pH Theory Guide

Practical
description of
how to
measure pH

Laboratory
environment

A Guide to pH Measurement

Theory & Practice of Laboratory pH Applications

METTLER TOLEDO

This guide focuses on giving a clear and practical description of how to measure pH in the laboratory environment. A lot of tips and hints are given for the important points and the whole measurement description is later backed up by the theoretical description of acidity and alkalinity measurements. Attention is also given to the different kinds of pH electrodes available and the selection criteria for choosing the right electrode for a specific sample.

1. Introduction to pH

1.1. Acidic or alkaline?

Why do we classify an everyday liquid like vinegar as being acidic? The reason for this is that vinegar contains an excess of hydronium ions (H_3O^+) and this excess of hydronium ions in a solution makes it acidic. An excess of hydroxyl ions (OH^-) on the other hand makes something basic or alkaline. In pure water the hydroniumn ions are all neutralized by hydroxyl ions and this solution is what we call at a neutral pH value.

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

Figure 1. The reaction of an acid and a base forms water.

If the molecules of a substance release hydrogen ions or protons through dissociation we call this substance an acid and the solution becomes acidic. Some of the most well-known acids are hydrochloric acid, sulfuric acid and acetic acid or vinegar. The dissociation of vinegar is shown below:

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

Figure 2. Dissociation of acetic acid.

Not every acid is equally strong. Exactly how acidic something is, is determined by the total number of hydrogen ions in the solution. The pH value is then defined as the negative logarithm of the hydrogen ion concentration. (To be precise, it is determined by the activity of the hydrogen ions. See chapter 4.2 for more information on the activity of hydrogen ions).

$$pH = -\log\ [H_3O^+]$$

Figure 3. The formula for calculating the pH value from the concentration of hydronium ions.

The quantitative difference between acidic and alkaline substances can be determined by performing pH value measurements. A few examples of pH values of everyday substances and chemicals are given in figure 4:

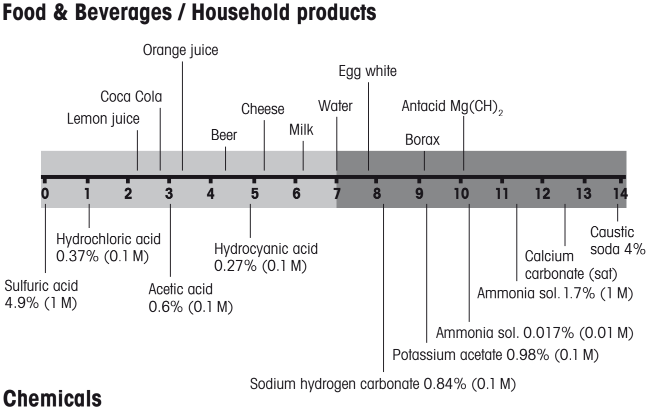


Figure 4. pH values for some chemicals and everyday products.

The alkaline end of the scale is between pH 7 and 14. At this end of the scale the hydroxyl or OH^- ions are present in excess. Solutions with these pH values are created by dissolving a base in an aqueous solution. The base dissociates to release hydroxyl ions and these make the solution alkaline. Some of the best known bases are sodium hydroxide, ammonia and carbonate.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Figure 5. The reaction of ammonia with water.

The whole scale of pH values in aqueous solutions includes both the acidic and alkaline ranges. The values can vary from 0 to 14, where pH values from 0 to 7 are called acidic and pH values from 7 to 14 are termed alkaline. The pH value of 7 is neutral.

1.2. Why are pH values measured?

We measure pH for a lot of different reasons, such as:

- to produce products with defined properties – during production it is important to control the pH to ensure that the end product conforms with the desired specifications. The pH can dramatically alter the properties of an end product such as appearance or taste.
- to lower production costs – this is related to the above mentioned reason. If the yield of a certain production process is higher at a given pH, it follows that the costs of production are lower at this pH.

- to avoid doing harm to people, materials and the environment – some products can be harmful at a specific pH. We have to be careful not to release these products into the environment where they can harm people or damage equipment. To be able to determine whether such a substance is dangerous we first have to measure its pH value.
- to fulfill regulatory requirements – as seen above, some products can be harmful. Governments therefore put regulatory requirements in place to protect the population from any harm caused by dangerous materials.
- to protect equipment – production equipment that comes into contact with reactants during the production process can be corroded by the reactants if the pH value is not within certain limits. Corrosion shortens the lifetime of the production line, therefore monitoring pH values is important to protect the production line from unnecessary damage.
- for research and development – the pH value is also an important parameter for research purposes such as the study of biochemical processes.

These examples describe the importance of pH in a wide range of applications demonstrating why it is so often determined.

1.3. The tools for pH measurements

To be able to measure pH one needs to have a measurement tool which is sensitive to the hydrogen ions that define the pH value. The principle of the measurement is that one takes a sensor with a glass membrane which is sensitive to hydrogen ions and observes the reaction between it and a sample solution. However, the observed potential of the pH-sensitive electrode alone does not provide enough information and so we need a second sensor. This is the sensor that supplies the reference signal or potential for the pH sensor. It is necessary to use the potential difference between these electrodes in order to determine the pH value of the measured solution.

The response of the pH-sensitive electrode is dependent on the H^+ ion concentration and therefore gives a signal that is determined by how acidic/alkaline the solution is.

The reference electrode on the other hand is not responsive to the H^+ ion concentration in the sample solution and will therefore always produce the same, constant potential against which the pH sensor potential is measured.

The potential between the two electrodes is therefore a measure of the number of hydrogen ions in the solution, which by definition gives one the pH value of the solution. This potential is a linear function of the hydrogen concentration in the solution, which allows quantitative measurements to be made. The formula for this function is given below in figure 6:

$$E = E_0 + 2.3RT / nF * \log [H_3O^+]$$

E = measured potential
E_0 = constant
R = gas constant
T = temperature in degrees Kelvin
n = ionic charge
F = Faraday constant

Figure 6. The relationship between the amount of acid in solution and the output potential of a pH electrode.

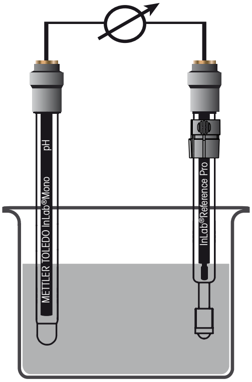


Figure 7. The measurement assembly of pH and reference sensor.

In figure 7 a pH measurement setup with two separate sensors, a pH sensor and a reference sensor is shown. Nowadays, a merger of the two separate sensors into one electrode is very common and this combination of reference and pH electrodes is called the combined pH electrode. Each of these three electrodes is different and has its own important features and properties.

a) The pH electrode

The pH electrode is the part that actually senses the pH in the solution. It consists of a glass shaft with a thin glass membrane at the end, sensitive to H^+ ions. The outside of this membrane glass forms a gel layer when the membrane comes into contact with an aqueous solution. A similar gel layer is also formed on the inside of the membrane glass, since the electrode is filled with an inner aqueous electrolyte solution. An example of this gel layer is shown in the figure below:

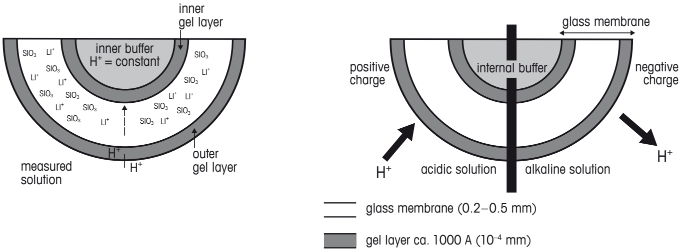


Figure 8. Cross sections through the glass membrane.

The H^+ ions in and around the gel layer can either diffuse into or out of this layer, depending on the pH value and thus H^+ ion concentration of the measured solution. If the solution is alkaline the H^+ ions diffuse out of the layer and a negative charge is established on the outer side of the membrane. Since the glass electrode has an internal buffer with a constant pH value, the potential on the inner surface of the membrane remains constant during the measurement. The pH electrode potential is therefore the difference between the inner and outer charge of the membrane. A drawing of a standard pH electrode is shown in figure 9.

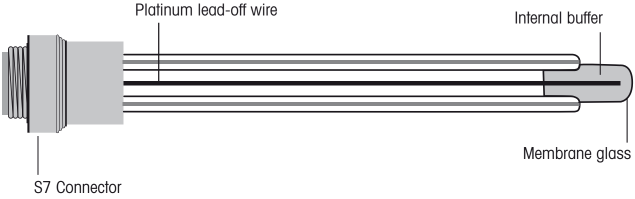


Figure 9. pH electrode with pH-sensitive membrane.

b) Reference electrodes

The purpose of the reference electrode is to provide a defined stable reference potential for the pH sensor potential to be measured against. To be able to do this the reference electrode needs to be made of a glass which is not sensitive to the H^+ ions in the solution. It must also be open to the sample environment into which it is dipped. To achieve this, an opening or junction is made in the shaft of the reference electrode through which the inner solution or reference electrolyte can flow out of into the sample. The reference electrode and pH half-cell have to be in the same solution for correct measurements. A picture of a typical reference electrode is shown below:

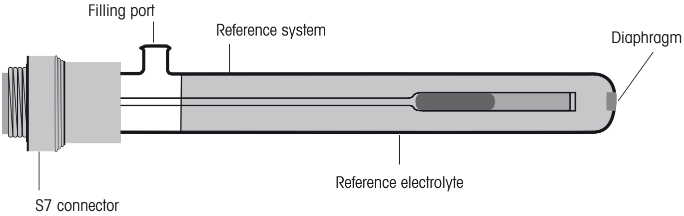


Figure 10. Reference electrode with reference electrolyte, reference element and junction.

The construction of the electrode is such that the internal reference element is immersed in a defined reference buffer and is indirectly in contact with the sample solution via the junction. This contact chain ensures a stable potential.

There are several reference systems available, but the one used almost exclusively today is the silver/silver chloride system. The potential of this reference system is defined by the reference electrolyte and the silver/silver chloride reference element. It is important that the reference electrolyte has a high ion concentration which results in a low electrical resistance (see chapter 4.4 for more details).

Since the reference electrolyte flows into the sample solution during measurement, one should be aware of any possible reactions between the reference electrolyte and the sample solution, as this can affect the electrode and measurement (see chapter 2.2 for more information).

c) Combined electrodes

Combined electrodes (figure 11) are much easier to handle than two separate electrodes and are very commonly used today. In the combined electrode the pH-sensitive glass electrode is concentrically surrounded by the reference electrode filled with reference electrolyte.

The separate pH and reference parts of the combined electrode have the same properties as the separate electrodes; the only difference is that they are combined into one electrode for ease of use. Only when the two components of the combined electrode are expected to have very different life expectancies is the use of individual pH and reference electrodes recommended rather than a single combined electrode.

To further simplify pH measurements, one can house a temperature sensor in the same body as the pH and reference elements. This allows temperature compensated measurements to be made. Such electrodes are also called 3-in-1 electrodes.

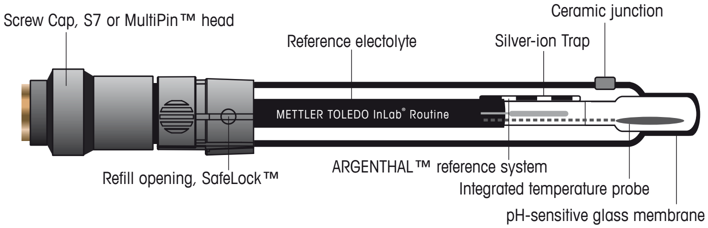


Figure 11. Typical combination pH electrode with inner pH sensor and outer reference element.

1.4. Practical guide to correct pH measurements

The tools necessary for pH measurements are relatively uncomplicated, easy to use and provide reliable measurements when they are used in the correct way. There are several important guidelines that must be followed and these are briefly discussed below. A step-by-step recipe for how to obtain correct and accurate pH measurements is then given at the end of the guidelines.

a) Sample preparation

When preparing the sample for measurement, one needs to take certain rules into consideration. It is very important to either measure the temperature of the sample or keep the temperature constant at a known value. The reason for doing this is that the pH value of a sample is temperature

dependent and the pH electrode gives a temperature dependent measurement result. This temperature dependence does not pose a problem as long as the temperature is recorded and compensated for.
Before starting a pH measurement, always stir the sample to ensure that it is homogeneous. This ensures that the measured value is valid for the whole sample and not just for the part where the electrode is situated.
There needs to be enough sample volume in the vessel so that the junction in the reference part is completely submerged in the sample. This is necessary to ensure that there is contact between the inner and outer part of the reference electrode and that the electrolyte can flow out into the sample.
It goes without saying that the basic rules of good laboratory practice such as only using suitable, clean and labeled glassware for the samples are also applicable for pH measurements.

b) Calibration

A pH electrode needs to be calibrated regularly. It is recommended that you do this at least once a day before you start measuring. In a calibration the slope and offset of an electrode are determined.
The theoretical slope and offset are given by the Nernst equation:

$$E = E_0 + 2.3RT / nF * \log [H_3O^+] = E_0 - 2.3RT / nF * pH$$

$$Slope = 2.3RT / nF$$
$$Offset = \text{Should be } 0 \text{ mV at pH } 7.00$$

Figure 12. Slope and offset for a pH electrode.

The calibration is necessary to adjust the slope and offset of an electrode to their true values for the measuring system in question. The calibration curve is then used to correlate the measured mV values of the electrode to the pH value of the solution measured.

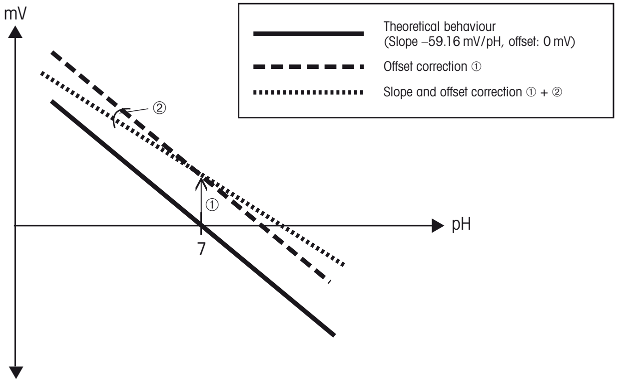


Figure 13. Correlation between mV value measured by pH electrode and pH value in sample. Curves shown are for the theoretical behavior, for offset compensated behavior and slope & offset compensated behavior.

Since an electrode is characterized by both its zero point and its slope, it is advisable to do a minimum of a two point calibration for reliable measurements and better precision. When measurements are performed over a large range of pH values it is recommended that one takes at least 3 calibration points. Most pH meters can do 3–5 point calibrations.
It is important to note that one should only measure samples within the chosen region of calibration.
When calibrating an electrode, most pH meters request that you input the type of buffers which will be used. There are several manufacturers of buffer solutions and the specifications of the most commonly used brands normally already come programmed as tables in the pH meters. These tables cover groups of buffers for a range of temperatures. In this way a whole group can be chosen at once allowing the temperature dependence of the individual buffers used for calibration, to be taken into account. The tables for the METTLER TOLEDO buffer groups can be found in Appendix 5.1. If no internal or external temperature sensor is used, ensure that you calibrate and measure at the same temperature. In this case remember to manually input the temperature to allow the meter to perform the buffer temperature correction.
The buffers which are used for the calibration are very accurate solutions with a guaranteed value and precision. To keep the buffer solutions suitable for calibrations for as long as possible after opening it is advisable that you follow these guidelines:

- Mark the date of first use on the bottle of the buffer solution.
- Keep the buffer solution bottles tightly sealed at all times and use the decanted buffer immediately.
- Never return used buffer back into the original bottle or mix calibration standards from different manufacturers.
- Ensure that no contaminants enter the buffer solution bottle and always keep the bottle sealed.
- Store the calibration standard at ambient temperature.
- Do not store the bottles of buffer solution in direct sunlight.
- Clean the electrodes before calibration and do not calibrate directly in the original buffer solution bottle.
- Never use a calibration standard with an expired use by date or that you suspect is contaminated.
- Replace the buffer solution with a new bottle after it has reached its expiry date.

Always repeat the calibration after cleaning your electrode, after electrode maintenance, regeneration or long term storage of an electrode, as all these factors have an influence on the pH electrode potential.

c) pH Electrode

pH electrodes have a very important role in performing correct pH value determinations, since they are responsible for the actual pH measurement. Electrode maintenance is therefore very important for prolonging the lifetime of the electrode and obtaining the best results.

If electrodes are not cleaned after use or are subjected to long term neglect they will lose their accuracy and the measurement precision of the whole system decreases. This can be observed as a steady decrease in the slope of the electrode.

When the slope value drops below 50 mV per decade (85 % slope efficiency) or the offset at the zero point exceeds ± 30 mV, extensive reconditioning may return the electrode to the level of expected performance, but a change of electrode may be necessary to ensure accurate pH measurements.

However, not only bad maintenance, but also other factors such as a reference junction blockage, electrolyte loss, glass bulb contamination and use of incorrect calibration buffers will all contribute to low slopes and poor performance.

A more detailed description of electrode maintenance is given in Chapter 2.
Temperature is also an important factor for electrodes. The electrode potential measured in a sample depends partly on the temperature of this sample. Since this is a known linear effect, it can also be compensated for. However, a problem arises when there is a temperature gradient between the electrode and the sample. This causes the pH measurement to drift until the temperature of the electrode and the sample becomes equal. Only then will the reading be stable. If one is not aware of this difference in temperature it may appear that the measurement is unstable or if the instability is not noticed a non-equilibrated pH determination is made.

d) Expected measurement accuracy

The accuracy of your measurement is influenced by different factors such as the accuracy of the buffers used for calibration, whether or not temperature compensation is used, if the right electrode is used for the particular sample measured, if the electrode has been given enough time to equilibrate and if the correct endpoint/measurement point is used in the meter, to mention just a few. When great care is taken with the measurements an accuracy of ± 0.05 pH units should be achievable.

Step-by-step guide to pH measurements

This step-by-step guide assumes that a combination pH electrode is used. If separate pH and reference electrodes are used, ensure that you always put the electrodes in the same solution during measurements. Also ensure that both electrodes are connected to the pH meter.

Preparation

1) Select the correct pH electrode for your sample (see Chapter 2).
2) Connect the electrode and temperature sensor to the pH meter.

Calibration

3) Switch on the pH meter and select the correct buffer group or buffer values for the calibration.
4) Set the meter to manual temperature correction if no temperature probe is attached.

5) Select the correct temperature for the buffers if no automatic temperature correction is done.
6) Prepare the buffer solutions intended for calibration by pouring a sufficient amount of the solutions into clean beakers.
7) Make sure that the buffer solutions are used in the correct order for the calibration unless the pH meter has auto-buffer recognition (All METTLER TOLEDO pH meters have auto-buffer recognition).
8) Take the electrode out of its holder and visually inspect it to see if there are any obvious problems with the electrode. Make sure that you have opened the electrolyte filling hole to ensure that there is no pressure build up or reduction in the electrode and to ensure that the electrolyte can slowly flow into the sample.
9) Rinse the electrode with distilled or deionized water.
10) Take the first buffer solution, stir gently and immerse the electrode.
11) Press the calibration (or equivalent) button on the pH meter.
12) Wait until the measurement is stable. METTLER TOLEDO instruments have automatic endpoint algorithms which freeze the measurement automatically as soon as the value is stable.
13) Take the electrode out of the buffer solution and rinse it.
14) Take the second buffer solution, stir gently and immerse the electrode.
15) Press the calibration (or equivalent) button on the pH meter.
16) Wait until the measurement has reached an endpoint.
17) Take the electrode out of the buffer solution and rinse it.
18) For a third calibration point, repeat steps 8 – 11. If the calibration is complete, end the calibration procedure on the pH meter by pressing the appropriate button.
19) Take the electrode out of the buffer solution, rinse it and store it in its holder.
20) Review the calibration results on the meter.
21) Save the results if they are acceptable.

Measurement

22) Pour enough sample solution into a measuring beaker so that the level of the sample is above the junction of the electrode.
23) Make sure that either the temperature of the sample is known or that it is measured during the pH determination with an internal or external temperature sensor.

24) Gently stir the sample and dip the pH electrode into the solution.
25) If the temperature of the sample and the electrode are very different, ensure that the measurement drift caused by the temperature gradient has stopped before taking the pH reading.
26) Press the measurement button on the pH meter and wait until a stable endpoint has been reached.
27) Take the electrode out of the solution and rinse with distilled or deionized water.
28) For additional samples repeat steps 1–6 until all samples have been measured.
29) After measurement, rinse the electrode with distilled or deionized water and store it in a wetting cap filled with reference electrolyte.

2. Electrode selection and handling

For optimal pH measurements, the correct electrode must first be selected. The most important sample criteria to be considered are: chemical composition, homogeneity, temperature, pH range and container size (length and width restrictions). The choice becomes particularly important for non-aqueous, low conductivity, protein-rich and viscous samples where general purpose glass electrodes are subject to various sources of error.
The response time and accuracy of an electrode is dependent on a number of factors. Measurements at extreme pH values and temperatures, or low conductivity may take longer than those of aqueous solutions at room temperature with a neutral pH.
The significance of the different types of samples is explained below by taking the different electrode characteristics as a starting point. Again, mainly combined pH electrodes are discussed in this chapter.

2.1. Different kinds of junctions

a) Ceramic junctions

The opening that the reference part of a pH electrode contains to maintain the contact with the sample can have several different forms. These forms have evolved through time because of the different demands put on the electrodes when measuring diverse samples. The 'standard' junction is the simplest one and is known as a ceramic junction. It consists of a porous piece of ceramic which is pushed through the glass shaft of the electrode. This porous ceramic material then allows the electrolyte to slowly flow out of the electrode, but stops it from streaming out freely. This kind of junction is very suitable for standard measurements in aqueous solutions; the METTLER TOLEDO **InLab® Routine Pro** is an example of such an electrode. A schematic drawing of the principle of this junction is shown below in figure 14.

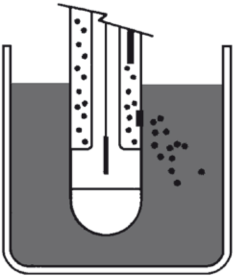


Figure 14. Electrode with ceramic junction.

Even though this is probably the most widely used junction because of its simplicity of use with aqueous solutions, it has one main drawback. Because of the porous structure of the junction it is relatively easy for samples to block the junction, especially if the sample is viscous or if it is a suspension.

One sometimes also has to be careful with some aqueous samples such as those with a high protein concentration, since proteins may precipitate within the porous junction if they come in contact with the reference electrolyte, which is often KCl. This reaction will cause the porous structure to be filled with protein debris blocking the junction and rendering the electrode useless. Measurements are not possible if the electrolyte cannot flow freely since the reference potential will no longer be stable.

The same problem can also be caused if the inner electrolyte reacts with the sample solution being measured and the two meet in the junction. This reaction can create a precipitate which may block the junction, e.g. if KCl electrolyte saturated with AgCl is used with samples containing sulfides, the silver and sulfides react to form Ag_2S which then blocks the ceramic junction.

b) Sleeve junctions

The ceramic junction has its limitations and is not suitable for more difficult samples, so several other junctions have been developed to facilitate the measurements with these samples. The problems that the ceramic junction has with viscous samples or suspensions can be solved with a larger junction which cannot be so easily blocked and which can be easily cleaned.

One such junction is the sleeve junction. This junction consists of an electrode shaft with a ground glass part over which a ground glass or plastic sleeve can be moved. The electrolyte comes out of the electrode via a hole which is covered with the ground glass or plastic sleeve. The sleeve can be pulled more or less securely over the ground glass part of the shaft to regulate the flow of the electrolyte out of the reference element. A representation of the ground glass junction is given in figure 15. METTLER TOLEDO has for example the sleeve junction electrode **InLab® Science**.

The advantage of this junction is that the electrolyte flow is faster than with the ceramic junction, which is beneficial for some samples such as ion-deficient media. Cleaning is also very easy with this junction as the sleeve can be lifted up completely and all the pollutants can be removed from the junction with deionized water or cleaned with a tissue (as long as the pH membrane isn’t touched!). This stronger electrolyte flow also makes the junction ’self-cleaning’ to a certain extend.

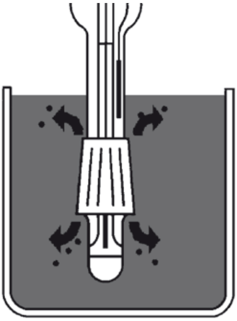


Figure 15. Drawing of electrode with sleeve junction.

The main application for this junction is in areas where the benefits of having fast electrolyte flow and a blockage resistant junction are required for accurate pH measurements.
The fast ion flow is particularly useful in media that have a low ion concentration of a few mmol or lower. These media are considered to be ion-deficient or ion-poor and have very low conductivity. This again causes increased resistance at the junction and leads to contact problems between the reference electrolyte and the measuring solution, giving a very unstable signal. However, this problem is solved by using a circular ground glass junction which creates optimal contact between the reference electrolyte and the measuring solution. Ion-poor media are also difficult to measure but this example will be discussed later on in this chapter.
The fact that the junction can easily be cleaned and is more resistant to blockages comes in handy with very viscous samples like oil, suspensions and emulsions e.g. milk. The electrode can perform longer without having to be cleaned and cleaning is easier. The larger junction contact area is also of benefit for oily samples as this solves the low ion concentration problem that oil samples generally have.

c) Open junctions

The third type of junction is the open junction. This reference electrode is completely open to the environment and has full contact between the reference electrolyte and the sample solution. This is only possible with a solid state polymer reference electrolyte. A schematic diagram of this junction is shown below.

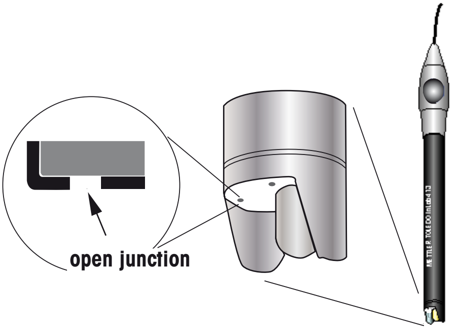


Figure 16. Example of electrode with open junction.

The great advantage of this junction is clearly the fact that it is completely open and can therefore seldom clog. Open junctions can easily cope with very dirty samples constantly providing good measurements. The disadvantage of the solid state polymer reference electrolyte which is used for this open junction is that it has slower reaction times and low electrolyte flow. This means that the samples measured need to have a high enough ion concentration for stable measurements to be possible. Nevertheless, these electrodes are suitable for most samples and are very robust.

2.2. Reference systems and electrolytes

Of all the possible reference systems developed for reference elements, only a few are of practical importance. These are the silver/silver chloride, iodine/iodide and the mercury/calomel systems, as well as some of their adaptations. Due to environmental considerations, however, the calomel reference electrode is no longer widely used. Here we only discuss the most important reference system, the silver/silver chloride system.
The potential of the reference electrode system is defined by the reference electrolyte and the reference element (silver/silver chloride). The conventional construction of this reference system is a silver wire coated with AgCl. For this version of the Ag/AgCl reference system it is important that

the reference electrolyte has a very high (saturated) AgCl concentration to ensure that the reference element wire doesn't get stripped of the AgCl. If this were to happen the reference element would stop working.
A recent improvement of this type of reference element was made with the development of the ARGENTHAL™ reference element. The ARGENTHAL™ reference element consists of a small cartridge filled with AgCl particles that provide the silver ions for the chemical reaction at the lead off wire. This cartridge contains enough AgCl to last the lifetime of the electrode.

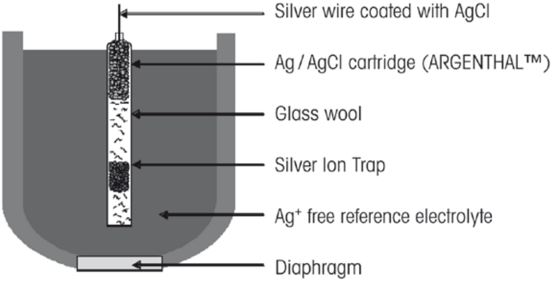


Figure 17. Schematic drawing of the ARGENTHAL™ reference system.

Which type of reference electrolyte is used in an electrode strongly depends on the reference system and on the type of sample used. Whereas the reference system can either be conventional silver wire or ARGENTHAL™, the sample can be divided into two classes namely aqueous and non-aqueous matrices.
For both aqueous and non-aqueous solutions it is important that the reference electrolyte contain plenty of ions to keep the reference system working well. Ideally, the salts used to provide these ions in the reference electrolyte are very soluble in the solvent, are pH neutral (so that they do not influence the measurements when flowing out of the electrode) and do not precipitate out by reacting with other ions present in sample or buffer. KCl matches these requirements best for aqueous solutions and LiCl is best suited for use with non-aqueous solutions.
The conventional Ag/AgCl reference system needs the presence of an electrolyte saturated with AgCl so that the lead off wire does not get stripped of AgCl. The reference electrolyte of choice is therefore, 3 mol/L KCl saturated with AgCl. The disadvantage of this electrolyte is that silver ions can react with the sample to form an insoluble precipitate thereby blocking the junction.

The ARGENTHAL™ reference system has a cartridge with AgCl granules which ensure that AgCl is constantly available. This cartridge contains enough AgCl to last the lifetime of the electrode. Typically this ARGENTHAL™ system comes in combination with a silver ion barrier which stops silver ions from passing into the electrolyte. The advantage of these features of the ARGENTHAL™ reference system is that one can use standard 3 mol/L KCl as a reference electrolyte rather than 3 mol/L KCl saturated with AgCl, so in combination with the silver ion trap there are no free Ag+ ions in the electrolyte which could cause a precipitate after reaction with the sample.

A phase separation in the contact area between electrolyte and sample solution at the junction can cause an unstable signal, therefore deionized water is used as a solvent for the reference electrolyte in aqueous samples, and ethanol or acetic acid is used as solvent for non-aqueous systems.

A brief overview of the possible reference system/electrolyte combinations is given below:

Electrolyte for aqueous samples		**Electrolyte for non-aqueous samples**
ARGENTHAL™	**Conventional**	**ARGENTHAL™**
3 mol/L KCl + H2O	3 mol/L KCl + AgCl + H2O	LiCl + Ethanol/ LiCl + Acetic acid

Figure 18. Overview of reference electrolytes to be used.

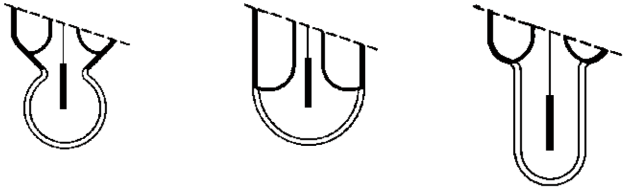
In addition to the above-mentioned liquid electrolytes, there are also gel and solid polymer electrolytes. Electrodes delivered with these electrolytes cannot be refilled.

The electrode response time is strongly dependent on the type of electrolyte used. Liquid electrolyte electrodes show a very quick response time and give the most accurate measurements. Gel and solid polymer electrolyte electrode both have longer response times, but they are virtually maintenance-free.

2.3. Types of membrane glass and membrane shapes

The pH glass membrane of an electrode can have several different shapes and properties, depending on the application the electrode is used for. The selection criteria here are sample consistency, volume and temperature, the required measurement range and the concentration of ions present in the sample.

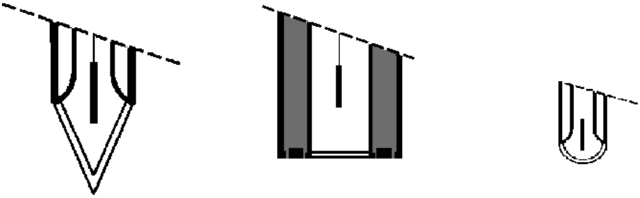
The most obvious property is the shape of the membrane and in figure 19 a selection of membrane shapes is shown together with their properties and proposed usage.



Spherical
For low temperature samples:
resistant to contraction

Hemispherical
Small sample volume:
pH membrane only
on the bottom

Cylindrical
Highly sensitive
membrane: large surface
area, lower resistance



Spear
For semi-solids and solids:
punctures the sample
easily

Flat
For surfaces and drop
sized samples:
very small pH-membrane
contact area

Micro
Samples in reaction
tubes: very narrow
electrode shaft

Figure 19. Differently shaped pH membranes.

The membrane glass is also important for the measurement properties of the electrode. The table below gives an overview of the various types of METTLER TOLEDO pH membrane glasses.

Type of membrane glass	**Properties/samples**
HA – High alkali glass	For high temperatures and high pH values: extremely low alkali error
LoT – Low temperature glass	For low temperatures and low ion concentrations: low resistance glass
A41	For high temperatures; resistant to chemicals
U – Universal glass	For standard applications
HF – Hydrofluoric acid resistant glass	For samples containing Hydrofluoric acid (up to 1 g/L)
Na – Sodium sensitive glass	Only used for sodium detecting electrodes: sodium specific glass

The HF membrane glass electrode is more robust in solutions with hydrofluoric acid than standard pH electrodes. Hydrofluoric acid above certain concentrations (> 1 g/L) and below pH 5 attacks glass and prevents the development of a gel layer on the standard pH glass membrane. This again leads to unstable measurement values and also reduces the life span of the electrode.
At higher hydrofluoric acid concentrations, an antimony electrode such as the Sb850-SC[1] with a special reference electrode (e.g. DX202-SC[2]) must be used.

2.4. pH electrodes for specific applications

Now that we have seen what different types of junctions, electrolytes and membranes exist in pH electrodes, we will have a look at what this means for the measurement of the pH in different systems.

Easy samples

A simple pH electrode is sufficient for routine measurements in chemistry labs where a lot of aqueous chemical solutions are tested. The advantage of the simple pH electrode is that it is very easy to use and isalso very robust. In general, these electrodes are made of glass and have a ceramic junction. They are also refillable, which means that you can refill the electrolyte thereby cleaning the electrode and prolonging its lifetime. An electrode of choice for these simple lab

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[1] The Sb850-SC electrode is a METTLER TOLEDO Antimony half cell electrode, 59904435

[2] The DX202-SC electrode is a METTLER TOLEDO plastic reference electrode, 51109295

measurements is the **InLab® Routine** with or without temperature sensor. The **InLab® Routine Pro** has an integrated temperature sensor for automatic temperature measurement and compensation during measurement.

Complex samples or such of unknown composition

Measuring the pH of complex samples can be somewhat tricky, since the dirt in the sample can hinder correct measurements. Examples of such applications are soil acidity measurements, quality control in foodstuffs such as soups and measurements in colloidal chemical systems. The risk of blockages with such samples would be very high if one were to use a pH electrode with a ceramic junction. Therefore it is best to use a pH electrode with an open junction such as the **InLab® Expert** which has a solid state polymer reference electrolyte. This electrode has a hole in the shaft which allows direct contact between the electrolyte and sample.
For temperature compensation during the measurement it is possible to use an electrode with a built-in temperature sensor such as the **InLab® Expert Pro**.

Emulsions

Another class of samples that require special care when doing pH measurements are emulsions, for example paints, oil in water dispersions, milk and other dairy products. Such samples can also block the junction of pH electrodes when the dispersed phase of the emulsion (the 'mixed-in' part) blocks the junction. The emulsion particles which can cause blockages are very small; therefore it is not necessary to measure with an open junction. Since electrodes with solid state polymers have relatively slow reaction times compared to electrodes with a liquid electrolyte, it is best to measure emulsions with electrodes that have a sleeve junction. The sleeve junction cannot be blocked easily and has a large contact area with the sample. If the junction should get blocked, it can easily be cleaned by moving the sleeve away from the junction and cleaning the electrode.
An example of this kind of electrode is the **InLab®Science**, or the **InLab® Science Pro** which has a built-in temperature sensor. Electrodes with a sleeve junction have a large contact area between the reference electrolyte and sample solution and therefore are also suitable for samples which cause an unstable signal.

Semi-solid or solid samples

Standard pH electrodes are generally not able to withstand the pressure of being pushed into a solid sample; therefore one needs a special electrode which is able to penetrate the sample in order to measure the pH. The shape of the membrane is also important as it needs to be formed in such a way as to ensure a large contact area with the sample, even if the electrode is pushed into the sample with force.

The METTLER TOLEDO electrodes most suitable for these kinds of applications are the **InLab® Solids** or **InLab® Solids Pro**. While their spear shaped point enables them to pierce the sample, the membrane shape ensures accurate measurements. The **InLab® Solids** also has an open junction, which further prevents the junction from being blocked by the (semi-) solid sample. This electrode is typically used for quality control or checking production processes of cheese and meat.

Surfaces and very small samples

One sometimes needs to measure the pH of a sample with a volume so small that it doesn’t cover the tip of a pH electrode. For these kinds of measurements there is only one solution, namely a flat pH electrode. This electrode only needs a surface to be able to measure pH.

Applications for this type of electrode include the determination of the pH of skin during a health check-up and the pH of paper as required in the manufacture of archival grade paper for important documents.

There are many other applications where only very small volumes are available for pH determinations, such as when measuring the pH of a drop of blood. Here the flat pH electrode is placed directly on the drop spreading out the sample over the surface of the flat membrane. Other applications involve very expensive biochemical samples of which only a tiny amount is available.

The METTLER TOLEDO electrode best suited for this purpose is the **InLab® Surface.**

Small samples and difficult sample containers

Some pH applications call for an electrode which only needs a small sample volume or can reach into difficult sample vessels, such as when measuring pH values in test tubes, Eppendorf tubes or narrow NMR sample tubes.

Such containers with small sample volumes generally require a small and narrow pH electrode which can reach the sample and allow for pH determinations. A good example of an electrode with these features is the **InLab® Micro (Pro)**.
For the smallest samples down to 15 µL a specialist like the **InLab® Ultra-Micro** is needed. The extremely small membrane and cleverly placed ceramic junction allow for measurements in well plates, centrifuge vials and other particularly small containers often used in life sciences.

High sample throughput or very viscous samples
For certain challenging applications it is advantageous to use an electrode with SteadyForce® reference. The **InLab® Power and InLab® Power (Pro)** has been designed so that the inner electrolyte is under pressure, which has the advantage of preventing the sample from getting into the electrode regardless of the characteristics of the sample or application. This means that the measurements are both reliable and fast since the electrolyte flow is always sufficient for stable measurements.
For very viscous samples the **InLab® Viscous** works best: the combination of SteadyForce reference and specially designed tip allows for quick measurements despite the applicative challenges.

2.5. Electrode maintenance

Regular maintenance is very important for prolonging the lifetime of any pH electrode. Electrodes with liquid electrolyte need the electrolyte to be topped-up when the level threatens to become lower than the level of the sample solution. This way a reflux of the sample into the electrode is avoided. The complete reference electrolyte should also be changed regularly, e.g. once a month. This ensures that the electrolyte is fresh and that no crystallization occurs despite evaporation from the open filling port during measurement.
Be careful not to get any bubbles on the inside of the electrode, especially near the junction. If this happens the measurements will be unstable.
To get rid of any bubbles, gently shake the electrode in the vertical motion like with a fever thermometer.

2.6. Electrode storage

Electrodes should always be stored in aqueous and ion-rich solutions. This ensures that the pH-sensitive gel layer which forms on the pH glass membrane remains hydrated and ion rich. This is necessary for the pH membrane to react in a reliable way with respect to the pH value of a sample.
Short term storage

In between measurements or when the electrode is not being used for brief periods of time, it is best to keep the electrode in a holder containing its inner electrolyte solution (e.g. 3 mol/L KCl), or in a pH 4 or pH 7 buffer. Ensure that the level of solution in the beaker is below that of the filling solution in the electrode.

For long term storage, keep the electrode wetting cap filled with the inner electrolyte solution, pH buffer 4 or 0.1 mol/L HCl. Make sure that the filling port for reference and combination electrodes is closed so as to avoid loss of the electrolyte solution through evaporation, which can cause the formation of crystals within the electrode and junction.
Never store the electrode dry or in distilled water as this will affect the pH-sensitive glass membrane and thus shorten the lifetime of the electrode. Although regeneration can restore an electrode that has been incorrectly stored, following these recommendations will ensure that your electrode is always ready to use.

Temperature sensors
Rinse the temperature sensors after use and store dry in the packing box to prevent damage.

2.7. Electrode cleaning

To clean the electrode, rinse it with deionized water after each measurement but never wipe it clean with a tissue. The rough surface of the paper tissue will scratch and damage the pH-sensitive glass membrane removing the gel-layer and creating an electrostatic charge on the electrode. This electrostatic charge causes the measured signal to become very unstable. Special cleaning procedures may be necessary after contamination with certain samples. These are described in greater detail below.

Blockage with silver sulfide (Ag_2S)
If the reference electrolyte contains silver ions and the sample being measured contains sulfides, the junction will get contaminated with a silver sulfide precipitate. To clear the junction of this contamination, clean it with 8% thiourea in 0.1 mol/L HCl solution[3].
Blockage with silver chloride (AgCl)

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[3] This thiourea solution can be ordered from METTLER TOLEDO (51340070)

The silver ions from the reference electrolyte can also react with samples that contain chloride ions, resulting in an AgCl precipitate. This precipitate can be removed by soaking the electrode in a concentrated ammonia solution.

Blockage with proteins

Junctions contaminated with proteins can often be cleaned by immersing the electrode into a pepsin/HCl (5 % pepsin in 0.1 mol/L HCl) solution for several hours[4].

Other junction blockages

If the junction is blocked with other contaminations, try cleaning the electrode in an ultrasonic bath with water or a 0.1 mol/L HCl solution.

2.8. Electrode regeneration and lifetime

Even electrodes that have been well maintained and properly stored may start performing poorly after some time. In such cases it may be possible to regenerate the pH-sensitive glass membrane and restore the electrode to its previous level of performance using an ammonium bifluoride regeneration solution. This regeneration solution is based on a highly diluted solution of hydrofluoric acid which etches away a very thin layer of the glass membrane, exposing a fresh surface area.

When using the regeneration mixture, do not to leave the electrode in the solution for longer than 1–2 minutes or the whole pH-sensitive membrane will be corroded away and the electrode rendered useless.

The expected lifetime of a correctly used and maintained pH electrode is around one to three years. Factors that contribute to a reduction of the lifetime of an electrode include high temperatures and measuring at extreme pH values.

2.9 Intelligent Sensor Management

Avoid mistakes and save time with Intelligent Sensor Management (ISM®). Whether you are measuring pH, conductivity or dissolved oxygen, the revolutionary ISM® technology supports you in your daily work

The SevenExcellence, SevenCompact and SevenGo Duo™ meters incorpo-

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[4] This pepsin solution can be ordered from METTLER TOLEDO (51340068)

[5] This regeneration solution can be ordered from METTLER TOLEDO under part number 51340073

rate Intelligent Sensor Management (ISM®). This ingenious system offers great advantages such as:

- **Secure and efficient** – After connecting an ISM® sensor the current sensor calibration data and the sensor ID are immediate transferred to the meter. No need to calibrate again.
- **Always up to date** – After the calibration of an ISM® sensor the new calibration data are instantaneously transferred from the meter to the sensor chip, where they belong!
- **Backup certificate guaranteed** – The initial factory calibration data of an ISM® sensor can be reviewed and transferred to a PC or printer. Print out your certificate any time.
- **Conclusive calibration history** – The last five calibrations data are stored in an ISM® sensor, including the current calibration; can be reviewed and transferred to a PC or printer.
- **Easy lifetime monitoring** – The maximum temperature that the ISM® sensor has been exposed to during measurement is monitored automatically and can be reviewed for valuation of electrode lifetime.

Intelligent pH electrodes for any imaginable pH application with ATC

METTLER TOLEDO supplies pH electrodes for all possible applications. The most important electrode models are available with ISM®. They all come with an integrated temperature probe for automatic temperature compensation (ATC):

- **InLab® Expert Pro-ISM (waterproof to IP67)**
  Easy-to-use pH generalist with polymeric XEROLYT® electrolyte and two open reference junctions
- **InLab® Routine Pro-ISM**
  Classical, refillable glass pH electrode for routine measurements of aqueous samples

- **InLab® Science Pro-ISM**
  pH generalist with movable glass junction for easy cleaning, ideal for complex sample matrices, emulsions, etc.
- **InLab® Solids Pro-ISM**
  Robust puncture pH electrode with spear tip shaft made of hardened glass, perfect for any solid or semi-solid sample like cheese, meat, fruit, etc.
- **InLab® Power Pro-ISM**
  Premium pH sensor with SteadyForce® pressurized reference system, ideal for all kinds of sample including complex sample matrices, emulsions, etc.
- **InLab® Pure Pro-ISM**
  Precise pH specialist for purified water, ultra-pure water, drinking water, etc.
- **InLab® Micro Pro-ISM**
  5mm shaft diameter for small containers or particularly precious samples

2.10. Additional information

For further information and the latest product offerings, please refer to the following METTLER TOLEDO internet pages:

Electrode selection and specifications guide:
www.mt.com/electrodes
www.mt.com/electrode-guide

pH meters:
www.mt.com/pH

Explore SevenGo Duo™ and intelligent sensors with 3D simulator, at:
www.MoreAbout7.com

3. Troubleshooting guide for pH measurements

Problems which arise during pH measurements can have different sources; from the meter, cable and electrode, down to the buffer solutions, measuring temperature and sample (application). Special note should be taken of the symptoms of the problem as these are useful for locating the origin of the fault. The following table gives an overview of symptoms and causes:

Readings too high/too low or off-scale readings "---"	Check meter, cable, electrode, calibration procedure and sample temperature
Value does not change	Check meter, cable and electrode
Slow response time	Check electrode and sample/application
High offset after calibration	Check electrode, buffer solutions and calibration procedure
Low slope after calibration	Check electrode, buffer solutions and calibration procedure
Calibration error	Check meter, cable, electrode, buffer solutions and calibration procedure
Drifting measurement values	Check electrode and sample/application

3.1. Checking meter and cable

Symptoms which are usually related to pH meter or cable problems are off-scale readings, readings that don't change or no reading at all.
To test if the problem comes from the meter or cable follow the steps described below:
Step 1: Check if the pH meter can be switched on. If not, replace the battery or check the power supply.
Step 2: Switch the instrument to mV mode. Check the potential with a shorting clip: The reading should be 0 mV (± the accuracy of the meter). If this is not the case, check that the unit is properly grounded or plugged into the wall outlet.
Step 3: Use a pH simulator and check the mV readings at pH 4.01, 7.00 and 10.00. Readings of about 0 mV and ±180mV should be obtained respectively. If these values are not obtained, a factory reset or a repair may be required.
Step 4: Check all the connections. If the electrode has a detachable cable, test it by replacing it with an identical one. If you are using an

electrode with fixed cable, then check to see whether there is a change in the signal when you bend the cable.
If the checks above show that the problem lies with the meter or cable, you should contact your local supplier for help.

3.2. Checking sample temperature and the application

The symptoms typically related to application problems are drifting measurement values, slow electrode response and an unusual number of electrode failures. Doing the following tests will show whether the problem is coming from the sample:
Step 1: Measure the mV signal of a fresh pH 4.01 or pH 7.00 buffer solution at constant room temperature and check the response time of the electrode. Then immerse the electrode in another buffer solution with a different pH and wait 30 seconds. Take note of the electrode potential and observe for a further 30 seconds. The potential should not change more than ±2 mV, nor should it drift in one direction.
Step 2: Check whether the sample temperature stays constant during the measurement. As the pH of a sample is temperature dependent (see also section 4.6) the values will keep drifting until the sample has reached a constant temperature.
Step 3: Check that you are using the optimal electrode for your application (see section 2.4 or consult our electrode selection guide at www.electrodes.net). The following is an example of a typical application problem that is easily solved by using another electrode:

- Electrodes in ion-poor solutions such as distilled water respond slower and measurements are likely to drift. In these solutions, stability may not be achieved for three or four minutes.

➪ Use an electrode with a higher electrolyte flow such as the **InLab® Science**.

3.3. Checking buffers and calibration procedure

Buffer related problems often result in inaccurate measurement values (higher or lower results than expected) or the inability to perform 2 point calibrations. The following five steps will help you identify whether the problem lies with the buffer solutions:
Step 1: Use fresh buffers. Open a new bottle of buffer solution in order to rule out the possibility of the problem arising from a contaminated buffer.
Step 2: Check the expiry date of your buffer solution.
Step 3: Check that you are using the right set of buffers. In the METTLER

TOLEDO pH meters there are several buffer groups that you can choose from (see also section 5.1).

Step 4: Make sure that you are using the buffers in the right sequence during calibration. METTLER TOLEDO meters all have automatic buffer recognition which allows calibration in any sequence, but other meters may require the calibration to be done in a pre-defined sequence.

Step 5: Make sure that the pH value of your sample lies within the calibration range. Each pH buffer has a certain tolerance (e.g. ±0.02 pH), so that measuring outside the calibration range leads to a measurement uncertainty which is higher than the tolerance given by the buffer solutions. The illustration below provides a graphical representation of this phenomenon.

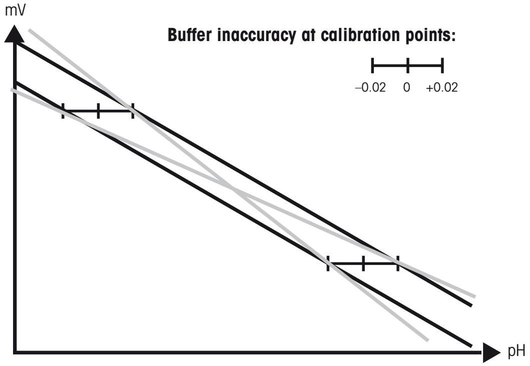

Figure 20. Measurement uncertainty inside and outside the calibration range. From the graph it can be seen that the potential inaccuracy outside the calibration limits gets larger the further the measurement is away from the calibration range (light grey lines). Within the calibration range the inaccuracy remains within the buffer defined inaccuracy of 0.02 pH units (dark grey lines).

Some tips for buffer usage

- Keep the buffer solution bottles tightly sealed at all times; use the decanted buffer immediately and only once.
- Ensure that no contaminants enter the buffer solution bottle.
- Store the calibration buffer at normal, ambient temperatures.
- Do not store the buffer solution bottles in direct sunlight.
- Never use a calibration buffer that is past its expiration date or that you suspect is contaminated.

3.4. Checking the electrode

There are a number of symptoms usually related to electrode failure: inaccurate or slow response, noisy and/or unstable readings, off-scale readings, no change in signal and the inability to perform a multipoint calibration.

Step 1: Check the mV signals. Always use fresh buffer solutions when doing this test.

- Check the zero potential by switching to mV mode and dipping the pH electrode in pH 7.00 buffer. The reading should be 0 mV ± 30 mV with a Ag/AgCl (ARGENTHAL™) reference system.
- Immerse the electrode in a pH 4.01 or pH 10.00 buffer solution, the meter reading should now be at least ±150 mV greater than the zero potential.

Step 2: Check the electrolyte.

- Check that there is enough reference electrolyte solution in the electrode (this is not applicable for gel filled electrodes). The electrolyte level must be above the internal elements and above the sample or storage solution.
- Make sure that the electrolyte filling hole (side aperture) of liquid filled electrodes is open during measurement. This is necessary to allow for contact between the sample and reference systems.
- Visually check the inside of the electrode. If precipitates are present, replace the electrolyte. Electrolyte crystals on the inside and salt deposits on the outside of the electrode can be removed with distilled water.
- Check that the electrode has been filled with the correct reference electrolyte solution and replace the electrolyte regularly: Empty the reference chamber, rinse with deionized water and refill with fresh electrolyte solution.

Step 3: Check the junction.

- Look for signs of blockage or discoloration of the junction. If the junction is blocked and the electrode has a replaceable ceramic junction, follow the description in the instruction manual to exchange it.
- If the fixed sleeve junction is blocked soak the electrode in hot (50 °C - 60 °C) reference electrolyte for a few minutes or until the reference electrolyte solution flows freely.
- With a movable sleeve junction ensure that the junction is clean and wet behind the sleeve by carefully moving the sleeve (with the filling aperture closed), cleaning and wetting behind it and again tightening it.
- Check that there are no air bubbles behind the junction.

- Soak electrode junction overnight in pH 4 buffer.
- Sometimes the material clogging the junction requires more specific action. In this case it is important to know the source of the blockage, so as to choose the solvent or reagent best suited to removing the material clogging the junction:
  - Blockages with AgCl: use a concentrated ammonia solution
  - Blockages with Ag_2S: use 8% thiourea in 0.1 mol/L HCl
  - Blockages with proteins: use 5% pepsin in 0.1 mol/L HCl
  - In the case of other contaminations, place the electrode with its junction in 0.1 mol/L HCl in an ultrasonic bath

After any of the above cleaning steps, a new calibration has to be carried out.

Step 4: Check the pH membrane:

- Check if the pH membrane is damaged, contaminated or dehydrated. Degrease the pH membrane by rinsing with ethanol, acetone or a soap solution. Then rehydrate the membrane by soaking it in an acidic solution (e.g. 0.1 mol/L HCl).
- If measurements have been made in samples containing protein, remove any protein deposits by soaking the electrode bulb in 5% pepsin in 0.1 mol/L HCl[5].
- If all of the above steps fail, try to regenerate the pH membrane in a reactivation solution containing NH_4HF_2 for 1-2 minutes[6]. This should only be done as the last measure and only for a very short time as the solution slowly etches away the pH membrane.

Step 5: Check the age of the electrode.

- If a METTLER TOLEDO electrode is used, the age of an electrode can be seen in the serial number of the electrode. The first number indicates the year and the following two numbers the week in which it was produced. An electrode that is simply too old or worn out needs to be replaced.

Most of the problems which arise during pH measurements come from the electrode or sample. In order to eliminate these as the problem source all tests should always be carried out with fresh buffer solutions at room temperature.

Once an electrode is found to be faulty, one has to consider that the sample may still be the initial reason for the problem as it may have

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[5] This can be obtained from METTLER TOLEDO under the part number 51340068

[6] This can be obtained from METTLER TOLEDO under the part number 51340073

damaged the electrode and another type of electrode may be required in future in order to ensure a longer electrode life expectancy (see chapter 2). Nevertheless, every electrode has a certain lifetime and depending on the application, sample temperature and electrode treatment this can vary from a few hours to several years.
Additional help with pH troubleshooting can be found at
www.electrodes.net

4. Comprehensive pH theory

In the previous sections the practical aspects of pH measurements were discussed. This chapter will principally deal with the theoretical background to pH measurements and is intended for readers wishing to acquire a more fundamental understanding of pH theory. First the basic pH theory is developed, then we will have a look at the sensor theory and at the end some special topics will be dealt with.

4.1. Definition of the pH value

According to Sørenson the pH is defined as the negative logarithm of the H_3O^+ ion concentration:

$$pH = -\log [H_3O^+]$$

From the equation we can see that if the H_3O^+ ion concentration changes by a decade, the pH value changes by one unit. This nicely illustrates how important it is to be able to measure even small changes in the pH value of a sample.
Often, the pH theory is described with H^+ ions in connection with pH values, although the correct ion to refer to is the hydronium (or as it is officially known according to IUPAC: oxonium) ion (H_3O^+):

$$H^+ + H_2O \leftrightarrow H_3O^+$$

Not only acids and bases show dissociation behavior to form hydronium ions or hydroxide ions, but pure water also dissociates to form hydronium and hydroxide ions:

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

The dissociation constant for this behavior is called Kw and is also known as the autoionization or autodissociation of water:

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]} = [H_3O^+][OH^-] = 10^{-14}\ mol/L\ (25\ °C)$$

From the K_w equation we can see that when equal amounts of H_3O^+ and OH^- are present the solution is neutral, and this is the case when both $[H_3O^+]$ and $[OH^-]$ are 10^{-7} mol/L, so at pH 7. When a higher concentration of H_3O^+ ions is present, then the pH value goes into the acidic region of the pH scale, e.g. a H_3O^+ concentration of 10^{-3} mol/L (and thus $[OH^-] = 10^{-11}$ mol/L) gives a pH value of 3.

To be able to measure this value in a sample solution we need to know how the pH sensors react to the acid concentration in the solution. We will have a look at this later on in this chapter.

4.2. Correlation of concentration and activity

Up to now we have only discussed the concentration of acids and bases as the determining factor for the pH value measurement. In reality though what is actually measured by a pH sensor is the activity of the hydronium ions in solution. The concentration is only used, as in many other chemical processes, as a simplification for using the activity of a solution.
In many conditions the use of the concentration is a very good approximation to using the activity.
The activity of the hydrogen ion (a_{H^+}) is defined by the concentration of hydrogen ions and the activity coefficient (γ_{H^+}). The concentration in this case is usually given as the molality (b = mol/kg solvent) and not the molarity (c = mol/L solution), as molality is a less ambiguous definition. The activity is then given by:

$$a_{H^+} = \gamma_{H^+} \cdot b_{H^+}$$

In dilute solutions the approximation $a_{H^+} = b_{H^+}$ can be made.
The activity constant is not a universal constant; the value of this number again depends on various factors, like temperature (T), total ion strength (I), the dielectric constant, ion charge (z), the size of the ions (in Angstroms) and also on the density (d) of the medium.
There are two main effects which can be observed when noting the difference between ion activity and ion concentration. These are the so-called salt effect and medium effect.
The influence of salts present in a solution of which the pH value is measured is called the salt effect. This salt effect is denoted by the symbol

$$\gamma^{x}_{H^+}$$

and is defined as:

$$log\gamma^{x}_{H^+} = \frac{-0.5 \cdot I^{1/2}}{1+3 \cdot I^{1/2}}$$

In this equation I is the symbol for the total ionic strength $\frac{1}{2}\sum c_i z_i^2$

If we assume in the case of pH measurement that both the anion and the hydrogen ion are monovalent, zi will be equal to 1 and the total ion strength I is determined by the molality. The influence of the salt effect on the activity coefficient of selected ion concentrations is shown in the following table.

Molality	0.001	0.005	0.01	0.05	0.1
Activity coefficient	0.967294	0.935044	0.915247	0.857205	0.829586

Figure 21. Table illustrating the salt effect on the activity molality relationship.

When we now compare a pH measurement in a solution of 0.01 mol/L HCl with or without salt present, we get the following comparison:

0.01 mol/L HCl solution:	0.01 mol/L HCl solution with 0.09 mol/L KCl:
$pH = -log\ (b_{H^+} \cdot \gamma^{x}_{H^+})$ $= -log(0.01 \times 0.915)$ $= -log(9.15 \times 10^{-3})$ $= 2.04$	$pH = -log\ (b_{H^+} \cdot \gamma^{x}_{H^+})$ $= -log(0.01 \times 0.829)$ $= -log(0.829 \times 10^{-3})$ $= 2.08$

From this example it can be seen that the pH value increases by 0.04 pH units (the H^+ activity decreases) in solutions with a higher ion strength. This explains why solutions with the same acid content may show different pH values if there are other salt ions present in the solution.
The second effect which links activity to concentration is the so-called medium effect. The medium effect is designated with:

$$\gamma^{m}_{H^+}$$

This effect shows what influence the medium (solvent etc.) will have on the H^+ ion activity. With this effect electrostatic and chemical interactions play an important role. For example, the H^+ activity is 200 times greater in ethanol than in water.
When taking both the salt effect and medium effect into account, the relationship between concentration and activity then becomes:

$$a_{H^+} = \gamma^{x}_{H^+} \cdot \gamma^{m}_{H^+} \cdot b_{H^+}$$

From these examples we can see that it is very important to have detailed knowledge of the measured sample, since the more accurately defined the measuring conditions are, the more reproducible the pH values obtained will be.

4.3. Buffer solutions

Buffer solutions are a very important part of an accurate pH measurement. Standard buffers are used to calibrate the pH sensors and to check their performance. The most important property of a pH buffer, hence its name, is its buffering capacity. This property enables a pH buffer to remain at a constant pH value, even if external substances are introduced into the buffer solution.

The buffering capacity of a buffer solution depends on the fact that weak acids only partly dissociate, causing the following equilibrium reaction:

$$HA \leftrightarrow H^{+} + A^{-}$$

In this equilibrium, the anion A^- can act as a base, since it can withdraw protons from the system. The non-dissociated acid HA, however, can supply the system with protons.

A buffer solution in its equilibrium state therefore has enough anions (A^-) to take up any protons added to the system, but also has enough non-dissociated acid available to replace any protons withdrawn from the system. Since the non-dissociated acid HA can act as an H^+ donor and the dissociated acid A^- as an H^+ acceptor, a buffer solution will be at its most powerful when both HA and A^- are present in equal concentrations.

If we first have a closer look at the theory of buffer solutions, we can then find out how suitable a certain solution is as a buffer. This depends on several properties of the buffer solution, such as buffer capacity, temperature influences, and changes of the pH value due to dilution of the buffer solution. These properties are documented for many standard buffer solutions and can be found in the literature.

From the formula above we can write the equilibrium constant for a dissociated acid is as follows:

$$Ka = \frac{[H^{+}][A^{=}]}{[HA]}$$

This can be then be re-written as

$$\frac{1}{[H^{+}]} = \frac{1}{K_a}\,\frac{[A^{=}]}{[HA]}$$ and then taking the logarithm on both sides:

$$log\left(\frac{1}{[H^{+}]}\right) = log\left(\frac{1}{K_a}\right) + log\left(\frac{[A^{=}]}{[HA]}\right)$$

Since $\log(1/[H^+]) = -\log[H^+] = pH$ and $\log(1/K_a) = -\log K_a = pK_a$, we then get:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad \text{(Henderson-Hasselbalch)}$$

This equation is known as the HENDERSON-HASSELBALCH equation. From this last equation we can see that if a buffer solution is at its strongest and therefore $[A^-] = [HA]$, that the pH value corresponds to the negative log of the dissociation constant,

$$pH = pK_a$$

This equation is very helpful when making a buffer solution of a weak acid with known pKa value.

Buffer capacity (ß)

The buffer capacity is defined as the ability of a buffer solution to maintain its pH value even after the addition of a strong acid or base.
As we have seen in the previous section, the greatest buffer capacity is when $pH = pK_a$, but the overall buffer capacity of a weak acid or base is limited to $pH = pK_a \pm 1$.
As an example of the buffer capacity of a weak acid we will look at a titration curve of acetic acid (CH_3COOH) with OH^- ions titrated into the solution (Figure 22). Acetic acid has a pK_a value of 4.8, so this solution starts with a low pH value and the pH value increases when more hydroxide ions are titrated into the solution. At the beginning the change is quite big with every drop of hydroxide solution, but when the concentrations of the non-dissociated acid and dissociated acid start becoming equal the curve gets flatter. As $[A^-] = [HA]$ when $pH = pK_a$, we expect the curve to become flat around pH 4.8, since this is the pH value where the buffering capacity should be most pronounced.

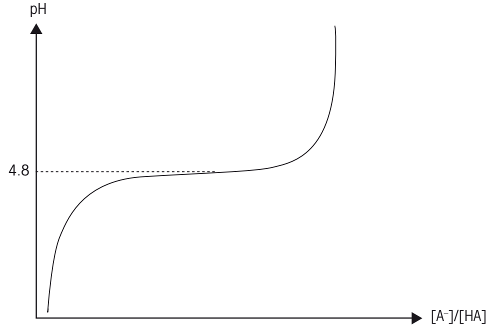

Figure 22. Buffering capacity of acetic acid.

When making and using buffer solutions one has to be aware of external influences on the acid/base equilibrium as well. One example of this could be the uptake of CO_2 from the air.

Dilution value (ΔpH)

The dilution value of a buffer solution indicates how much the pH value changes when the buffer solution is diluted with an equal amount of distilled water.

A positive dilution value means that the pH will increase whereas a negative dilution value means that the pH will decrease with increasing solution.

Temperature effect (ΔpH/ΔT)

We have seen the pH value is derived from the activity of the H^+ ions in the solution. Since the ion activity is temperature dependent, the temperature will also influence the pH value.

The temperature coefficient expresses changes of the pH value per °C.

4.4. The measurement chain in the pH measurement setup

We saw in chapter 1.3, that a pH measurement is actually the measurement of a potential. The changing potential of a pH-sensitive electrode is measured against the stable potential of a reference electrode. A measurement setup was shown in Figure 7.

The principle of the setup is that metal conductors within the 2 electrodes are connected to each other through one or more electrolytes to form a galvanic chain. To this galvanic chain (pH and reference electrode) a meter with a high input resistance is attached and this connects the two electrodes internally and measures the chain potential E.

This galvanic potential E is defined by the Nernst equation:

$$E = E_0 + 2.3\,\frac{RT}{nF} \cdot \log a_{H^+}$$

which we have seen before in figure 6.

In order to be able to compare the galvanic potentials of different electrodes with different reference systems, the standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) was introduced as a universal reference electrode. The potential of the SHE is by definition zero at all temperatures. The SHE consists of a platinized platinum sheet, which is immersed in a solution of $a_{H+} = 1.0$ and surrounded by hydrogen gas at 1 bar.

In the Nernst equation E0 is the standard potential at $a_{H+} = 1$. The factor 2.3 RT/nF (E_N) is the slope of the pH electrode and gives the change in measured potential with tenfold change in H^+ activity, or per pH unit. The value of E_N depends on the temperature T in Kelvin, and is often referred to as the slope factor. Some examples for the slope at certain temperatures are given below in figure 23.

Temperature	E_N Value (mV)
0 °C	E_N = 54.2 mV
25 °C	E_N = 59.2 mV
50 °C	E_N = 64.1 mV

Figure 23. Temperature dependence for the pH electrode slope factor.

When we look at the measurable chain potential E from the Nernst equation in a bit more detail, we find that this chain potential consists of several intermediate potential points, which are shown in figure 24.

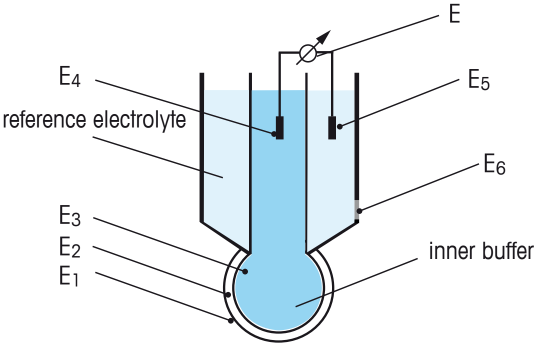

Figure 24. Different sources of potential in a combination electrode

pH electrode

The chain potential starts at the contact area between the sample solution and the pH electrode glass membrane, where the potential E1 is measured in correlation with the pH value of the sample solution. In order to measure E1 and assign a definite pH value to it, all other single potentials in the chain E2 – E6 have to be constant, the only variable signal is caused by the potential difference between inner electrolyte and sample solution over the pH membrane. The last point in the chain is E6, the potential between the reference electrode electrolyte and the sample solution again, which has a constant potential since the reference electrode is insensitive to the pH value of the sample.

The other potentials E2, E3, E4 and E5 are the consecutive steps in the chain from the sample through the pH electrode to the meter, and back again from the meter through the reference electrode to the sample solution. All these separate steps can be seen in figure 24.

The potential E1 is transferred to the inside of the pH membrane glass via the gel layer on the glass membrane and the pH glass membrane (as shown in figure 8), where another gel layer is present as an interface between the inside of the pH electrode and the inner buffer solution. The potential difference between the outside of the pH glass membrane and the inside of the pH glass membrane is the potential E2 in Figure 24.

Physically this works by transferring the potential via an equilibrium of the hydrogen ions which arises at the interface between the measuring solution and the outer pH membrane gel layer. If the activity of the hydrogen ions is different in the two phases, hydrogen ion transport will occur. This leads to a charge at the phase layer, which prevents any further H^+ transport. This resulting potential is responsible for the different hydrogen ion activities in the sample solution and the gel layer. The number of hydrogen ions present in the gel layer is given by the silicic acid skeleton of the glass membrane and can be considered a constant and therefore independent of the measuring solution.

The potential in the outer gel layer of the pH-sensitive membrane is then transferred by the Li^+ ions found in the glass membrane to the inside of the glass membrane, where another phase boundary potential arises (E3 in figure 24).

The potential E3 is then transferred to the lead-off wire in the pH electrode (E4) via the inner buffer solution of the pH electrode and from there to the meter.

Reference electrode

When the pH electrode potential chain (E1 – E4) signal goes to the meter, there needs to be a reference signal available in the meter as well to measure the pH signal against. This is done with the reference part of the electrode, where another potential chain (E5 – E6) ensures this stable potential independent of the sample solution.

From the meter there is a connection to the reference element of the reference electrode and from there an interface between the reference element and the reference electrolyte solution (potential E5).

Of the different reference elements, the silver/silver-chloride element has become the most important one. Compared to the calomel electrode the silver/silver-chloride reference has some important advantages, but it is mainly because of environmental reasons that the calomel reference electrode has almost completely disappeared.

The next step is the potential E6, which is the connection between the reference electrolyte on the inside of the reference electrode and the sample solution on the outside of the electrode. Again, it is important that the potential is stable here as it is used as a reference signal. The junction is naturally very important for this particular contact since it allows the diffusion of the ions through the junction.

The critical property of the junction is the diffusion of ions through it which generates the diffusion potential ($E6/E_{diff}$). The diffusion potential depends not only on the type of junction and its properties, but also on the diffusing ions.

Since E_{diff} is a part of the potential in every measuring chain, the pH values of different measuring solutions can, strictly speaking, only be compared if the diffusion potential is identical in all solutions. In practice this is not always possible, so one tries to keep E_{diff} small and constant to limit the measurement error.

The migration velocity of ions is determined by their charge and size. The size of an ion is determined not by its 'net' size, but by the size of its hydration cover. All ions in aqueous solutions are surrounded by polar water molecules. This means that a small but highly hydrated lithium ion for example migrates slower than a much larger but only slightly hydrated potassium ion. Since the H^+ and the OH^- ions migrate in accordance with completely different mechanisms, they have a much higher ion mobility compared to all other ions. Examples of migration speeds for different ions are shown below in figure 25.

Ionic mobilities (in 10^{-4} cm^2 / s·V) at 25 °C			
H^+	36.25	OH^-	20.64
Li^+	4.01	F^-	5.74
Na^+	5.19	Cl^-	7.91
K^+	7.62	NO_3^-	7.41
NH_4^+	7.62	CH_3COO^-	4.24

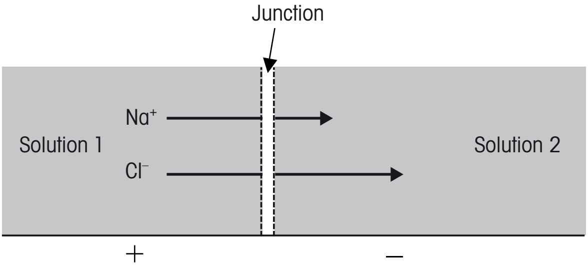

Figure 25. Ion mobility and diffusion of ions through a junction.

Using the example of sodium and chloride ions we see from the table and figure above that the sodium and chloride ions diffuse through a junction from solution 1 into solution 2 at different speeds. Since Cl^- ions in the solution migrate much faster than Na^+ ions, a charge separation occurs.

This charge separation then causes a diffusion potential which counteracts the initial migration. This in turn leads to a dynamic equilibrium which takes a long time to stabilize. This means that the different diffusion speeds of the ions in the reference electrolyte through the junction cause a slower response time of the electrode. So it is very important that the junction is highly porous allowing a strong electrolyte flow so that the response time is kept as short as possible.

The charge separation and therefore the diffusion potential E_{diff} increases when the mobility of the cations and anions is very different. This effect is particularly noticeable in strongly acidic and basic solutions, the typical solutions often used in pH measurements.

Another factor which determines E_{diff} is if one of the two solutions is very dilute. A typical example of such a pH measurement is an ion-deficient sample such as pure water. In this case the diffusion potential also increases since the charge difference is amplified by the ion-deficient sample outside the junction.

To keep the diffusion potential as small as possible, one should ensure that the reference electrolyte is a concentrated and equitransferent solution (equal mobility of anions and cations). This is the case with the most commonly used KCl and KNO_3 reference electrolytes, as can be seen in the figure 25.

However, despite taking such precautions, the diffusion potential at extreme pH values is considerable even with ideal reference electrolytes. This is demonstrated in the example below (at 25 °C):

Inner electrolyte	Sample solution	Diffusion potential	ΔpH
KCl (sat.)	HCl (1 mol/L)	E_{diff} = + 14.1 mV	0.238 pH units
KCl (sat.)	NaOH (1 mol/L)	E_{diff} = - 8.6 mV	0.145 pH units

This description of the diffusion potential makes it clear that some pH measurements will therefore be more difficult than others. Care should be taken with very dilute solutions, or solutions which are ion-poor, such as non-aqueous solutions. In such cases the diffusion potential will become quite high resulting in an unstable reference signal. Contaminated junctions also have this effect as the blockage of the junction inhibits the free flow of electrolyte.

4.5. Calibration/ adjustment of the pH measurement setup

There are two settings in the meter which are adapted to the specific electrode attached to the meter and are affected when the pH electrode and the meter setup is adjusted, namely the zero point offset (mV) and the slope (mV/pH) of the electrode. Since there are two settings that have to be adjusted it follows that a two-point calibration is the minimal adjustment that should be performed.

An adjustment of the zero point and the slope has to be performed to compensate for any deviations from the theoretical values. These deviations occur due to non-ideal behavior of the electrode. A buffer solution with a pH value of 7.00 corresponds to the zero point of most glass pH electrodes and is especially intended for the zero point calibration. In most cases, depending on the expected measurement range, buffer solutions of pH 4.01 or pH 9.21 (or 10.00) are recommended to adjust the slope.

In the figure below both these adjustments are illustrated. The drawing on the left depicts the offset adjustment, so that the mV deviation from the theoretical 0 mV at pH 7.00 is shown. The slope adjustment is illustrated on the right. Here the deviation from the theoretical 59.16 mV/pH at 25 °C is depicted.

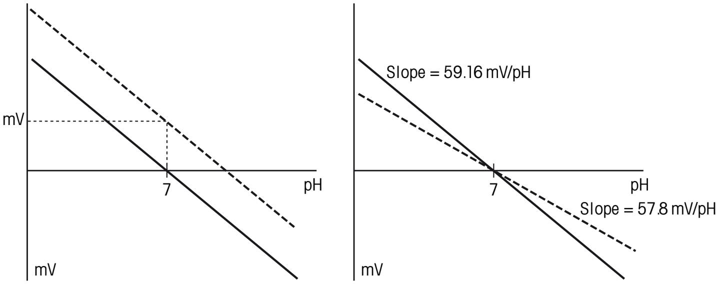

Figure 26. Left: offset adjustment of a pH electrode in the pH meter, right: slope adjustment of a pH electrode. Solid lines show ideal behavior, dashed lines show real behavior.

4.6. The influence of temperature on pH measurements

Temperature has an influence on both the electrode and the sample. We will take a closer look at this influence in the sections below.

Temperature dependence of the electrode

Temperature influences a pH electrode in several different ways:

Slope

Looking at the Nernst equation, which gives the relationship between measured mV values and pH value of the sample for a pH electrode, we see that the slope contains the temperature in Kelvin:

$$E = E_0 + 2.3\,\frac{RT}{nF} \cdot \log a_{H^+}$$

When we fill in all the numbers, except the temperature in Kelvin (T), we get:

$$E = E_0 - 0.198 \cdot T \cdot pH$$

From this equation we can now clearly see that the slope of an electrode is linearly dependent on the temperature. Because of this linear dependence the behavior is fully predictable and can be compensated for by a pH meter and electrode with integrated temperature sensor.

Isothermal intersection

The isothermal intersection depends on the behavior of the individual potentials E1 to E6 and is a characteristic of every electrode. For an ideal electrode the calibration lines of different temperatures would intersect at the zero point of the electrode (pH 7.00/0 mV) and the slope would always be proportional to the absolute temperature.

Since the overall potential of the pH electrode is composed of the sum over E1–E6, which all have their respective temperature dependencies, the isothermal intersection may not always coincide with the zero point of the electrode.

It is important for an electrode to have the isothermal intersection and the zero point as close together as possible, since the nearer these are to pH 7 the smaller the error in the temperature compensation will be. The measuring error increases with an increasing temperature difference between the calibration and sample solutions, these errors can be in the order of 0.1 pH units. The most accurate pH value is obtained when the temperature of the calibration and sample solutions is identical.

These measurement errors are illustrated in figure 27.

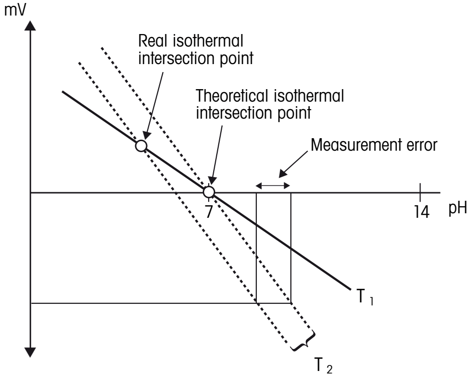

Figure 27. Isothermal intersection, theory and practice.

If the real isothermal intersection does not coincide with the theoretical one the measurement error can be quite large, depending on the temperature difference between samples or between sample and calibration. Furthermore, the error can become significant if the real isothermal intersection is very far from the theoretical intersection, and measurement and calibration differ in temperature.

Further temperature phenomena

The response time of the electrode can also be affected if the temperature changes between or during measurements.
If the change in the temperature of the medium is rapid, a conventional pH electrode will drift until the temperature of the electrode and the medium becomes equal. In order for a combination electrode to react rapidly to the temperature changes in the sample, the temperature of the inner pH electrode and the outer reference electrode must always be identical. This is only possible with a symmetrical arrangement of the pH and reference elements.

Temperature dependence of the measured sample

Every sample solution has a characteristic temperature and pH behavior which can be expressed with the so-called temperature coefficient. This describes how the pH value changes when the temperature changes. Since this pH change is different for every sample, it is almost impossible to compensate for it.
The first point to note is that the dissociation constant of water itself is temperature dependent. In pure water when the temperature increases from 0 and 100 °C, the neutral point shifts 1.34 pH units downwards as a result of the temperature dependent ion product. In other words the Kw of water decreases with increasing temperature. A similar behavior is seen in weak acids and bases, since their dissociation constants are also temperature dependent.
The temperature coefficient is determined by two parameters:

- activity coefficient (γ)
- acid constant

The temperature dependence of the activity constant γ becomes larger when γ is further away from 1, i.e. when there is a large deviation between the concentration and the activity of a solution. This is especially the case for concentrated solutions and in the presence of ions with a high electrical charge.
The acid constant pK_a is also temperature dependent, but this relationship is non-linear, which means that the dissociation behavior of an acid changes with temperature. This dissociation behavior causes a change in the H^+ concentration with a change in temperature and thus a real pH value change.

In general, organic acid/base systems show a higher temperature coefficient than inorganic systems, and alkaline solutions are more temperature dependent than acidic solutions.
This is illustrated by the following examples:

pH value at:	**20 °C**	**30 °C**
0.001 mol/L HCl	3.00	3.00
0.001 mol/L NaOH	11.17	10.83
Phosphate buffer	7.43	7.40
Tris buffer	7.84	7.56

These examples clearly show that large temperature coefficients can even occur in nearly neutral solutions and therefore that temperature has to be taken into account when comparing pH measurements obtained at different temperatures. Ideally, samples should be measured at the same temperature to be able to make comparisons between them.

In general it is not possible to do temperature compensation for real changes in pH for chemical solutions. However, temperature compensation tables have been determined for standard buffer solutions. The tables for the standard METTLER TOLEDO buffer solutions are provided in appendix 5.1. These tables are also programmed into all METTLER TOLEDO pH meters and are automatically used when a temperature sensor is plugged into the pH meter. This ensures that the correct pH value is used for the buffer at the temperature at which the calibration is performed.

4.7. Phenomena in the case of special measuring solutions

Different problems may occur when measuring in samples that do not consist of easy to measure clear, aqueous solutions. These problems can be of electrical or chemical origin and are briefly discussed in this section.

Alkaline error

The alkaline effect is the phenomenon where H^+ ions in the gel layer of the pH-sensitive membrane are partly or completely replaced by alkali ions. This leads to a pH measurement which is too low in comparison with the number of H^+ ions in the sample. Under extreme conditions where the H^+ ion activity can be neglected the glass membrane only responds to sodium ions.

Even though the effect is called the alkaline error, it is actually only sodium or lithium ions which cause considerable disturbances. The effect increases with increasing temperature and pH value (pH > 9), and can be minimized by using a special pH membrane glass. An example of electrode behavior under these conditions is given in figure 28.

Acid error

In strongly acidic media, acid molecules are absorbed by the gel layer leading to a decrease in the H^+ ion activity in the gel layer. Consequently an artificially high pH value is registered. The acidic error is less disturbing than the alkaline error and is only relevant at very low pH values.
An illustration of this is also given in figure 28.

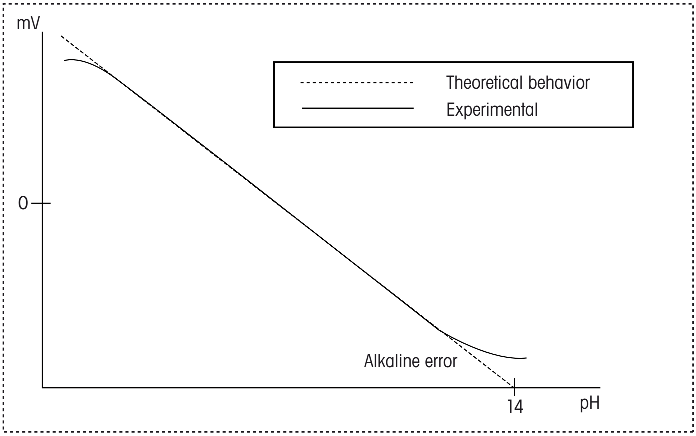

Figure 28. Illustration of alkaline and acid error electrode behavior.

Reactions with the reference electrolyte

Another problem source can be the occurrence of chemical reactions between electrolytes and the measured solution. The resulting precipitates block the pores of the junction and thus increase the electrical resistance considerably.
When using KCl as a reference electrolyte the following ions can precipitate and form compounds of low solubility:
Hg^{2+}, Ag^+, Pb^{2+}, ClO_4^-
Silver chloride may further react with bromide, iodide, cyanide, and especially with sulfides and sulfide compounds such as cystine and cysteine.

Contamination due to silver sulfide results in a black coloration of the junction. As described in chapter 2.1, contamination of the junction may result in unsatisfactory measurements because of:

- an increase in the response time of the electrode, or
- a diffusion potential (E_{diff}), which enters into the pH measurement as a direct error

In order to prevent such reactions between the electrolyte and the sample solution, one can either use an electrolyte which does not react with the above ions, or one can use an electrode with a double junction and a bridge electrolyte which does not react with the sample.

Organic media

The measurement of pH in organic media or non-aqueous solutions (less than 5% water) presents a special challenge, since the classical definition of pH does not apply for such samples.

When determining the pH value in non-aqueous samples it is important to note that the conventional pH range of pH 0 to pH 14 as based on the dissociation behavior of water and is therefore not valid. In this case the dissociation equilibrium, i.e. the ion product of the solvent used and not the ion product of water is relevant. This can result in completely different concentration ranges for H+ ions in the solvent and thus a completely different pH scale. Figure 28 illustrates this by showing the actual valid pH ranges for some common solvents.

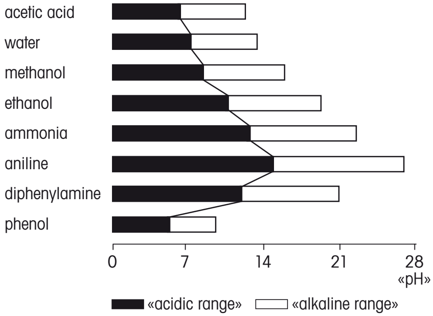

Figure 29. pH scale in different solvents

In applications involving non-aqueous solvents it is common to measure relative rather than absolute pH, e.g. titrations in oil. In this case it is the potential jump observed when the reaction goes to completion and

not the pH scale that is important. When doing a pH measurement in a non-aqueous sample it is important to remember that the measurement will not give an absolute pH value. Furthermore, the electrode will loose its hydrated gel layer around the pH-sensitive membrane. To ensure that measurements can still be performed, one has to take care to rehydrate the gel layer in an ion-rich aqueous solution between experiments.
If one wants to measure quantitatively in non-aqueous solvents, one can prepare a calibration curve for the pH glass electrode with different samples that have a known composition corresponding to the conditions of the samples to be measured. This makes it possible to differentiate the different sample compositions during the measurement, without having to quantify an absolute value during the measurement.
Remember that non-aqueous solvents are usually very ion-deficient and that this can result in measurement instabilities.

5. Appendices

5.1. Temperature tables for METTLER TOLEDO buffer solutions

Temperature	**METTLER TOLEDO standard pH buffer solutions**								**NIST/DIN 19266**		
5.0	1.67	2.02	4.01	7.09	9.45	10.65	10.25	11.72	4.004	6.950	9.392
10.0	1.67	2.01	4.00	7.06	9.38	10.39	10.18	11.54	4.001	6.922	9.331
15.0	1.67	2.00	4.00	7.04	9.32	10.26	10.12	11.36	4.001	6.900	9.277
20.0	1.68	2.00	4.00	7.02	9.26	10.13	10.06	11.18	4.003	6.880	9.228
25.0	**1.68**	**2.00**	**4.01**	**7.00**	**9.21**	**10.00**	**10.01**	**11.00**	**4.008**	**6.865**	**9.183**
30.0	1.68	1.99	4.01	6.99	9.16	9.87	9.97	10.82	4.015	6.853	9.144
35.0	1.69	1.99	4.02	6.98	9.11	9.74	9.93	10.64	4.026	6.845	9.110
40.0	1.69	1.98	4.03	6.97	9.06	9.61	9.89	10.46	4.036	6.837	9.076
45.0	1.70	1.98	4.04	6.97	9.03	9.48	9.86	10.28	4.049	6.834	9.046
50.0	1.71	1.98	4.06	6.97	8.99	9.35	9.83	10.10	4.064	6.833	9.018

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