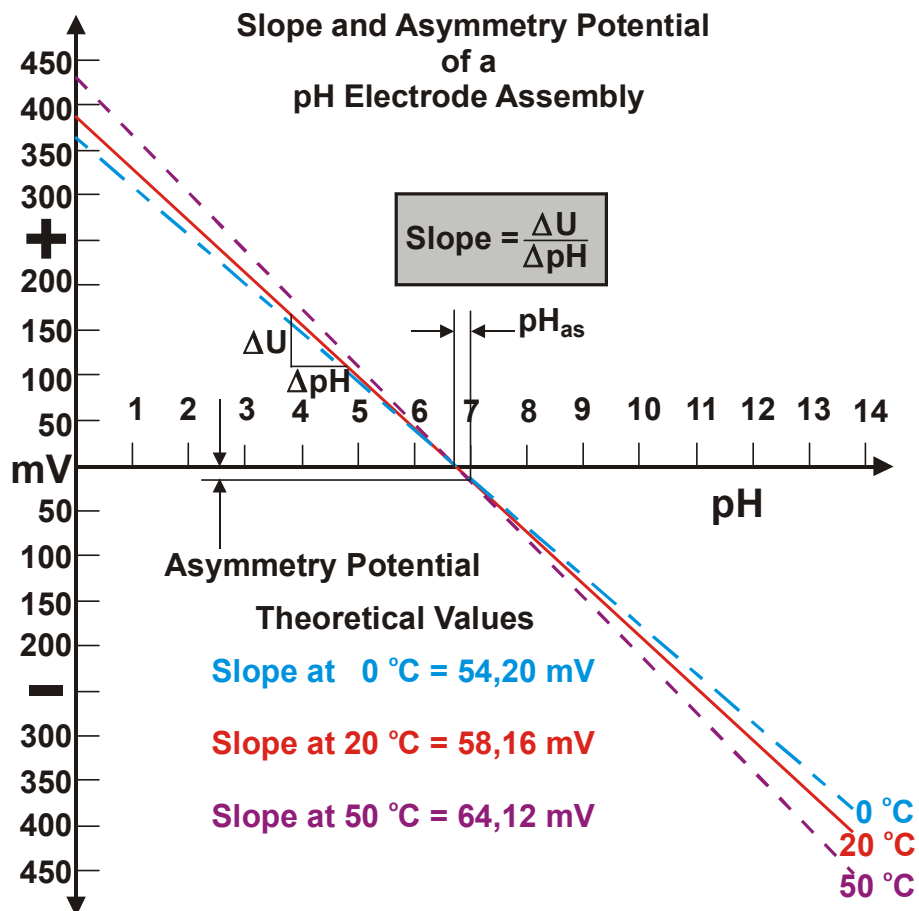
3.3.5 The Isotherm Intersection Point

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 diagram below.

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 *isotherm intersection point (U_{is} = isotherm potential)*.

In order to perform an accurate pH measurement, the position of the isotherm intersection point has to be established. Two buffer solutions are required. The position of the isotherm intersection point can then be determined by measuring the potential difference of the pH 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 isotherm intersection point is established. The voltage and polarity of the established isotherm potential U_{is} can only be compensated for if the pH meter/transmitter used is equipped with an U_{is} potentiometer. Nowadays, only the 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.

Slope and Isotherm Potential of a pH electrode Assembly

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

Theoretical Values

Slope at 0 °C = 54,20 mV

Slope at 20 °C = 58,16 mV

Slope at 50 °C = 64,12 mV

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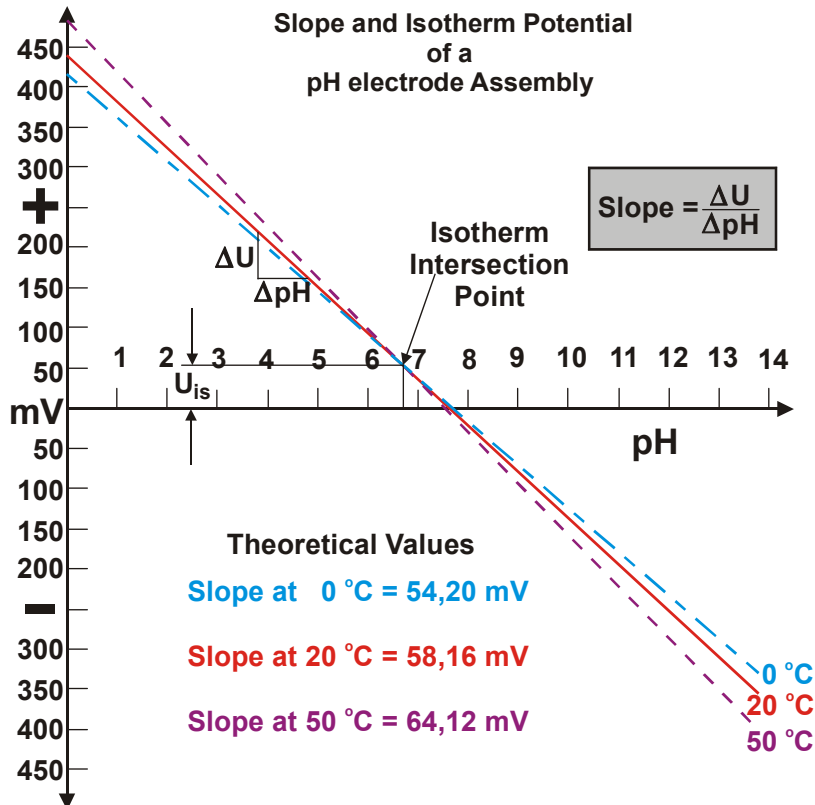
3.4 The Diaphragm

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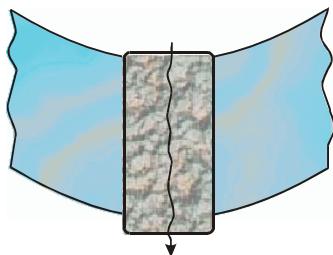
The **porous ceramic diaphragm** is probably the most frequently used today. It possess a high chemical resistance and it is easy to manufacture.

This junction provides a reproducible electrolyte flow but because of its large surface it is very vulnerable to contamination.

b) Platinum Fibre Diaphragm
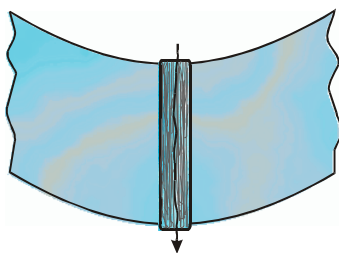
Platinum fibre diaphragms consist of very fine platinum wires which are spun loosely together and fused into the glass.

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

c) SINGLE PORE (Trademark of HAMILTON) Diaphragm
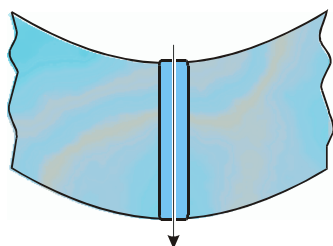
The **SINGLE PORE diaphragm** is strictly speaking not a diaphragm at all. It is a very small glass capillary which allows a larger leakage rate than a ceramic or platinum diaphragm. A constant and very reproducible electrolyte flow is assured. Clogging or contamination is barely possible. It gives the most accurate and repeatable results.

In combination with a polymeric electrolyte the **SINGLE PORE** principle is adapted 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)

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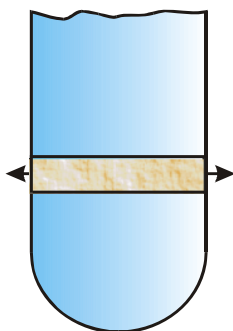
The **annular ceramic diaphragm** is formed by a porous ceramic layer between two glass tubes. The direction of the measured medium is not critical due to the annular shape of this junction. The electrolyte flow is not reproducible. Hence it is mainly applied in gel-type electrodes.

e) Ground Sleeve Diaphragm

Electrolyte
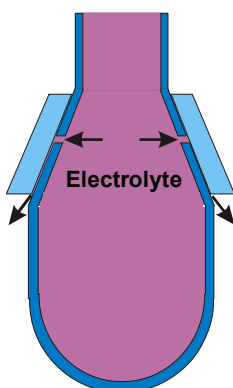
Ground sleeve diaphragms are ideally suited for applications in suspensions and emulsions, as these diaphragms can be cleaned easily by only pulling up the glass sleeve. Another successful application of this diaphragm is the pH measurement in low ionic solutions or in non-aqueous media. The electrolyte 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 measuring 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 pressurised.

There are pH electrodes on the market where the electrolyte storage vessel can be pressurised in order to counteract the penetration of the measured solution through the diaphragm. As a rule of thumb a pressure of 100 kPa 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 the stopper which closes the refill opening must be removed. Periodic inspection of the electrolyte level should be part of the electrode maintenance programme.

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 two electrolytes of different concentration or composition. The diffusion potential can be contributed to the different migration velocities of ions, which again depends on the polarity and size of the ion type.

The illustration below explains the diffusion potential between two HCl solutions of different concentration:
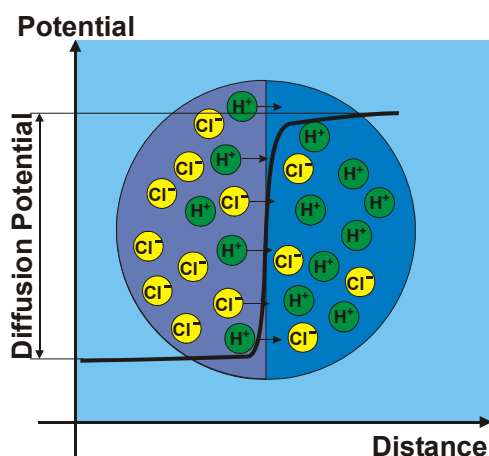
The H^+ ions diffuse nearly five times faster to the right than the Cl^- ions. This creates a potential across the boundary of the two solutions. In order to keep the diffusion potential at the diaphragm of a reference electrode as small as possible, the different ions in the reference electrolyte should have identical ionic mobility. With a 3 mole 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 KCl	=	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 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 falsified measuring results. The reference electrolyte contains silver chloride which is prone to chemical reactions, especially with sulphides. For this reason great care must be taken when measuring pH in solutions containing sulphides, as the diaphragm may be contaminated with silver sulphide deposits.

Silver sulphide 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 it may be impossible to calibrate such a contaminated electrode assembly***.

3.4.2.1 The EVEREF Reference System

Reference conductor Silver wire

Silver chloride reservoir

Diffusion pipe filled with cotton wool

Reference electrolyte with constant chloride concentration, but free of AgCl
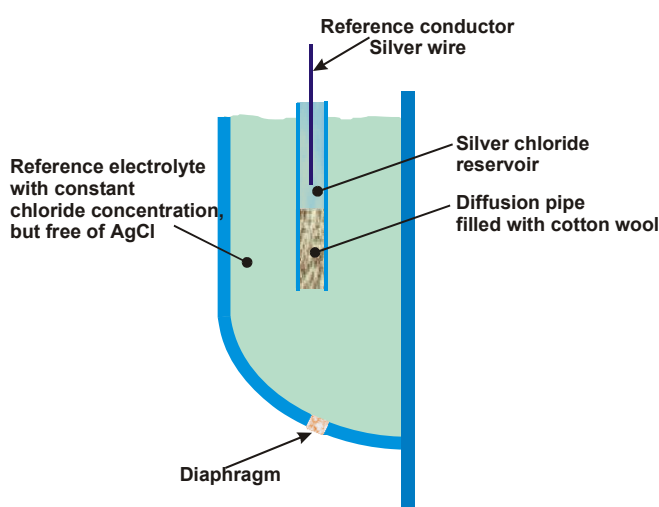
Diaphragm

In order to counteract silver sulphide contamination at the diaphragm HAMILTON have invented the EVEREF reference system. This system consists of a silver chloride reservoir from which the silver reference wire leads to the electrode plug. 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.

The EVEREF reference system enhances the stability of the reference potential and extends the life of the combination electrode considerably.

3.4.2.2 The EVEREF-B Double Liquid Junction

If a chemical reaction at the diaphragm is unavoidable, the application of a reference electrode having an ***inter-mediate electrolyte provides a solution***.

The ***EVEREF-B double liquid junction system from HAMILTON*** with its intermediate electrolyte reservoir provides such a solution. The reference electrolyte is completely separated from the EVEREF reference system by an internal diaphragm situated in a second reservoir filled with an intermediate electrolyte. The life of the pH electrode is greatly prolonged as the reference electrolyte is absolutely silver-free. The ***EVEREF-B*** system performs well in media containing sulphides and in media with low ion concentration or partly aqueous solutions. Owing to the maintenance-free ***EVEREF-B*** system only the main reference electrolyte needs to be refilled (see electrode drawing on next page).

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3.5 Alkaline and Acid Error

3.5.1 Alkaline Error

**pH Electrode
"Chemotrode Bridge"
with Intermediate Electrolyte**

- Electrode Head
  (Variopin or SMEK)
- Refill opening
- Intermediate electrolyte
- Reference system EVERREF-B
- Internal diaphragm
- 3 mole KCl
- Internal conductor electrode (Ag/AgCl)
- Internal buffer plus KCl
- External diaphragm
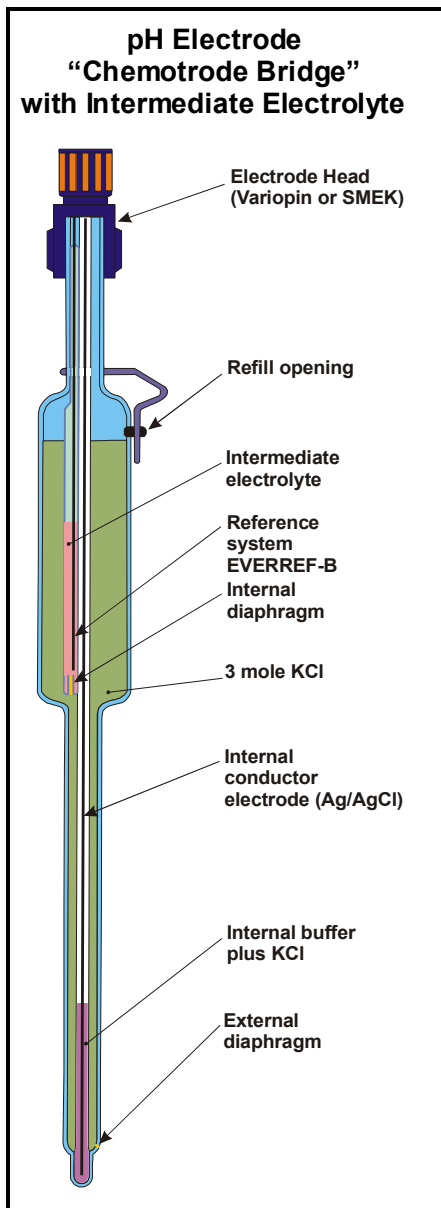
At a value above pH 10 the gel layer structure at the membrane of a measuring electrode is subject to certain changes which lead to a measuring inaccuracy, the *alkaline error*. This alkaline error is caused by the presence of a high concentration of alkaline ions, especially sodium ions (Na^+). These 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 already developed 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.
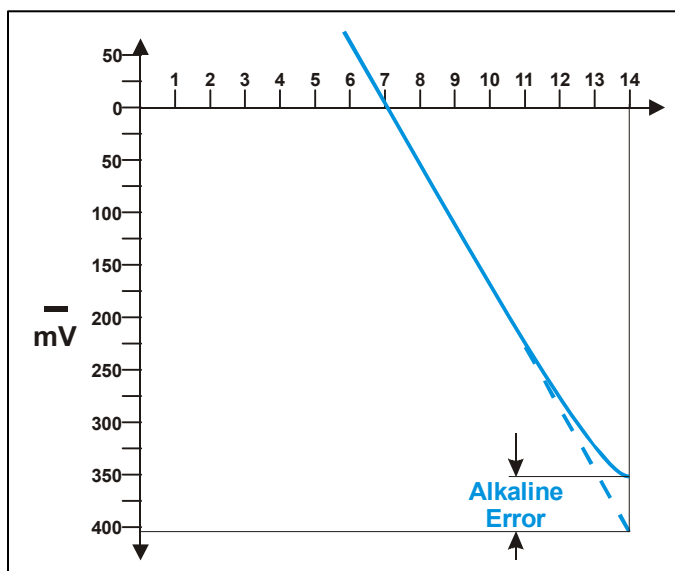
3.5.2 Acid Error
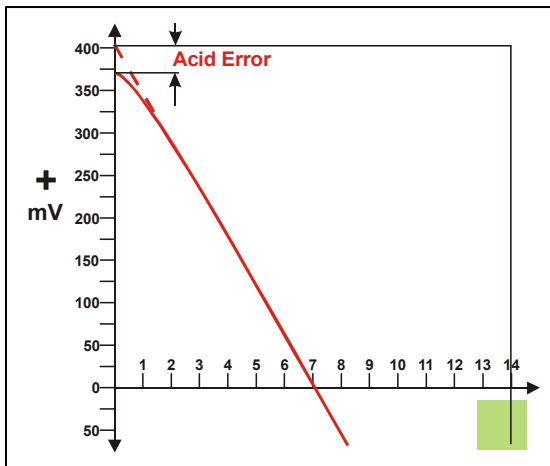
At low pH values (< pH 2) the potential difference between measuring and reference electrode will not conform exactly to the NERNST equation. Through experiments it has been proven that the gel layer of the membrane will absorb acid molecules at very low pH values.

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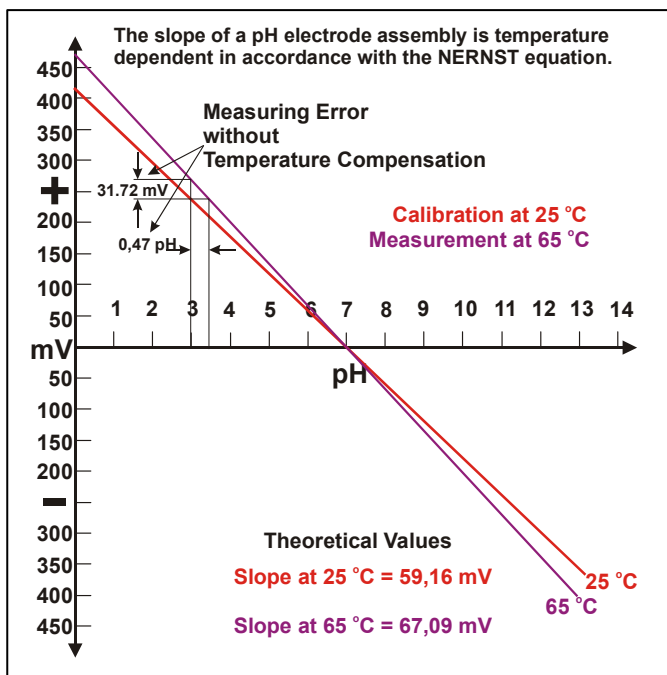
The temperature dependency of the Nernst equation and with it the temperature dependency of the theoretical slope of a pH electrode assembly has already been discussed in paragraph 3.1.

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 measuring products. The adjacent graph illustrates the theoretical error which is compensated for by conventional temperature compensation.

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

Measuring Error with Temperature Compensation

450
400
350
300

+

200
150
100
50

Calibration at 25 °C
Measurement at 65 °C

← Measuring Error after Temperature Compensation

Isotherm Intersection Point

1 2 3 4 5 6 7 8 9 10 11 12 13 14

mV

pH

50
100
150
200

–

300
350
400
450

Theoretical Values

Slope at 25 °C = 59,16 mV

25 °C
65 °C

Slope at 65 °C = 67,09 mV
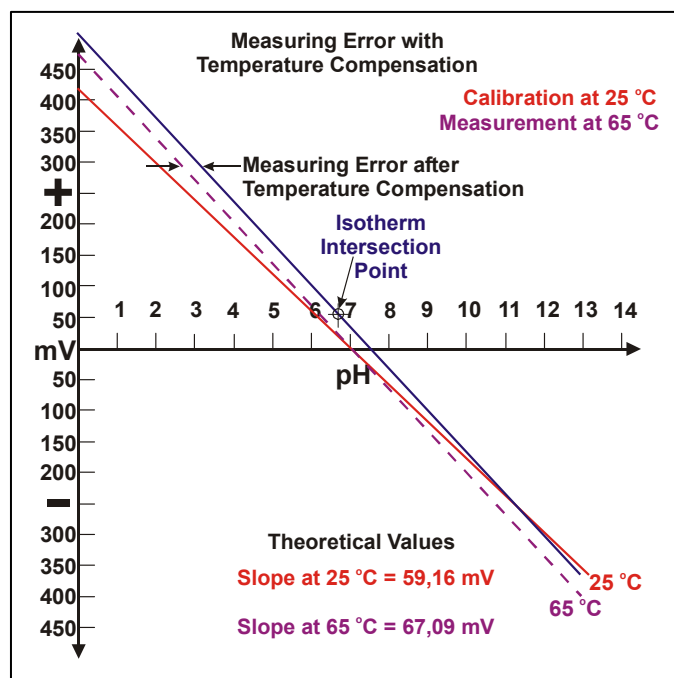
Today electrode manufacturers try to produce pH measuring electrodes which have the isotherm intersection point positioned as near as possible to the theoretical zero point (pH 7). This will reduce the residual error of conventional temperature compensation, as instrument manufacturers nowadays omit the U_{is} potentiometer, which could be found in earlier days on quality pH meters/transmitters. Nowadays only microprocessor based pH meters/transmitters have the capacity to correct the position of the isothermal intersection point (U_{is}).

The third factor is ***the pH/temperature dependency of the measured solution*** which is also called ***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 and cannot be described as a measuring error.

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***.

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3.7 Various Electrode Shapes

It is not possible to use one electrode shape for every application. More often in the laboratory 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. Measuring, reference and combination electrodes are manufactured using this construction.

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 construction example includes two electrode features: a ground sleeve diaphragm and a pipe connector. In order to minimise maintenance time and to pressurise 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 in power stations.

Form d)

This electrode construction 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 pressurised and also sterilised with hot steam. A special electrode holder is required for this electrode. No laboratory application.

Form e)

The above electrode construction is used in the laboratory where small samples have to be measured.

Form f)

The feature of this construction is the flat membrane which enables the operator to measure the pH of surfaces, e.g. 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 construction, pointed electrode, are normally applied in the food laboratory and in the dairy industry. They facilitate the pH measurement in meat and cheese.

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3.8 Ageing

3.8.1 The Ageing of a Measuring Electrode

Every glass measuring 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 measuring 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 measuring electrode, especially as a combination of the above given reasons for ageing may cause the deterioration of the electrode performance. An electrode, with a potential operating life of 18 months if used continuously in aqueous solution of pH 4 to pH 8 at ambient temperature and if handled correctly, could last only 2 months if operated above at 90 °C. Often an electrode already stops performing after 2 to 3 weeks if it is subjected to high alkalinity of higher than 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.

A deteriorating response time is a certain indication of ageing. 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.

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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.

The reference electrode always has to be topped-up with an identical electrolyte used originally by the manufacturer, otherwise the reference potential becomes unstable, the response time of the 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 measuring solution 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 they are to a certain degree pressure resistant (up to 200 kPa) diffusion over the diaphragm does take place in both direction and will gradually reach the 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 the above reasons 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 electrode with gel-electrolyte should never be used 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** 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 (conventional polymer electrolytes are limited to   90 °C only), 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** electrolyte may easily be used up to 12 month.

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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 measuring 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 characterised 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 measuring 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 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. Especially alkaline buffer solutions are affected by CO_2 contamination from the atmosphere.

Not so for the new ***DURACAL pH buffer solutions from HAMILTON***. 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 expiry date. The certification is traceable to primary standards from NIST and PTB.

pH Values of Standard Buffer Solutions according to NIST

NBS Code Temp. C	A Potassium tetra-oxalate	B Potassium hydrogen tartrate	H Potassium dihydrogen citrate	C Potassium hydrogen phthalate	D Phosphate	E Phosphate	F Borax	I Sodium carbonate/ sodium hydrogen carbonate	G Calcium hydro-xide
0	-	-	3,863	4,010	6,984	7,534	9,464	10,317	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	-	-

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Stability Comparison of HAMILTON Alkaline Buffer to Conventional Alkaline Buffer

Both buffer solutions have been exposed to blowing air
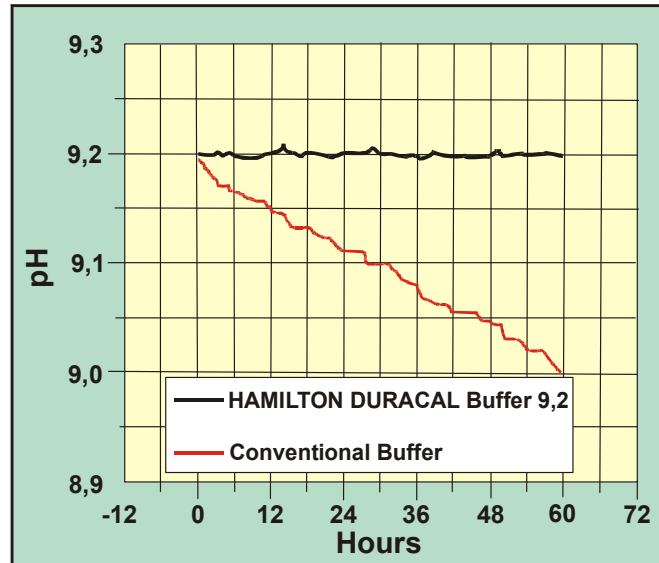
Used buffer solutions should always be discarded and never be returned to their original storage bottle. For this reason HAMILTON have developed a unique storage bottle which includes a calibration compartment with a non-return valve at the bottom, preventing the used buffer solution to be returned into the storage bottle. This **CALPACK** bottle is practical: no additional calibration container is required, and it is economical: only the required amount of buffer solution is used.

The Practicality of the HAMILTON CALPACK Calibration Bottle

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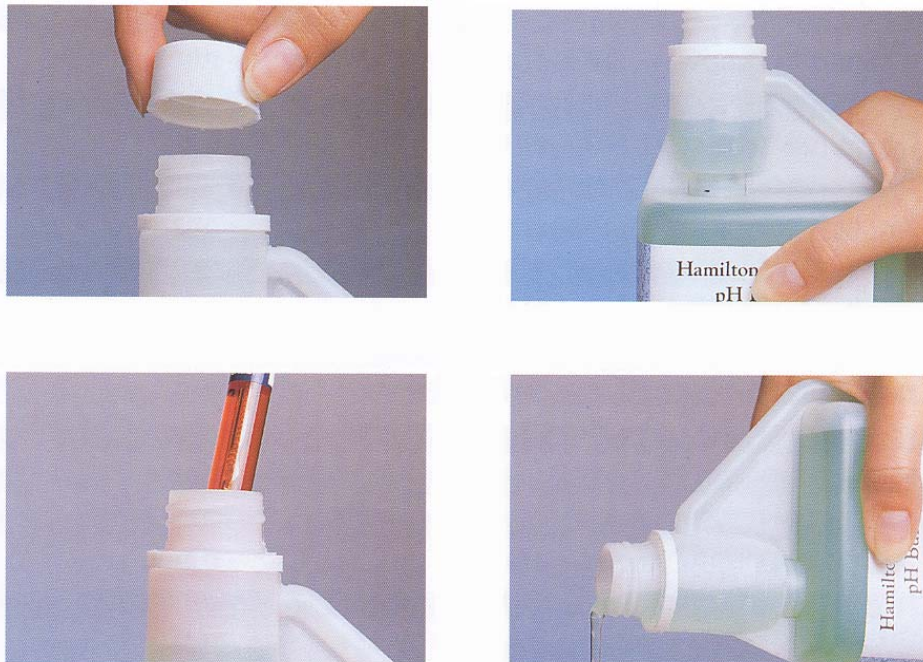
Values and Accuracies of HAMILTON Buffer Solutions

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 measuring 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 behaviour 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 measuring 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.

Please note: 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 utilised 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 measuring system (pH electrode assembly plus instrument) against buffer solutions having definite pH values.

There is a difference in the calibration procedure between analogue and microprocessor controlled pH meters. In principle the calibration procedure should be described in the operating instructions supplied with all pH meters/transmitters.

A brief description of the calibration procedure for analogue and microprocessor pH meters follows on the next page.

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3.9.2.1 Calibration of Analogue pH Meters

1) Two buffer solutions of different pH values have to be selected. The pH value of one buffer solution should be as close as possible to the zero point of the electrode assembly, which is, under normal circumstances, pH 7.

   The second buffer solution should have a pH value which lies as near as possible at the end of the anticipated measuring range and the value should differ as much as possible from the zero buffer solution, at least 2 pH units.

   If the measuring range covers the acidity and the alkalinity range then a third buffer solution is required. The pH value of the second buffer solution should lie in the acid region and the third buffer solution should lie in the alkaline region of the desired measuring range. Both values should differ as much as possible.

pH Scale

| 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |

measuring range I

measuring range II

Slope Calibration   Zero Calibration   Verifying

HAMILTON Buffer Solutions
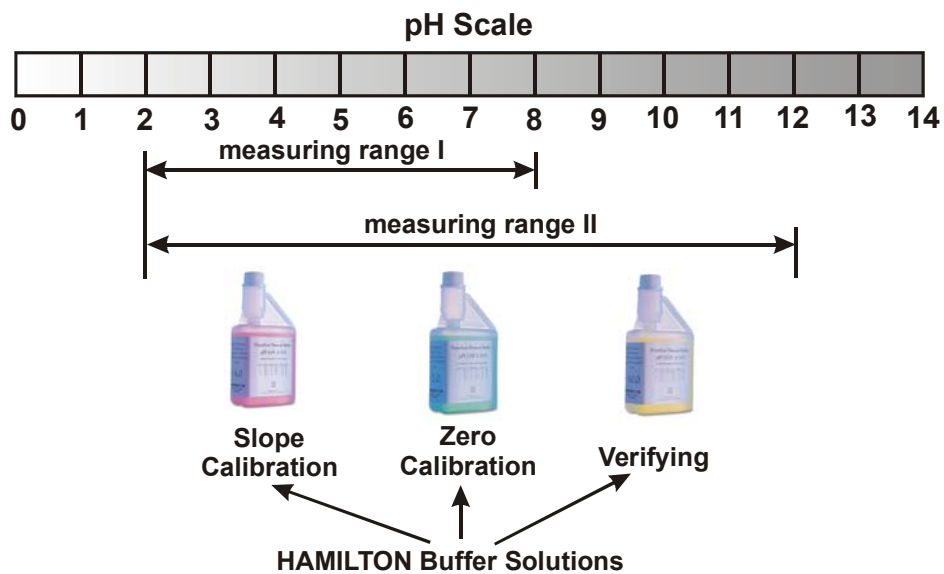
2) The pH value of any buffer solution is temperature dependent. Therefore the temperature of the applied buffer solution has to be measured in order to establish the correct pH value of the buffer solution.

   The temperature adjustment potentiometer (manual temperature compensation) must be set to the buffer temperature. With automatic temperature compensation the temperature sensor, connected to the pH measuring instrument, must be immersed into the buffer solution.

Manual Temperature Compensation

7,00 pH

U_is   zero   °C   slope

pH 7,00   pH 10,01   pH 4,01
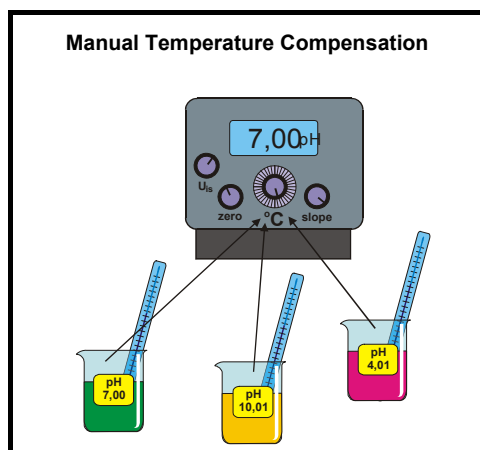
Temperature Dependency of Technical buffer Solutions

°C	HAMILTON Buffer Solutions		
5	4,01	7,09	10,19
10	4,00	7,06	10,15
15	4,00	7,04	10,11
18	4,00	7,03	10,08
20	4,00	7,02	10,06
22	4,00	7,01	10,04
25	4,01	7,00	10,01
30	4,01	6,99	9,97
35	4,02	6,98	9,92
40	4,03	6,97	9,86
45	4,04	6,97	9,83
50	4,05	6,97	9,79

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3) After rinsing the electrode assembly with de-ionised water, it is immersed into the first buffer solution for the zero point compensation (normally pH 7 = 0 mV). The electrode assembly has to stay in the buffer solution for a short time, at least for one minute, till the indication of the pH meter settles near the pH value of the buffer solution (pH 7) and becomes stable. Thereafter the indicated value has to be adjusted with the zero potentiometer to the exact value of the buffer solution. The zero potentiometer is sometimes marked **@pH** or **pH$_{as}$**.

For analogue pH meters it is important that the zero point calibration is always performed before the slope calibration.

4) After the zero point calibration, the electrode assembly has to be rinsed again with de-ionised water and dried with tissue paper. When drying the electrode, 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 might introduce static electricity into the glass shaft of the electrode and could make an accurate pH measurement impossible for hours.

No rubbing!
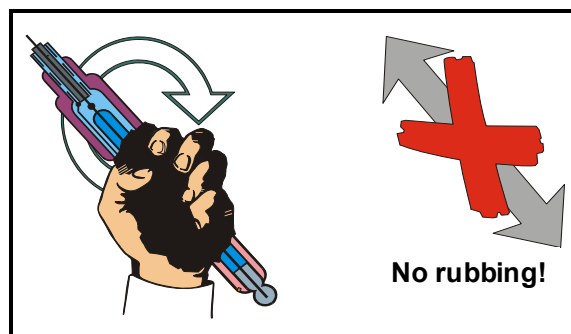
5) The electrode assembly is then immersed into the second buffer solution (acid or base – according to the measuring range). After the indication of the pH meter has stabilised, the indicated value has to be adjusted with the slope potentiometer to the exact pH value of the second buffer solution. The slope potentiometer is sometimes marked **ΔmV/ΔpH**.

It is advisable to re-check the zero point after the slope calibration has been performed.

It is of utmost importance that the above calibration sequence must be adhered to, otherwise no valid calibration will be obtained.

6) If the measuring range covers both the acidity and the alkalinity range the third buffer solution serves as a *verifying solution*. After the zero point (with the first buffer) and the slope calibration (with the second buffer) has been accomplished, the calibration over the entire measuring range has to be verified with the third buffer solution (be aware of acid and alkaline errors).

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

8) After the successful calibration the used buffer solution should be discarded. *Never re-use buffer solution and never return it to its original storage container*.

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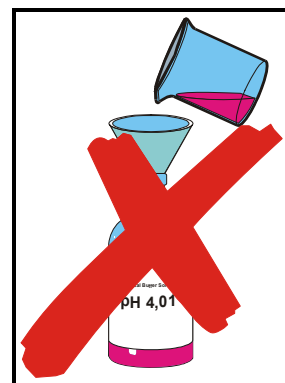
3.9.2.2 Calibration of Microprocessor-based pH Meters

Microprocessor-based pH meters are more and more employed in laboratories and as on-line instruments in industrial plants. Even portable pH meters are nowadays microprocessor controlled. Their handling is relatively simple. 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 differs slightly from the calibration procedure with conventional analogue pH meters. Although two buffer solutions still have to be used, it is not necessary anymore to calibrate the zero point with buffer 7. The two buffer solutions required should represent the start and the end of the selected measuring span. The zero point, the slope and even the isotherm intersection point are all determined by the microprocessor during the different stages of calibration.

In general the calibration is performed as follows:

1) Two buffer solutions of different pH values have to be selected. The pH value of one buffer solution should lie somewhere in the region of the beginning of the desired measuring span and the pH value of the second buffer solution should lie somewhere at the end of the measuring span.

   After the calibration mode of the pH meter is activated, the calibration menu guides the operator through the calibration procedure. Sometimes the buffer values still have to be entered manually, very often the microprocessor identifies the buffer values automatically.

2) The temperature of the buffer solutions has to be measured, either with the incorporated temperature sensor in the pH electrode or separately with a glass thermometer. The temperature values are either entered manually into the microprocessor or, with an incorporated electrode sensor, detected automatically.

The electrode handling is identical to the electrode handling during the calibration procedure of analogue pH meters as explained in point 3) and 4) of paragraph 3.9.2.1.

3.9.3 Re-calibration

The pH calibration has to be repeated periodically. 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 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 re-calibrate as often as possible. If no significant change of the calibration values is noticed, the frequency of the calibration may be progressively extended.

The Frequency of re-calibration has to be established experimentally
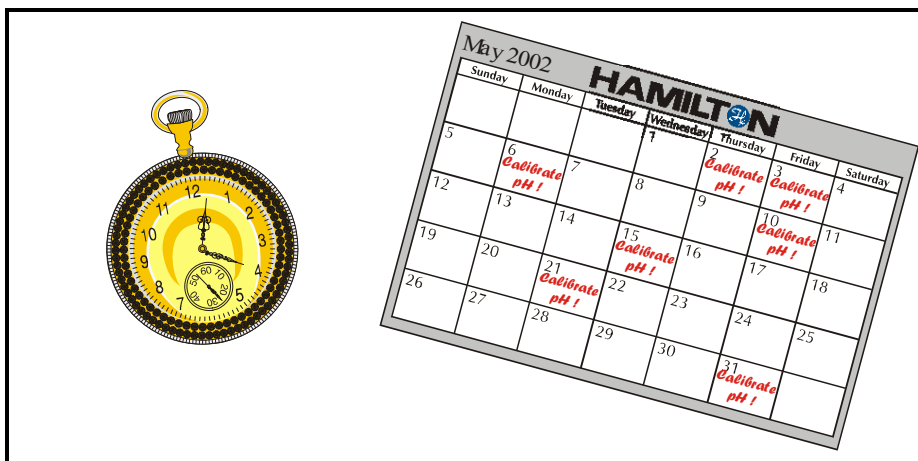
3.9.4 Response Time

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.

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.

A further point to consider is the storage medium used for electrode assemblies. Never store pH electrode assemblies which are not in use, in distilled water, as this will slow down the response time of that electrode assembly considerably. It has been found that a 3 mole KCl solution is the best storage medium for glass electrode assemblies.

Modern microprocessor based pH meters/transmitters are fitted with a programme for early detection of a stabilised calibration value (Auto-Read). Verification measurements have shown that the Auto-Read values do not differ more than 0,01 pH units from the end value of the adapted electrode assembly when dealing with new electrodes.

3.9.5 Reasons for calibration problems

Three common problems might be encountered when calibrating a pH measuring 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)

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

a) the utilised buffer solutions are either contaminated or out-dated. It could be that the buffer solution used is incorrect – *therefore never store buffer solutions in unmarked bottles*

b) the electrolyte of the reference electrode is contaminated and/or the diaphragm is blocked

c) a time-worn electrode assembly is utilised

d) an electrode assembly is utilised which has not been hydrated long enough (after dry storage or after cleaning with an acid solution)

e) hair cracks are present in the membrane of the measuring electrode

f) electrostatic charge on the electrode assembly caused by rubbing the electrode shaft with cloth instead of gently dabbing it with tissue paper

g) a temperature difference between electrode assembly and buffer solution of more than 10 °C

h) the zero point of the pH electrode assembly and the measuring instrument differ. This is seldom the case as normally both have pH 7 as their zero potential. In exceptional cases the pH electrode assembly could have a zero point which differs from pH 7

i) the connection between electrode assembly and measuring instrument could also cause problems: either open-circuit in the cable or short-circuit in cable and/or connection plug (usually due to moisture ingress)

3.10 The Accuracy to be Expected

The accuracy of a pH measurement depends on many factors of which some cannot be controlled while others can. In order that the non-controllable factors do not influence the result of the pH measurement to too great a degree, the controllable factors must be monitored and kept as small as possible.

The calibration of the pH measuring system is one of the most important factors. To ensure a high measuring accuracy one has to follow the correct calibration procedure, use new and accurate buffer solutions and wait long enough for stable indication values of the electrode assembly to be calibrated. The time interval between re-calibration should be as short as practically possible. Remember: *no pH measurement can be more accurate than its calibration accuracy*.

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

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The reference electrode must be kept pressurised by approximately 100 kPa (1 bar) above the pressure of the measured medium to keep the reference electrolyte flowing and prevent the ingress of measured solution into the reference electrolyte vessel. ***The diaphragm must be kept clean at all times***. The ***correct matching of the diaphragm type to the measuring problem*** will drastically improve the measuring accuracy.

The conducting system and electrolyte of measuring and reference electrode must be identical.

The membrane of the measuring electrode must also be kept clean at all times. Deposits on the membrane glass will reduce the measuring accuracy dramatically 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 electrode assembly connected to an accurate, state-of-the-art pH measuring instrument having the required high impedance of at least 10^{12} ohms. In the laboratory accuracies of +/- 0,02 pH units are achievable.

4 ELECTRODE HANDLING

pH measuring 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 measuring system.

Incorrect handling might shorten the life of the electrode assembly considerably or cause an unreliable measuring result. ***Correct handling of the pH electrode assembly does not only improve the measuring 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 has to differentiate between the types of electrodes: measuring electrode, reference electrode or combination electrode. The time of storage 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 Measuring Electrodes

Measuring electrodes can be stored dry for long periods. However before using the measuring 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 measuring 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.

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If a measuring 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 re-use.

4.1.2 The Storage of Reference Electrodes

Reference electrodes should always be stored wet, i.e. the diaphragm has to 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 crystallise and subsequently cover the complete bottom of the electrode. The crystallisation itself does not cause a problem but the reference electrode might dry out completely which will result 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 measuring errors or even make a measurement totally impossible.

Closed refill aperture

KCl
3 mol/l

Rubber or
plastic cap
filled with
reference electrolyte (3 mol/l KCl)

Therefore for short or long periods of time it is essential to store reference electrodes in their respective reference electrolyte, with the refill aperture closed by 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 and will significantly falsify the subsequent pH measurement.

4.1.3 The Storage of Combination Electrodes

A combination electrode consists of a measuring electrode and a reference electrode combined into one single-rod electrode. ***The storage conditions must therefore be suitable for a measuring and for a reference electrode***. As every reference electrolyte is an aqueous solution it has been found that the optimum storage liquid is the respective reference electrolyte of that combination electrode. 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 electrodes 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 3 mol/l KCl solution***.

This statement ***applies to polymer electrodes*** as well.
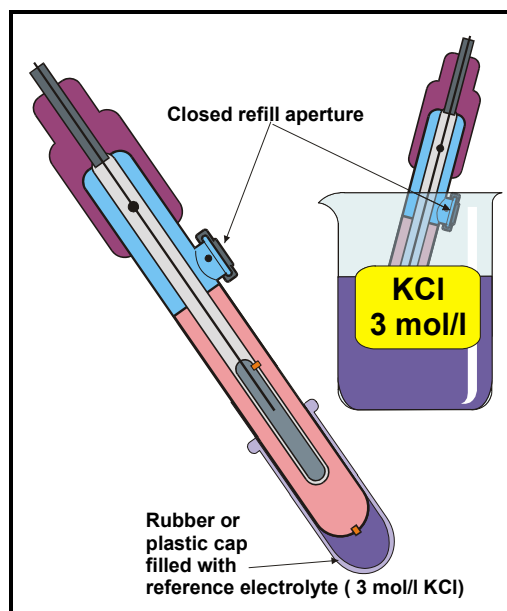
4.2 Cleaning of Electrode Assemblies

Industrial pH electrode assemblies are often immersed into process solutions which tend to contaminate the membrane of the measuring 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*

Principally the electrode assembly has to be clean at all times in order to guarantee an ideal pH measurement. Therefore the periodic cleaning of the electrode assembly should be part of any regular plant maintenance schedule. As the cleaning frequency depends solely on the measuring solution, a cleaning time cycle has to be established individually for each pH measuring application. The cleaning interval could vary between hours and weeks.

The 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.

♦ Calcium deposits may be removed by soaking the electrode for several minutes in a solution of 0,1 mol/l HCl.

♦ 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.

♦ Measuring solutions containing proteins tend to contaminate the membrane and diaphragm of the electrode assembly. Soaking the electrode assembly for several hours in a solution of 1% pepsin in 0,1 mol/l HCl is normally a remedy.

♦ Inorganic coatings can be removed using commercially available glass cleaning solutions.

♦ Measuring solutions containing sulphides will react with the silver chloride present in most reference electrolytes. This reaction will lead to the contamination of the diaphragm with silver sulphide deposits (black diaphragm). To remove the silver sulphide deposit the electrode has to be soaked in a thiourea/HCl solution until the diaphragm is totally bleached.

♦ Highly resistant deposits may be removed with hydrogen peroxide or sodium hypo-chloride.

♦ Any other acid or alkaline soluble deposits may be removed by either rinsing the electrodes in 0,1 mol/l HCl or in 0,1 mol/l NaOH for a few minutes only.

It is very important that after each above mentioned cleaning process the cleaned electrode has to be soaked in its respective reference electrolyte (normally 3 mol/l KCl) for at least 12 hours, or preferably a day (hydration process). As the cleaning solution may have penetrated the diaphragm which will change the diffusion potential, it is absolutely necessary to perform a re-calibration after the soaking time in the reference electrolyte and before a new pH measurement takes place with the cleaned electrode (see paragraph 3.8)

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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 3.8.2).

4.3 Refilling or Replacing the Reference Electrolyte

A reference electrode or a combination electrode utilising 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 MEASURING INSTRUMENT

5.1 Measuring Electrode Connection Cable

The pH measuring electrode has inherently a high internal resistance (up to 5×10^9 ohms in some cases) and, therefore the electrical connection to a pH meter or transmitter is prone to all kinds of electro-magnetic interference. For this reason special and high demands are made to the quality of the cable which connects the pH measuring electrode to its measuring instrument.

A measuring electrode is always connected with a low-noise screened coaxial cable to the measuring instrument. *This cable must have a very high insulation resistance*, always higher than the input impedance of the measuring instrument (normally 10^{12} Ω). The market offers coaxial cables having an insulation resistance of 10^{14} Ω to 10^{17} Ω per metre 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 measuring 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 measuring instrument is not problematic, as long as the cable is protected from any electro-magnetic 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 measuring 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 semiconductor layer. This layer suppresses voltages which might be created when moving the coaxial cable. It is of importance that this black layer must be carefully removed when preparing the cable ends for connection to the electrode plug and/or to the measuring instrument. *If the black layer is not 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 always be dry and clean. After stripping, the cable ends should be cleaned with alcohol or ether, which can be done with a cloth or a brush, both of which should be absolutely clean. Touching the stripped cable ends with wet or fat-stained 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 becomes impossible.

When routing the pH connection cable care must be taken not to route the pH connection cable parallel to power cables. Parallel situated power cables in the vicinity of the pH connection cables would 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 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 metres.

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: PVC external insulation, screen, PE insulation, internal conductor, black semiconductor layer

Triax cable: PVC external insulation, PVC insulation, screen 1, PE insulation, internal conductor, black semiconductor layer, screen 2

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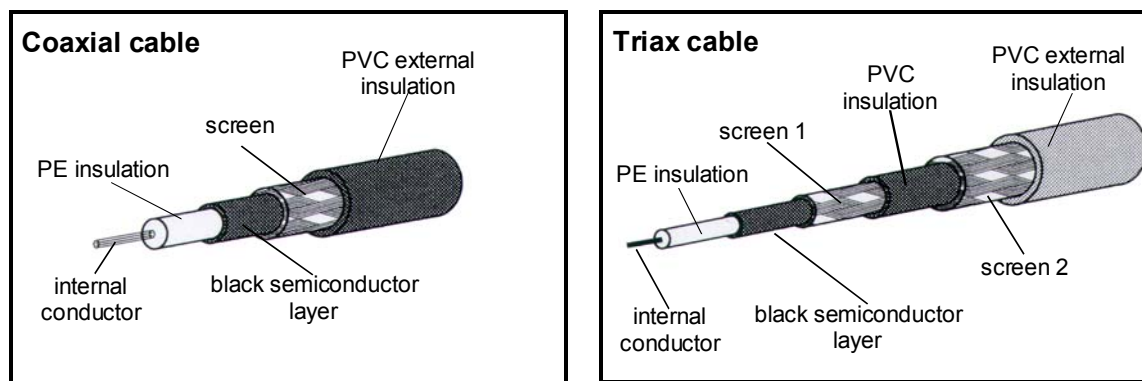
5.5 Plug or Cable?

Various electrode manufacturers supply their pH electrodes in *two configurations: either with an integrally installed cable (normally 1 metre in length), or with an electrode plug connection*. Both configurations have their advantages and disadvantages.

If the cable is installed to the electrode by the manufacturer, 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.

An electrode 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 connect the electrode 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 recognised that all liquids, gases and solids could be analysed 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 visualisation 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 paragraph "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 realised 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*.

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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 Bohr Atom

$2 \times 7^2 = 98$ electrons
$2 \times 6^2 = 72$ electrons
$2 \times 5^2 = 50$ electrons
$2 \times 4^2 = 32$ electrons

Electron
Nucleus

In each shell there are $2n^2$ electrons

Shells maximum 7 shells
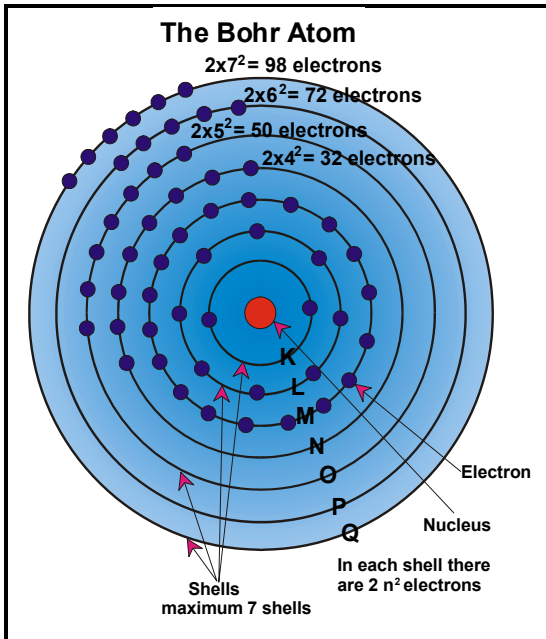
The electron shells are built up in a regular fashion from a first shell to a total of seven shells, each of which has an upper limit of the number of electrons that it can accommodate. The shells are named from inner shell to outer shell: **K-shell, L-shell … to Q-shell**. The K-shell is complete with 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 behaviour of the 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

Electron orbit

Electron⁻   Proton⁺

Atomic number   Atomic weight

1   1.0079
H
Hydrogen

Symbol

Element name

The Oxygen Atom

Neutron

Proton⁺

8   15.9994
O
Oxygen
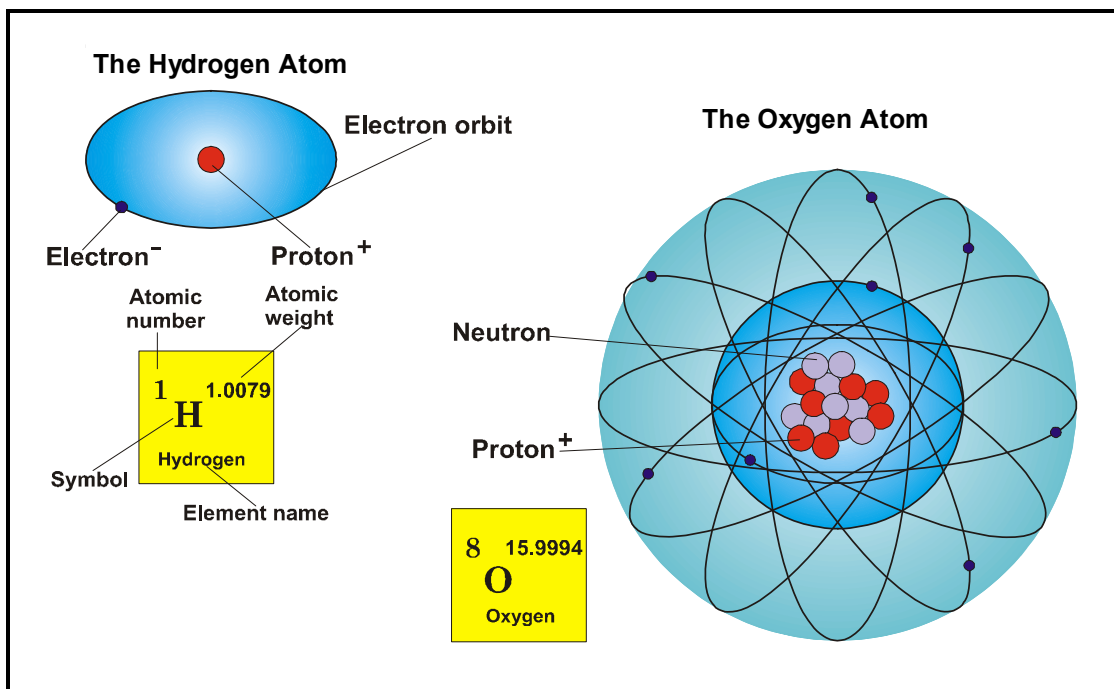
6.3 The Periodic Table of Elements

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 50. 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 maximise 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.
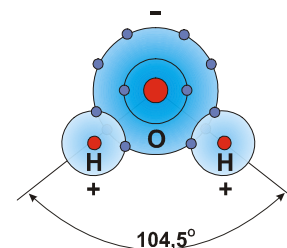
The Water Molecule H_2O

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	

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.

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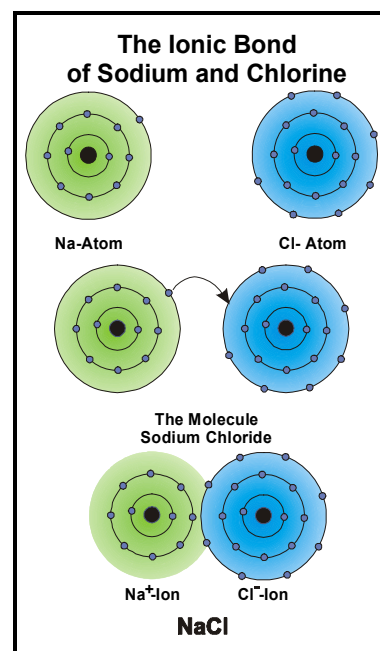
Periodic Table of the Elements

Group																	
IA																	VIIIB
1 1.0079 H Hydrogen	IIA											IIIB	IVB	VB	VIB	VIIB	2 4.0026 He Helium
3 6.941 Li Lithium	4 9.01218 Be Beryllium											5 10.81 B Boron	6 12.011 C Carbon	7 14.0067 N Nitrogen	8 15.9994 O Oxygen	9 18.9984 F Fluorine	10 20.179 Ne Neon
11 22.9897 Na Sodium	12 24.305 Mg Magnesium	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	13 26.982 Al Aluminium	14 28.086 Si Silicon	15 30.974 P Phosphorus	16 32.06 S Sulfur	17 35.453 Cl Chlorine	18 39.948 Ar Argon
19 39.098 K Potassium	20 40.08 Ca Calcium	21 44.956 Sc Scandium	22 47.9 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.847 Fe Iron	27 58.933 Co Cobalt	28 58.7 Ni Nickel	29 63.546 Cu Copper	30 65.38 Zn Zinc	31 69.72 Ga Gallium	32 72.59 Ge Germanium	33 74.922 As Arsenic	34 78.96 Se Selenium	35 79.9 Br Bromine	36 83.8 Kr Krypton
37 85.468 Rb Rubidium	38 87.62 Sr Strontium	39 88.906 Y Yttrium	40 91.22 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.9 Rh Rhodium	46 106.4 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	51 121.75 Sb Antimony	52 127.6 Te Tellurium	53 126.9 I Iodine	54 131.3 Xe Xenon
55 132.9 Cs Caesium	56 137.3 Ba Barium	57 138.9 La Lanthanum	72 178.5 Hf Hafnium	73 180.9 Ta Tantalum	74 183.9 W Tungsten	75 186.2 Re Rhenium	76 190.2 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.2 Pb Lead	83 208.98 Bi Bismuth	84 (209) Po Polonium	85 (210) At Astatine	86 (222) Rn Radon
87 (223) Fr Francium	88 226.0 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Db Dubnium	106 (263) Sg Seaborgium	107 (262) Bh Bohrium	108 (265) Hs Hassium	109 (266) Mt Meitnerium	110 (269) Uun Unun-nilium	111 (272) Uuu Unun-unium	112 (277) Uub Unun-bium						

58 140.1 Ce Cerium	59 140.9 Pr Praseodymium	60 144.2 Nd Neodymium	61 (145) Pm Promethium	62 150.4 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.5 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Yterbium	71 174.97 Lu Lutetium
90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 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 (260) Lr Lawrencium

Legend:
- Gas
- Noble Gases
- Liquid
- Solid
- Synthetically prepared

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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.

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

Na-Atom   Cl- Atom

The Molecule Sodium Chloride

Na^+-Ion Cl^--Ion

NaCl

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.

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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
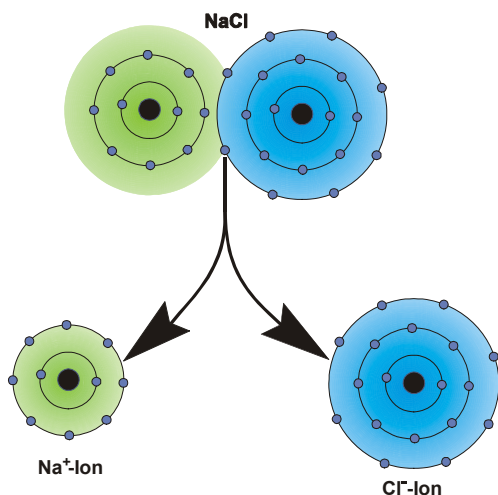
Electrolytes
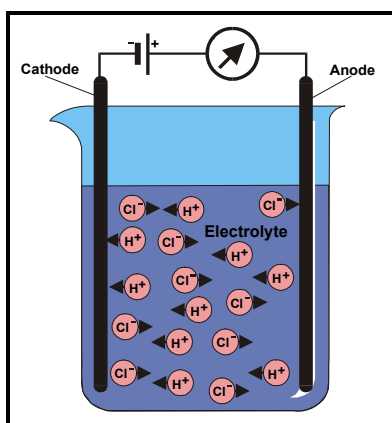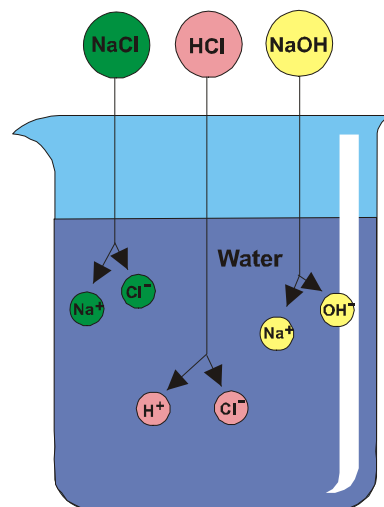
If two electrodes are immersed into an electrolyte and a potential difference is applied to these electrodes, the negatively charged ions will be attracted by the positively charged electrode (anode) and by reaching the anode will lose their charge (lose electrons). Hence the name *anion*. Similarly 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
Sulphuric 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 neutralisation reaction occurs. This reaction takes place very rapidly and generally produces water and a **salt**. For example, sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH), yield water and sodium sulphate (Na_2SO_4).

$$H_2SO_4 + 2NaOH = 2H_2O + Na_2SO_4$$
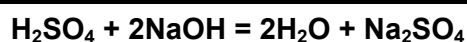
Salts are produced by substituting the H^+ ion with a base part or by substituting the OH⁻ ion with an acid part. Cations and anions combine to form an electrically neutral compound.

Examples:

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

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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 12g of carbon-12 (the atom against which other substances are measured) is **6,0221367 x 10^{23}**. This number is known as the **Avogadro's number** in honour 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.

$$
\begin{array}{llll}
1 \text{ mole} & H_2 & = & 2 \text{ g} \\
1 \text{ mole} & H_2O & = & 18 \text{ g} \\
1 \text{ mole} & Cl_2 & = & 71 \text{ g} \\
1 \text{ mole} & Rn & = & 222 \text{ g} \\
1 \text{ mole} & HCl & = & 36,5 \text{ g} \\
1 \text{ mole} & NaOH & = & 40 \text{ g}
\end{array}
$$

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^-).

$$\boxed{H_2O = H^+ + OH^-}$$
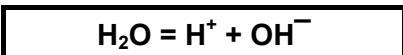
H^+ = Positive electrically charged hydrogen ion with acidity action

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 generalised theory of acids and bases, be viewed as the simplest acid-base neutralisation:

$$\boxed{2H^+ + 2e^- = H_2}$$
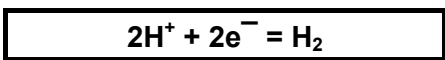
Actually hydrogen ions, or protons, do not exist freely in solution but are associated with water molecules. The ionisation of water should thus be written more correctly as:

$$2HOH = H_3O^+ + OH^-$$
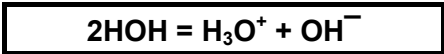
H_3O^+ is called the **hydronium ion** and is, in aqueous solutions, the ion responsible for acidic properties. For simplicity, equations are normally written using H^+.

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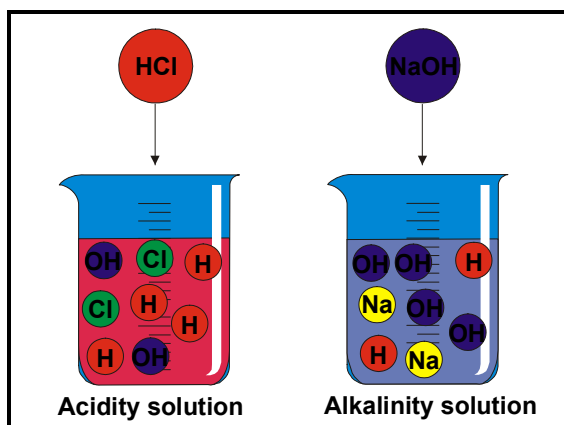
All aqueous solutions of acid and bases owe their chemical activity to their relative hydrogen ion (H^+) and hydroxyl ion (OH^-) concentration.

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/litre) 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:

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

(please refer to page 5 of this publication).

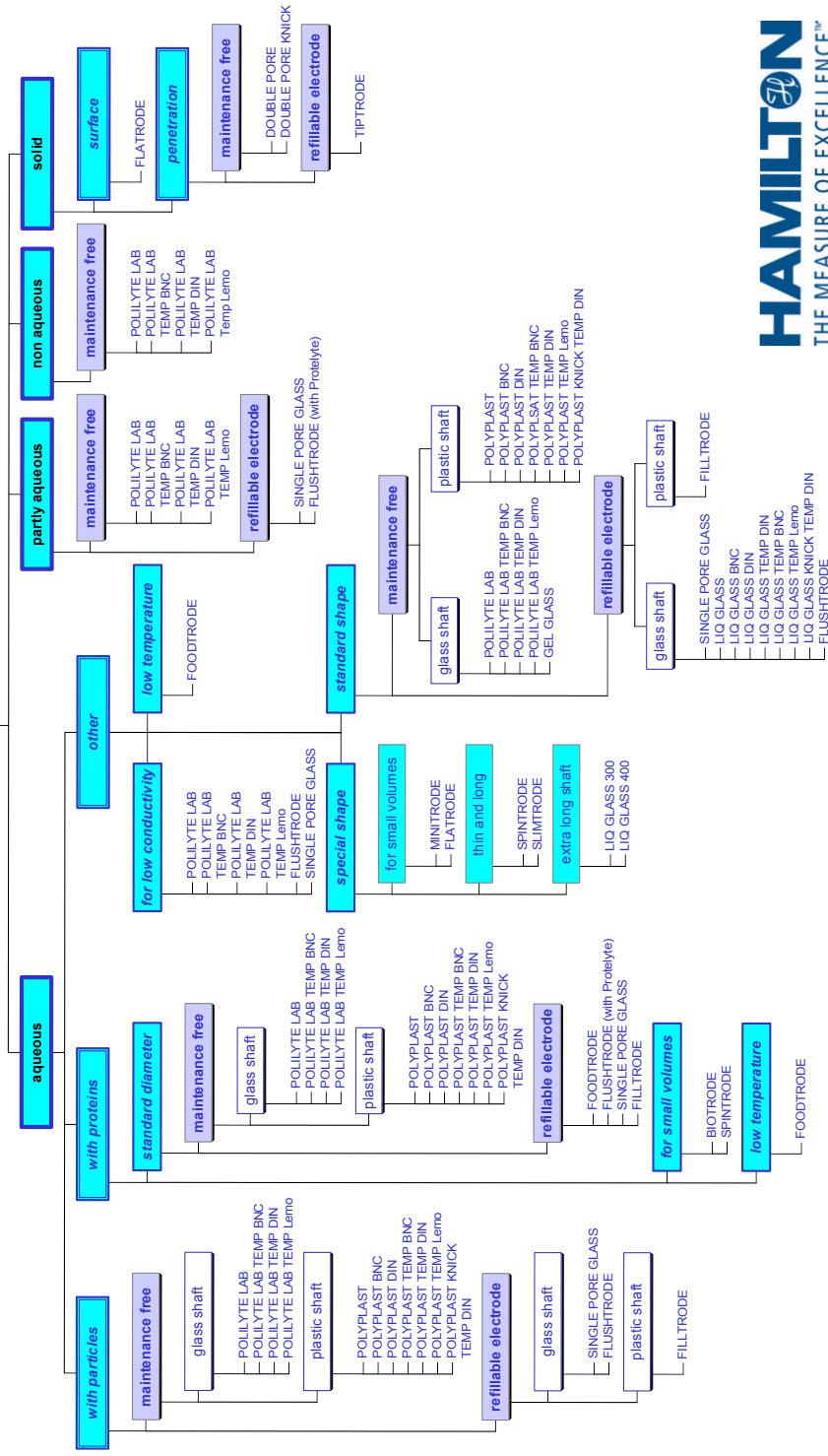**For detailed technical specifications and application notes**

on HAMILTON's pH electrodes please visit HAMILTON's website at
http://www.hamiltoncompany.com

or contact your local dealer

Theory is necessary – Experience is essential

Good luck with your pH measurement!

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Notes

Notes

Notes

Laboratory pH-Electrode Pathfinder

Laboratory Electrode for sample type:

aqueous

with particles

maintenance free
- glass shaft
  - POLILYTE LAB
  - POLILYTE LAB TEMP BNC
  - POLILYTE LAB TEMP DIN
  - POLILYTE LAB TEMP Lemo
- plastic shaft
  - POLYPLAST
  - POLYPLAST BNC
  - POLYPLAST DIN
  - POLYPLAST TEMP BNC
  - POLYPLAST TEMP DIN
  - POLYPLAST TEMP Lemo
  - POLYPLAST KNICK TEMP DIN

refillable electrode
- glass shaft
  - SINGLE PORE GLASS
  - FLUSHTRODE
- plastic shaft
  - FILLTRODE

with proteins

standard diameter

maintenance free
- glass shaft
  - POLILYTE LAB
  - POLILYTE LAB TEMP BNC
  - POLILYTE LAB TEMP DIN
  - POLILYTE LAB TEMP Lemo
- plastic shaft
  - POLYPLAST
  - POLYPLAST BNC
  - POLYPLAST DIN
  - POLYPLAST TEMP BNC
  - POLYPLAST TEMP DIN
  - POLYPLAST TEMP Lemo
  - POLYPLAST KNICK TEMP DIN

refillable electrode
- FOODTRODE
- FLUSHTRODE (with Protelyte)
- SINGLE PORE GLASS
- FILLTRODE

for small volumes
- BIOTRODE
- SPINTRODE

low temperature
- FOODTRODE

other

for low conductivity
- POLILYTE LAB
- POLILYTE LAB
- TEMP BNC
- POLILYTE LAB
- TEMP DIN
- POLILYTE LAB
- TEMP Lemo
- FLUSHTRODE
- SINGLE PORE GLASS

low temperature
- FOODTRODE

special shape

standard shape

maintenance free
- glass shaft
  - POLILYTE LAB
  - POLILYTE LAB TEMP BNC
  - POLILYTE LAB TEMP DIN
  - POLILYTE LAB TEMP Lemo
  - GEL GLASS
- plastic shaft
  - POLYPLAST
  - POLYPLAST BNC
  - POLYPLAST DIN
  - POLYPLAST TEMP BNC
  - POLYPLAST TEMP DIN
  - POLYPLAST TEMP Lemo
  - POLYPLAST KNICK TEMP DIN

refillable electrode
- glass shaft
  - SINGLE PORE GLASS
  - LIQ GLASS
  - LIQ GLASS BNC
  - LIQ GLASS DIN
  - LIQ GLASS TEMP DIN
  - LIQ GLASS TEMP BNC
  - LIQ GLASS TEMP Lemo
  - LIQ GLASS KNICK TEMP DIN
  - FLUSHTRODE
- plastic shaft
  - FILLTRODE

for small volumes
- MINITRODE
- FLATRODE

thin and long
- SPINTRODE
- SLIMTRODE

extra long shaft
- LIQ GLASS 300
- LIQ GLASS 400

partly aqueous

maintenance free
- POLILYTE LAB
- POLILYTE LAB
- TEMP BNC
- POLILYTE LAB
- TEMP DIN
- POLILYTE LAB
- TEMP Lemo

refillable electrode
- SINGLE PORE GLASS
- FLUSHTRODE (with Protelyte)

non aqueous

maintenance free
- POLILYTE LAB
- POLILYTE LAB
- TEMP BNC
- POLILYTE LAB
- TEMP DIN
- POLILYTE LAB
- Temp Lemo

solid

surface
- FLATRODE

penetration

maintenance free
- DOUBLE PORE
- DOUBLE PORE KNICK

refillable electrode
- TIPTRODE

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Miniature Valves

Laboratory Automation for:
Drug Discovery
Genomics
Proteomics
Forensics
In Vitro Diagnostics

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POLYCLAVE
SINGLE PORE
SKYLYTE

HYDROGEN VALUES by pH LEVELS

1. **pH 1.6**
   - Hydrogen ion concentration: ($[H^+] \approx 200,000,000$
   - PPM: Approximately **200,000 PPM**

2. **pH 2.0**
   - Hydrogen ion concentration: ($[H^+] \approx 79,621,434$
   - PPM: Approximately **79,622 PPM**

3. **pH 2.5**:
   - Hydrogen ion concentration: ($[H^+] \approx 25,278,508$
   - PPM: Approximately **25,279 PPM**

4. **pH 3.0**:
   - Hydrogen ion concentration: ($[H^+] \approx 7,962,143$
   - PPM: Approximately **7,962 PPM**

5. **pH 3.5**:
   - Hydrogen ion concentration: ($[H^+] \approx 2,517,850$
   - PPM: Approximately **2,518 PPM**

6. **pH 4.0**:
   - Hydrogen ion concentration: ($[H^+] \approx 796,000$
   - PPM: Approximately **796 PPM**

7. **pH 4.5**:
   - Hydrogen ion concentration: ($[H^+] \approx 31,600$
   - PPM: Approximately **31.6 PPM**

8. **pH 5.0**:
   - Hydrogen ion concentration: ($[H^+] \approx 10,000$
   - PPM: Approximately **10 PPM**

Remember that as the pH decreases (becomes more acidic), the hydrogen ion concentration increases, leading to higher PPM values. Conversely, as the pH increases (becomes more basic), the hydrogen ion concentration decreases, resulting in lower PPM values.

Hydrogen Water Competitive Levels

Purify Hydrogenator Bottle

- 5 minute program – yields 1.6 ppm
- 10 minute program – yields 3.0 ppm