

A GUIDE TO pH MEASUREMENT

- the theory and practice of laboratory pH applications

INTRODUCTION

This guide to pH measurement has been produced to accompany the latest development in laboratory pH technology.

As well as an insight into the theoretical aspects of pH measurement, sections covering applications and electrode troubleshooting have been included to make this a comprehensive review of the subject.

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SECTION 1 pH Measurement: Basic theory and practice

Why are pH values measured?

The qualitative determination of the pH value of foodstuffs is probably the oldest analysis method in the world. All foodstuffs are tested with the taste organs. Thereby some are noticed to be acidic and some to be alkaline. With modern pH electrodes these taste sensations can be measured in exact figures (see fig. 1).

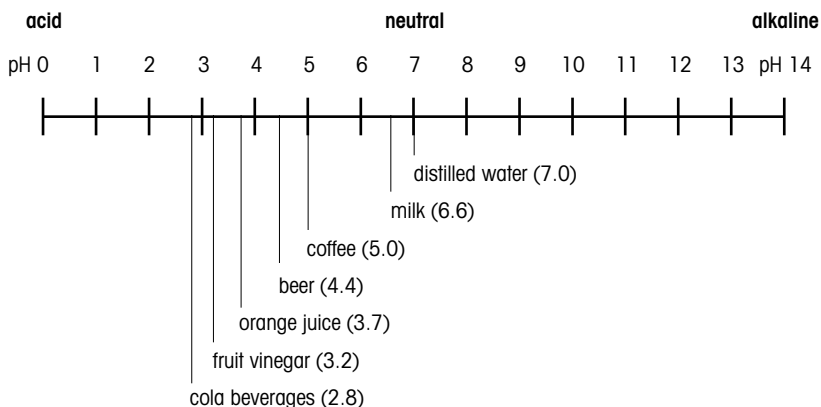


Fig. 1: pH values of various foodstuffs

Whether something is perceived as acidic or alkaline depends on the hydrogen ion (H^+) concentration in the solution.

The pH value is defined, by the Sorenson Equation, as the negative logarithm of the H^+ concentration in a given solution (see table 1).

In other words, at a high concentration, e.g. $1 \text{ mol/L} = 10^0$, $\text{pH} = 0$ (ACIDIC)

at a low concentration, e.g. 10^{-14} mol/L , $\text{pH} = 14$ (ALKALINE)

Hence, different substances are objectively compared with each other, where pH 0 is extremely acidic, pH 14 extremely alkaline, and pH 7 neutral.

In the last few years the measuring of pH has gained in importance. In the control and regulation of chemical and biological processes, it has become indispensable to monitor the pH values.

Thanks to accurate pH control it is possible to:

- manufacture a product with defined attributes
- produce a product at low cost
- prevent damage to the environment, materials and humans
- satisfy legal regulations
- gain further knowledge in research

range	pH	H ⁺ concentration (mol/L)	OH ⁻ concentration (mol/L)
acid	0	1	0,000000000000001
	1	0,1	0,00000000000001
	2	0,01	0,0000000000001
	3	0,001	0,000000000001
	4	0,0001	0,00000000001
	5	0,00001	0,0000000001
neutral	6	0,000001	0,00000001
	7	0,0000001	0,0000001
alkaline	8	0,00000001	0,000001
	9	0,000000001	0,00001
	10	0,0000000001	0,0001
	11	0,00000000001	0,001
	12	0,000000000001	0,01
	13	0,0000000000001	0,1
	14	0,00000000000001	1

Table 1: pH scale

How are pH values measured?

In order to measure a pH value, a measuring electrode (pH electrode) and a reference electrode are needed. In many cases, a combination electrode, housing both measuring and reference elements, is used.

Glass electrodes

A 'gel layer' develops on the pH-sensitive glass membrane when a pH glass electrode comes into contact with an aqueous measuring solution. Such a 'gel layer' arises also on the inside of the glass membrane which is in contact with a defined buffer solution (the inner buffer).

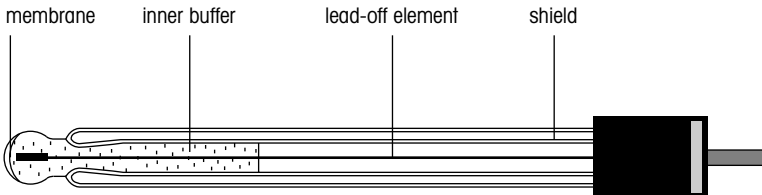


Fig. 2:
Structure of a glass electrode

The H^+ ions either diffuse out of the gel layer, or into the gel layer, depending on the pH value of the measured solution. In the case of an alkaline solution the H^+ ions diffuse out and a negative charge is established on the outer side of the gel layer. Since the glass electrode has an internal buffer with a constant pH value, the potential at the inner surface of the membrane is also constant during the measurement. The total membrane potential is a result of the difference between the inner and outer charge.

$$E_{el} = E^0 - S (pH_a - pH_i)$$

- E_{el} = electrode potential
- E^0 = zero potential
- S = slope (mV per pH unit)
- pH_i = pH value of the internal buffer
- pH_a = pH value of the measured solution

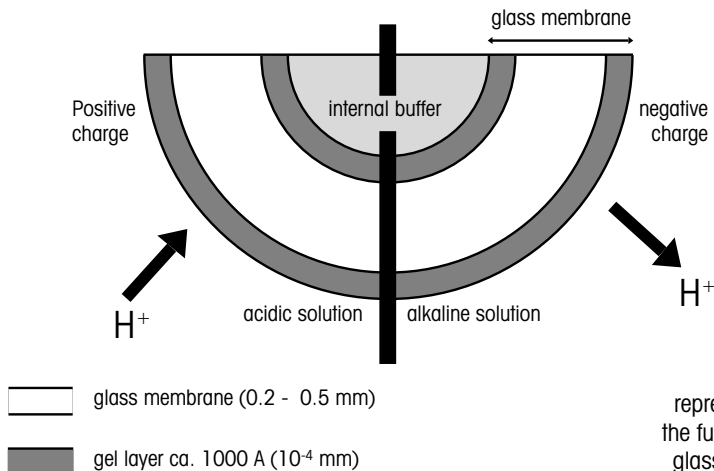


Fig. 3:
Schematic representation of the function of the glass membrane

Reference electrodes

The whole pH measuring circuit (fig. 4) consists of a measuring electrode (glass electrode; fig. 2) and a reference electrode (fig. 5), which are both immersed in the same solution. In order to obtain a definite pH value the reference electrode must have a defined stable potential which is independent of the measured solution.

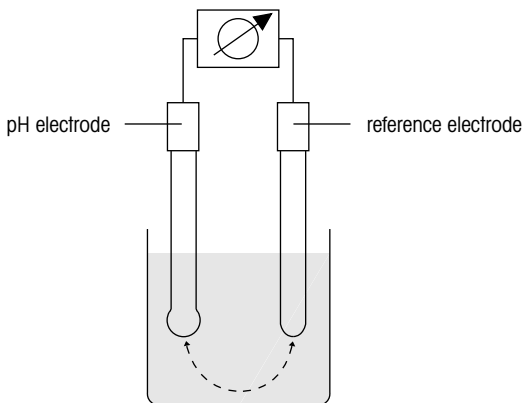


Fig. 4: Measuring circuit

Every reference electrode consists of a reference element which is immersed in a defined electrolyte. This electrolyte must be in contact with the measured solution. This contact most commonly occurs through a porous ceramic junction.

Of the many reference systems, only the mercury/calomel and the silver/silver chloride systems, along with certain modifications of them, have attained practical importance. Due to environmental considerations, however, the mercury electrode is rarely used today.

The potential of the reference electrode system is defined by the reference electrolyte and the reference element (e.g. silver/silver chloride). Here it is important that the reference electrolyte has a high ion concentration which results in a low electrical resistance.

Ideally no reaction between the reference electrolyte and the measuring solution should occur over a wide temperature range.

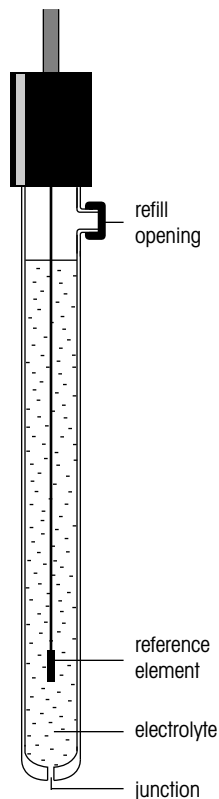


Fig. 5:
Structure of a reference electrode

Combination electrodes

Since the combination electrode (fig. 6) is much easier to handle than the separate electrodes, the former is used almost exclusively today. In the combination electrode the glass electrode is concentrically surrounded by the reference electrolyte.

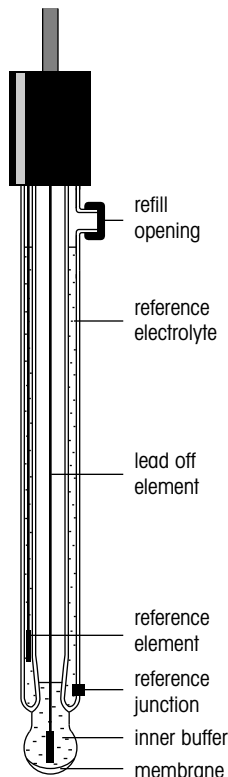
Only when the different parts of the electrode are expected to have very different life expectancies is the use of separate electrodes recommended instead of a single combination electrode.

Three-in-one electrodes

A recent innovation is the addition of a temperature sensor to the pH combination electrode.

By housing the temperature sensor in the same body as the pH and reference elements, temperature compensated readings can easily be made with a single probe.

Fig. 6:
Structure of a
combination
electrode



pH measuring system

Successful pH measurement can only be achieved by choosing the correct system to meet the demands of the sample under examination. As well as the correct apparatus, a supply of suitable reagents is vital.

Consideration has to be given to:

Type of pH meter:	Specification, ease of operation
Electrode(s):	Is it suitable for this measurement? Is a pH electrode with built-in temperature sensor available?
Temperature probe:	Is temperature compensation required?
Buffer solutions:	Pure, correct value
Reagents:	Distilled water, electrolyte solutions, cleaning solutions
Glassware:	Clean, labelled
Electrode holder:	For housing electrode(s)

For optimal pH measurement, the correct electrode must first be selected. The following criteria must be considered: Chemical composition, homogeneity, temperature, pH range, 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 error sources. The response time and accuracy of an electrode is dependant upon 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 accuracy of pH readings will depend upon continued maintenance of the electrode, as well as experimental conditions such as temperature, clean or fresh buffer solutions and state of the sample.

A pH electrode is characterised by its zero point and its slope, and a two point calibration is chosen for greater precision.

The response of a pH electrode is defined by the **Nernst Equation**

$$E = E^{\circ} - 2.3 \frac{RT}{nF} \bullet \text{pH}$$

Where E° is a constant

R is the gas constant

F is the Faraday constant

T is the temperature in Kelvin

and n is the ionic charge

When measuring hydrogen ions (i.e. $n = +1$), the slope factor at 25 °C (298 K) has a value of 59.16 mV. This is termed the IDEAL SLOPE FACTOR. It follows that for a unit change in pH, an ideal measuring system will sense a mV change of 59.16 mV. This measurement of slope factor gives an indication of the performance of the electrode system.

If electrodes are not cleaned after use, and are subject to long term neglect, then the accuracy of the system is lost.

This loss of performance can be monitored by a steady decrease in the measured slope value of the system.

When the slope value drops below 50 mV per decade (85 % slope efficiency) or drift 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, it should be remembered that factors such as reference junction blockage, electrolyte loss, glass bulb contamination and use of incorrect calibration buffers will all contribute to 'low slope values'.

All of these must be considered when there are doubts about the performance of the pH system.

Temperature compensation

Automatic temperature compensation (ATC) is generally used in laboratories, except when both calibration and pH measurement occur at a constant temperature. If the sample temperature does differ from calibration temperature by more than 10 °C, lack of appropriate temperature compensation will result in a measuring error of 0.15 pH units or more (between pH 3 and 11).

The pH range (0-14) is determined through the ion product of the water. Water dissociates to a small extent into H⁺ and OH⁻ ions.

$$I = [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ Molar (@ 25}^\circ\text{C)}$$

The ion product I is strongly dependant on temperature.

The temperature influences the pH measurement through four factors:

- temperature coefficient of the measured solution
- temperature dependence of the slope (see Nernst equation)
- position of the isothermal intersection
- differing response time of the electrode (caused by temperature changes)

Temperature coefficient

Every measuring solution has a characteristic temperature and pH behaviour (temperature coefficient). In general one has to assume that a temperature change results in a pH change (see buffer/temperature table). The reason for this is the temperature dependent dissociation which causes a change in the H⁺ concentration. This pH change is real, not a measuring error, and cannot be compensated for by use of ATC.

Example:

	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

This has to be taken into consideration if pH values obtained at different temperatures are to be compared. Experimentally, samples should be measured at the same temperature.

Temperature dependence of slope

It can be seen that the slope factor of the Nernst equation contains a temperature term.

$$E = E^0 - \frac{2.3 RT}{nF} \text{pH}$$

When making pH measurements, the effect of temperature can be compensated for in a number of ways. The majority of pH meters have the facility for manual or automatic temperature compensation (ATC). ATC is the use of a separate temperature probe or a temperature sensing device fitted into the pH electrode. Each measures solution temperature and the meters electronically adjust the pH reading according to the Nernst equation factor.

Calibration line and isothermal intersection points

An electrode would have an ideal temperature behaviour if its calibration lines (isothermals) intersect at the zero point of the electrode (pH 7 = 0 mV) at different temperatures (see fig. 7).

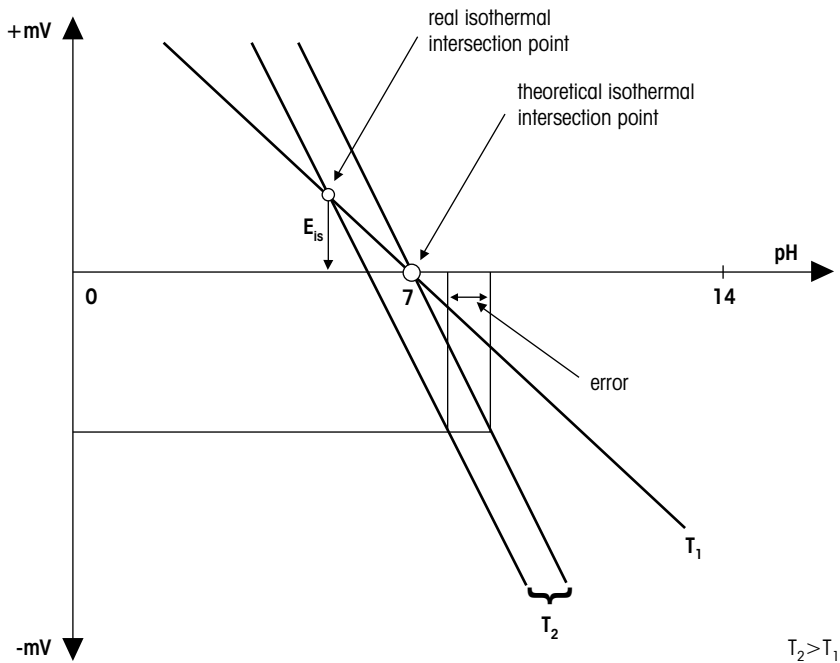


Fig. 7: Calibration line and isothermal intersection points

Since the overall potential of the pH electrode is composed of the sum of many single potentials, which all have their respective temperature dependencies, the isothermal intersection hardly ever coincides with the zero point of the electrode (the ideal case would be: 0 mV at pH = 7/25 °C).

In the last few years, the development of the electrode has concentrated on bringing the isothermal intersection and the zero point as close together as possible, since the nearer they are to pH 7 the smaller the error in the temperature compensation. The measuring error increases with an increasing temperature difference between the calibration and sample solutions. As a rule the errors can be in the order of 0.1 pH units. The most exact pH value is obtained when the temperature of the calibration and measured solutions are identical.

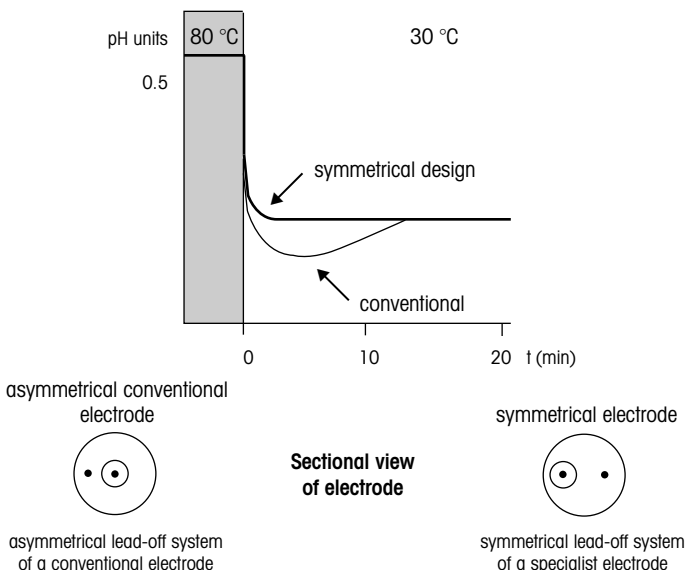
Response time of the electrode

When the temperature change of the medium is rapid, a conventional pH electrode will drift until the temperature of the electrode and the medium become equal. In order for a combination electrode to react rapidly to the temperature changes of the medium, the temperature of the inner lead-off element and the outer reference element must always be identical. Alternatively the temperature dependence of the lead-off elements have to be equal to zero.

Optimal electrodes are above all distinguished by the symmetrical warming up or cooling down of their lead-off elements. They also have the same temperature coefficient and isothermal intersection at pH 7 and 0 mV.

Thereby a short response time to temperature compensation can be guaranteed (see fig. 8).

Fig. 8:
Temperature-time
behaviour of
combination
electrodes



SECTION 2 Laboratory measurements

This section will highlight problems encountered in pH measurement, and electrode features that have been developed to solve these problems. In many cases the pH of samples which cannot be measured with standard electrodes can now be measured routinely with special electrodes.

Standard measurement

Laboratory measurements are generally made with a conventional combination electrode.

Usually the following conditions exist:

The measuring range is between pH 2 and pH 12, the temperature between 10 °C and 50 °C, and the ion concentration between 0.5 and 4 mol/L. Additionally, the system is buffered, aqueous and homogeneous.

Ion deficient media

Media that have an ion concentration of a few mmol or lower are considered to be ion deficient. Such a low ion concentration leads to poor conductivity. In ion poor media an increased resistance arises at the junction. This transition resistance leads to contact problems between the reference electrolyte and the measuring solution which in turn may cause diffusion potentials. Furthermore the signal can be affected by stirring.

The above problems can be solved by using circular ground junctions (see fig. 9) which create optimal contact between the reference electrolyte and the measuring solution.

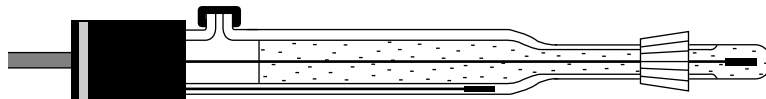


Fig. 9: Combination electrode with circular ground junction

Semi-aqueous or non-aqueous solutions

In non-aqueous solutions (less than 5 % water) it is possible to obtain only relative pH values (see page 46). Semi-aqueous solutions are in general also ion deficient. If the sample contains more than 5% water, the classical definition of pH measurement may be used, i.e., an absolute and not a relative value is obtained.

A phase separation often arises in the contact area between electrolyte and measuring solution (junction), causing an unstable signal. Furthermore, there is a risk of precipitation at the junction. This occurs, for instance, when concentrated KCl solutions are used as the reference electrolyte.

To minimise problems with such measurements the electrolyte and sample solution should be matched for mobility and solubility.

This is achieved by using LiCl in ethanol or LiCl in acetic acid as the reference electrolyte for non-aqueous samples.

Protein rich solutions

With high protein concentrations the proteins may precipitate at the junction if they come in contact with the KCl reference electrolyte.

The use of special electrolytes may overcome these problems. Junctions contaminated with proteins can sometimes be cleaned by immersing the electrode into a pepsin/HCl solution for several hours.

Solutions containing sulfides

When working with an Ag/AgCl reference system, the reference electrolyte always contains dissolved silver. When the dissolved silver at the junction comes into contact with the sulfide in the measuring solution, nearly insoluble silver sulfides result. Silver sulfide clogs the junction and colors it black. This leads to a slow and unstable measurement signal.

By using a reference system with a silver ion barrier, AgCl-free electrolytes can be employed. Sulfide-contaminated junctions can sometimes be cleaned by immersing the electrode in a thiourea/HCl solution. This eliminates silver sulfide contamination.

Solutions containing hydrofluoric acid

Hydrofluoric acid attacks the glass membrane chemically and prevents, even in small concentrations, the development of a gel layer. This leads to unstable measuring values and also reduces the life span of the electrode. Hydrofluoric acid attack occurs only at pH values below 5.

It is possible to measure pH at total fluoride concentrations of 0.2g/L (pH 1; 20 °C) up to 1g/L (pH 3; 20 °C). Special electrodes are available for such applications. At higher concentrations, an antimony (Sb) electrode and a special reference electrode must be used.

Applications of pH measurement

Agriculture

The pH of soils is important since plants grow best within a rather narrow pH range. The optimum pH varies with each type of plant. In hydroponics, pH control is even more important than in the soil since too high or too low pH can cause precipitation of some of the chemicals. Helpful soil bacteria grow best in slightly acid soil. Plant nutrients form insoluble compounds if soil pH is too high. Toxic amounts of some metals become available if pH is too low.

Brewing

pH is important for proper ageing and for all stages of the brewing process. A decrease in pH decreases the solubility of the bitter parts of hops and permits the use of stronger hops without an increase in harshness. The beer should be at a pH of 3.9 to 4.1 when bottled, to ensure stability while on the shelf.

Corrosion Prevention

The corrosion of iron occurs below pH 4.3 but a semi-protective layer is formed above 4.3. Acid soils may be below this level. A more resistant coating is formed above pH 10.5. The thickness of oxide coatings can be estimated by emf measurements. If the emf is near that of the oxide the coating is complete and non-porous but if the emf is near that of the base metal then the coating has little protective value.

Dairy Industry

Since milk curdles at a pH of 4.7 it must not be allowed to drop to this value. The ageing of cheese can be followed by both emf and pH measurements. For example, a pH of 4.9 is about right for cheddar cheese. Ice cream can be spoiled by the addition of fruits or juices with too low a pH. The pH of cooling brines must be controlled to prevent corrosion of the pipes.

Example: Cheese Production

pH measurements are required for soft, fresh cheese and hard, mature cheese. Cheese contains a large amount of protein and fat so the choice of electrode is important. Often puncture electrodes are used.

Why are pH values measured?

pH measurements enable both production control during the cheese fermentation, as well as quality control.

The pH development during the first hours and days is characteristic for every cheese variety. Fig. 10 shows clearly the difference in pH value during the first hours of a typical cheese fermentation process. The process influences the consistency, color and taste.

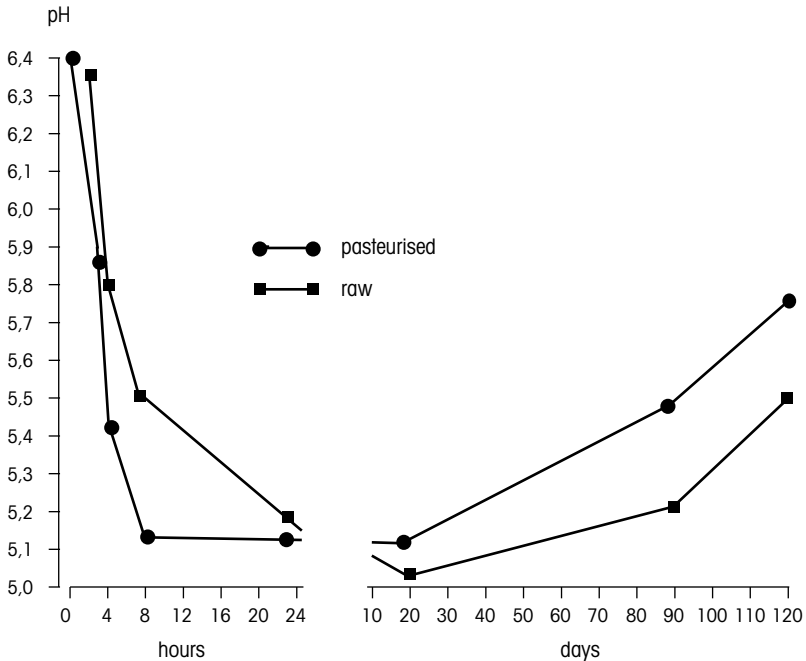


Fig. 10: pH variation during cheese fermentation process. (Federal research institute of milk industry, 3097 Liebefeld-Bern)

The main problem with this application is the contamination of the junction, especially by proteins and fats. This leads to a slow and unstable measurement and a loss of slope. The electrode also has to be resistant to mechanical stress, as it is inserted into relatively hard cheese.

A combination pH electrode with a needle membrane and an open aperture reference system solves the problem. Instead of the conventional ceramic junction, direct contact between the measuring solution and the solidified electrolyte is established through a hole or aperture.

The possibility of clogging is therefore drastically reduced. Solids in the hole may be dissolved by briefly immersing the electrode in lukewarm water.

A fatty layer on the electrode may be removed by rinsing the electrode with ethanol. Daily calibration of the electrode is recommended.

Dyeing

Processes such as bleaching and dyeing with different types of dye must be made with a definite pH in order to obtain good results and still not damage the fabrics. Wool, for example,

must be neutralized to a definite pH for effective dyeing, and in addition, the pH will vary depending upon the nature of the dye itself. The acid content of the dye also has to be determined which is normally done by means of a titration using a pH meter to determine the endpoint.

Electrical Equipment

The pH of feedwaters should be controlled in order to prevent pipe and boiler corrosion. In most cases minimum corrosion occurs between a pH of 7.4 and 8.0. Feedwater can be monitored in order to detect certain types of contamination. The soda lime softening process requires a pH of 9.4 for the removal of calcium and 10.6 for the removal of magnesium.

Fermentation Reactions

Each fermentation process requires a specific pH for the best results. A change in pH with some bacteria even changes the product. The pH during a fermentation process changes by itself, and must be adjusted periodically. This maintains optimum conditions and prevents manufacture of unwanted or even harmful by-products.

Fertilizers

The pH of acid type fertilizers is controlled in order to prevent waste of acid, and to ensure a more uniform product.

Flour Milling

The quality of flour can be determined by making pH measurements, with the better flours having a lower pH. The overall range is from 5.9 to 6.5. The buffering qualities of flours are determined by noting the decrease in pH with the addition of a measured amount of acid.

Gelatin and Glue Manufacturing

The properties of gelatin and glue vary considerably with the pH during manufacture. pH needs to be controlled accurately to ensure a consistent product. Colorimetric methods require special sample treatment and are less accurate.

Iron and Steel

pH measurements determine effectiveness of pickling baths and neutralization of waste pickle baths. Sand used in sand casting can be improved by pH control. Proper pH makes the sand hold its shape better.

Jam and Jelly Manufacturing

Jams and jellies have narrow ranges for proper gelling. A pH of 3.3 is best for jelly. At 3.1 it becomes stiff and at 3.5 quite tender. No gelling occurs at all above 3.5. Control is effected by using tartaric or citric acid.

Laundries

The efficiency of soaps and detergents can be improved by proper pH control. Undyed cottons can stand a maximum pH of 11, wool about a pH of 10, colored cloths 9.6 and silks 9.2. In general, the higher the pH the more efficient the washing process, but the pH should not exceed the maximum value for the material being cleaned. Proper pH of starch solutions helps prevent sticking during pressing.

Leather

Close pH control of leather processing is required to obtain maximum efficiency without damaging the leather. The pH of tanning and dyeing baths actually determine the texture and colour of the finished product. The dehairing process is normally done at a pH of 12.3, but this must be completely neutralized to assure good keeping qualities of the leather. Minimum swelling of the collagen is obtained at pH 4.7.

Meat and Fish Processing

The pH measurement of meat and fish gives a good indication of the keeping qualities and freshness of the product. This is a typical application for a puncture electrode.

Metal Finishing

The effectiveness of the pickling and cleansing baths are determined by pH measurements. The pH of plating baths determines the quality and speed of the plating process. Some alloys can be plated if very strict pH control is maintained. The plating thickness can be found during destructive testing by noting the change in millivolt readings when penetration of a coating has been accomplished. This is an industry where colorimetric methods cannot be used directly.

Neutralization

Neutralizing acids or bases is best controlled electrometrically with a pH meter which indicates the neutral point more precisely than any other method. The pH meter is especially useful in colored solutions where a color indicator is of no use.

Printing

The pH of paper and inks must be controlled to assure proper penetration and drying of the ink. Too high a pH causes gumminess and too low a pH slows up the drying process.

Pharmaceuticals

Antibiotics produced from molds are grown at a precise pH. Incorrect pH can possibly produce a poison rather than a medicine. Many pharmaceuticals must be prepared using very close pH control.

Sewage

The pH of sewage is controlled to assure efficient coagulation of sludges. A pH of either 3.4 or 7.4 may be used for good results. Also the pH of the effluent water must be controlled to prevent contamination. The best digestion range is 6.8 to 7.6. The pH of filtration depends upon the chemicals used; for example, pH 3.4 for ferric chloride and 4.4 for alum.

Swimming Pools

pH levels in swimming pools should be maintained near the neutral range or slightly alkaline to prevent skin irritations. High pH accelerates deposition of solid salts in heater lines and filters. Low pH causes corrosion of iron pipes etc.

Tropical Fish Breeding

Expensive tropical fish thrive within definite pH ranges. Each species has its own best pH environment, which is even more critical during breeding. The Neon Tetra Fish, for example, prefers water as close to pH 7.0 as possible, while an Angel Fish requires pH 6.8. The general range for freshwater fish is pH 6.0 to 8.0. Salt water aquariums should be kept at 8.3. If the pH of the salt water gets as low as 7.0 the fish become sickly.

Water

The pH of water sources such as rivers, lakes and oceans is measured to study natural conditions of wildlife. These tests are made by oceanographic institutes, fish and wildlife services and water authorities. pH measurements also assist in determining the extent of pollution in domestic and industrial supplies.

In measuring the pH in water, there are two extreme situations. One is the pH measurement in pure water (boiler feed water), and the other is the pH measurement in waste water (sewage purification plants). In the first case the medium is very low on ions, which leads to poor conductivity. In the second case the medium is heavily polluted, which leads to clogging of the junction.

Example: Boiler feed water

Power stations use boiler feed water to create steam. The goal is to have as pure water as possible, which fully evaporates without leaving any residue. Lime deposits must especially be avoided. In order to keep the use of boiler feed water within reasonable costs, the condensed steam is pumped back in. Thus, boiler feed water is very pure distilled water with a conductivity of sometimes less than 1 $\mu\text{S}/\text{cm}$.

Why are pH values measured?

Despite the low conductivity of the boiler feed water, the tank and pipes will corrode if the pH value of this medium is acidic.

In order to keep costly maintenance and repair work of the whole structure to a minimum, the pH value ought to be regularly, if not continuously, controlled. If required, the pH value is brought up to 9 through suitable additions, (e.g., ammonia soln.), and kept there.

Through monitoring pH values, any acid or base breakthroughs from the ion exchangers can be determined immediately.

	Boiler feed water	Steam generator water
pH value @ 25°C	9 - 10	9 - 10
Conductivity @ 25°C	_____	< 50 μ S/cm
Hydrazine, N ₂ H ₄	> 0.1 mg/kg	_____
Iron (total), Fe	< 0.3 mg/kg	< 5 mg/kg

Table 2: Standard values for water used by steam generators

Sleeved combination electrodes have been developed to overcome the problem of low ionic strength solutions.

An open reference aperture covered by a molded ground glass sleeve offers a larger reference contact area. This leads to stable, and accurate, pH readings from problem water samples.

Example: Sewage treatment

In biological purification plants, organic substances are decomposed by bacteria. This is done in the activated sludge basin. Further anaerobic fermentation takes place in the septic tank.

The pH has to be monitored. Firstly, the activity of the micro-organisms has to be maintained. Secondly, the output of methane gas can be used economically as an energy source.

The problem is that the high solid content and dissolved sulfide compounds quickly leads to the clogging of the reference junction in conventional electrodes.

Cleaning of the electrodes used for such measurements is very important and open aperture or replaceable ceramic reference junctions overcome the possible blockage problems.

SECTION 3 pH Electrode systems

Troubleshooting guide

The first important step in troubleshooting is to isolate the problem to one of the six major elements of the pH measuring system, which are:

- pH meter
- pH electrode
- reference electrode
- buffer solution
- operator
- application

Once this is done, action can be taken to correct the problem.

pH Meters

Symptoms usually related to pH failure are offscale readings and readings that will not change. To confirm that the meter is the source of the problem, refer to the instruction manual accompanying the meter.

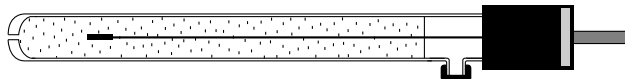
Electrodes

There are three types of electrode used in the determination of pH:

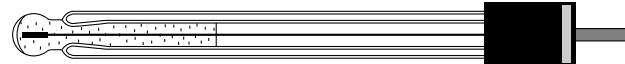
- Reference Electrodes
- pH Electrodes
- Combination Electrodes (pH and reference electrode in one sensor)

Fig. 11: Electrode types

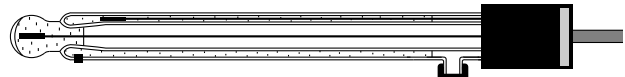
Reference electrode



pH electrode



Combination electrode



(i) Reference Electrode

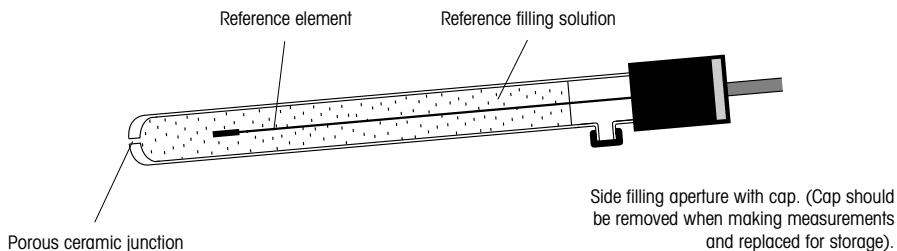


Fig. 12: Reference electrode

Symptoms usually related to reference electrode failure are: inaccuracy or sluggish response, noisy or unstable readings and offscale readings.

Carry out the following check procedure:

1. Check that the filling solution is above the internal elements (not applicable for gel filled electrodes).
2. Check side aperture is open (if applicable).
3. Look for sign of blockage or discoloration of reference junction (if electrode has a replaceable ceramic junction this can be replaced as instructed).
4. Connect a working pH half-cell and reference electrode to pH meter. In mV mode the system should display a stable reading. Drift or noise indicate an unshielded cable or a poor connection.

If the reference electrode does not meet the above checks it should be cleaned thoroughly.

Proceed as follows:

1. Empty the reference chamber, rinse with deionised water, empty and refill with the specified filling solution.
2. Soak the electrode in hot (50 °C - 60 °C) reference electrolyte for a few minutes or until the filling solution flows freely.
3. Soak electrode junction overnight in pH 4 buffer.
4. Remove any exterior salt deposits with distilled water.
5. If the filling solution does not flow through the junction by this time (generally due to an unusually low junction porosity) the following procedure should be followed:
 - hang electrode in air for some time and let KCl creep out and crystallize
 - use gentle suction to pull filling solution through if necessary
 - repeat from step 2
 - try the check procedure again

6. Sometimes the material clogging the junction requires more severe action. Should the above fail, proceed as follows:
 - use a solvent specific to the solution or material plugging the junction, if possible
 - soak membrane overnight in 0.1 M HCl
 - if measurements were made in solutions containing protein or sulfides, remove deposits by soaking electrode in appropriate deproteinising cleaning solution
 - repeat from step 1
7. Soak electrode in ammonium bifluoride regeneration solution.

If all these fail, the electrode should be replaced with a new electrode.

(ii) pH electrode

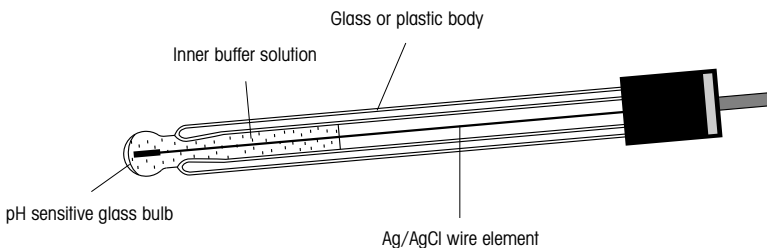


Fig. 13: pH electrode

Symptoms usually related to pH electrode failure are: noisy or unstable reading, offscale readings, and 2 point calibration cannot be performed.

In order to ascertain whether the pH electrode is at fault the following procedure should be followed:

1. With the meter set to read absolute mV, dip the pH electrode in question, with a working reference, in pH 7.00 buffer.
2. The reading should be $0 \text{ mV} \pm 30 \text{ mV}$ with an Ag/AgCl reference. (This is checking the zero potential).
3. Lower the electrodes into pH 4.00 or pH 10.00 buffer and the reading should be greater than 150 mVs different from the zero potential.

If the electrode responds outside of this test, clean the electrode as follows:

1. Degrease the membrane with cotton wool soaked in acetone (CAUTION - HAZARDOUS SUBSTANCE) or soap solution. N.B. Acetone should not be used on plastic bodied electrodes.
2. Soak membrane in 0.1 M HCl overnight.

3. If measurements have been made in samples containing protein, remove protein deposits by soaking electrode bulb in 0.1 M HCl + pepsin solution.
4. Soak electrode in ammonium bifluoride regeneration solution.

If all these fail, the electrode should be replaced with a new electrode.

(iii) Combination electrode

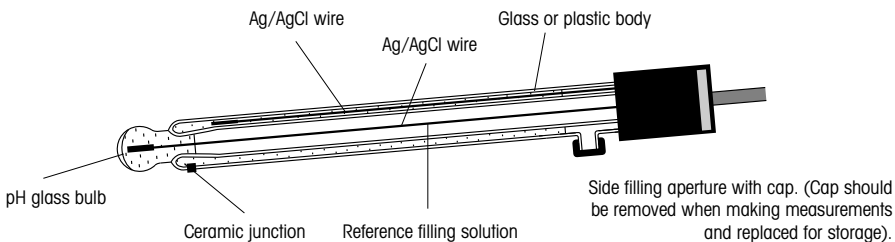


Fig. 14: Combination electrode

Should a faulty combination electrode be suspected, a mixture of steps described for pH and reference electrodes should be tried. Commonly the reference is at fault and the reference procedure should be tried first. If this fails to return electrode to the expected level of performance replace with a new electrode.

For short term storage, the electrode should be immersed in 15 mm depth of reference filling solution. Ensure that the level of solution in the beaker is below that of the filling solution in the electrode (see below).

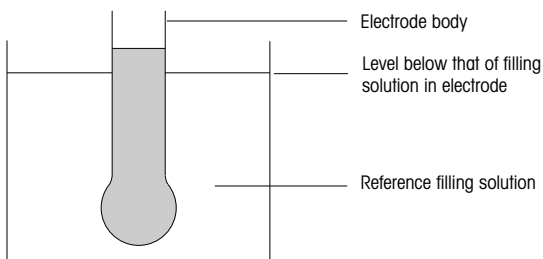


Fig. 15: Electrode storage

For longer term storage, the wetting cap, filled with filling solution, should be replaced and the side filling aperture closed.

Other sources of error

A. Buffers

Symptoms usually related to buffers are: inaccurate readings or inability to perform 2 point calibration.

1. Check for aged or contaminated buffers and rectify by substituting fresh ones.

B. Operator

Symptoms usually related to operator error are: offscale reading, noise, inability to perform 2 point calibration and inaccuracies of reading.

Check for the following common operator faults:

1. Ensure that the unit is properly grounded or plugged into the wall outlet.
2. Ensure that the electrodes are plugged into proper terminals and are seated firmly.
3. Ensure that the calibration of the meter is being performed according to the operating instructions outlined in the Instruction Manual.
4. Ensure that the meter is being calibrated to the actual buffer required and that the buffers have not been reversed.
5. Check that the reference electrode has not been filled with the wrong filling solutions. (Calomel electrode solution becomes very milky if AgCl solution has been used.)

Before making a measurement check that the wetting cap and side filling aperture have been removed and RINSE THE ELECTRODES BEFORE measuring a different buffer or sample.

Note - A short time spent reading the electrode product insert and the instruction manual for the instrument being used should eliminate most operator errors.

C. Applications

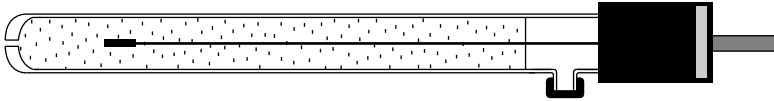
Symptoms usually related to applications problems are: drift, slow response and an unusual number of electrode failures.

Examples of typical application type problems are:

1. Electrodes in unbuffered solutions such as distilled water respond more slowly, appearing to drift. In these solutions, stability may not be achieved for three or four minutes.
2. Some applications require a particular type of electrode to be used, and if the correct one is not used a large number of electrode failures will result - contact the manufacturer for advice on applications.
3. The use of Ag/AgCl reference electrodes in a sample which contains halides.

Electrode storage

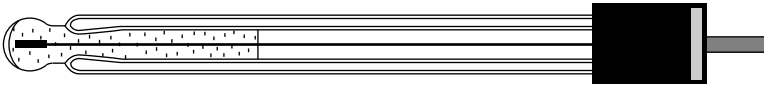
Reference electrode



Short term
Immerse in reference filling solution.

Long term
Store with wetting cap attached filled with reference filling solution. Close side aperture.

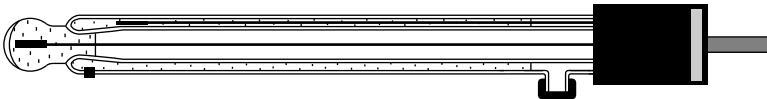
pH electrode



Short term
Immerse in reference filling solution.

Long term
Store with wetting cap attached filled with reference filling solution.

Combination electrode



Short term
Immerse in filling reference solution.

Long term
Store with wetting cap attached containing reference filling solution. Close side aperture.

Fig. 16: Electrode storage

Directly after use and before a period of storage the electrodes should be rinsed thoroughly with distilled water.

ATC probes

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

SECTION 4 Electrochemistry theory

In the previous sections the practical aspects of pH measurements have been discussed. This chapter will principally deal with the theoretical background of pH measurement and also explain its main mathematical equations.

The theory of potentiometric measurements (Nernst Equation)

The pH measurement is a potentiometric measurement (i.e. it measures a potential). The potential of a measuring electrode (e.g. a pH electrode) is measured against that of a reference electrode.

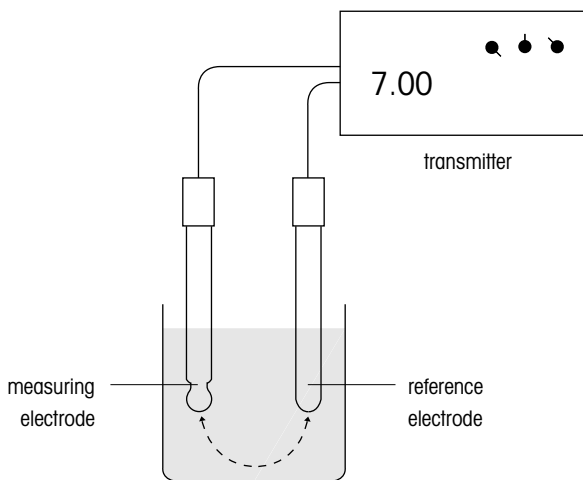


Fig. 17: Principle of a potentiometric measurement

Two or more metal conductors which are connected to each other through one or more electrolytes form a galvanic chain. A measuring device with as high an input resistance as possible connects the two conductors (electrodes) and allows the chain potential E to be measured. This quasi-nonelectrical measuring method does not alter the chemical composition of the measuring solution. A charge exchange takes place at the interphases of the electrode of a galvanic chain, leading to galvanic potentials. These cannot be determined separately, since at least two interphases are present.

The measurable chain potential E is composed of several components:

$$\begin{array}{c} \text{Metal A / Electrolyte 1 // Electrolyte 2 / Metal B} \\ \hline E = E' \qquad + E'' \qquad + E''' \end{array}$$

whereby:

E': Potential of the measuring electrode

E'': Diffusion potential

E''': Potential of the reference electrode

E is dependant on the concentration (c) or activity (a) of the measured ion.

The mathematical link between activity and galvanic potential is defined by the **Nernst** equation:

$$E_{\text{Ag}^+} = E_{0\text{Ag}} + \frac{2.3 RT}{nF} \cdot \log a_{\text{Ag}^+}$$

whereby:

E_{Ag^+} = Galvanic potential of the silver electrode

$E_{0\text{Ag}}$ = Galvanic potential under standard conditions

($a_{\text{Ag}^+} = 1.0$)

R = Gas constant

T = Absolute temperature (Kelvin)

F = Faraday constant

n = Charge (silver electrode: n = 1)

a_{Ag^+} = Activity of the silver ions

The factor $2.3 RT/F$ is defined as the Nernst potential E_N and is identical to the change in potential resulting from a tenfold change in activity.

In order to be able to compare the galvanic potentials of different electrodes the standard hydrogen electrode (SHE) 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 $a_{\text{H}^+} = 1.0$ and surrounded by hydrogen gas at 1 bar.

In order to calculate the galvanic potential of the measuring electrode E', all other measurable components of the chain potential E have to be constant.

Potential of the pH measuring system

pH electrode

As discussed earlier the potential between a pH glass electrode and a reference electrode is defined by the Nernst equation, which is as follows for a pH measurement:

$$E = E^0 + 2.3 \frac{RT}{F} \cdot \log a_{H^+}$$

E^0 is the standard potential at $a_{H^+} = 1 \text{ mol/L}$. The factor $2.3 RT/F$ is summarised as the Nernst potential E_N and is identical to the change in potential per pH unit. The value of E_N depends on the absolute temperature T Kelvin. (E_N is often referred to as the slope factor):

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

The measurable chain potential E consists of several sources of potential, which are shown in fig. 18.

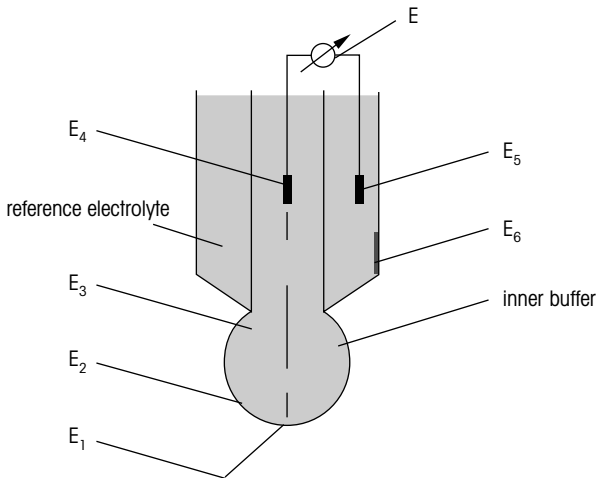


Fig. 18: Different sources of potential in a combination electrode

In order to measure E1 and assign a definite pH value to it, all other single potentials E2 - E6 have to be constant.

Fig. 19 shows that ΔE is zero when the inner pH value is equal to the outer pH value. A small residual potential is defined as the asymmetrical potential (E2). The Nernst equation also shows that the zero point of the glass electrode is determined by the pH value of the inner buffer.

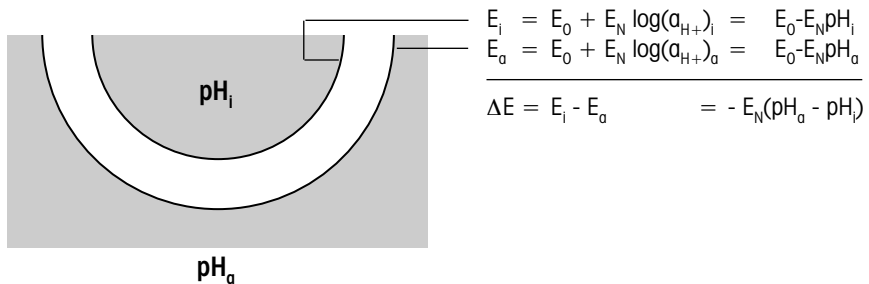


Fig. 19: A model representing the pH potentials at the glass membrane

To explain the phenomenon of the development of a potential at the glass membrane of a pH electrode a knowledge of the structure of the gel layer is of crucial importance. The phenomenon can be explained through the following model.

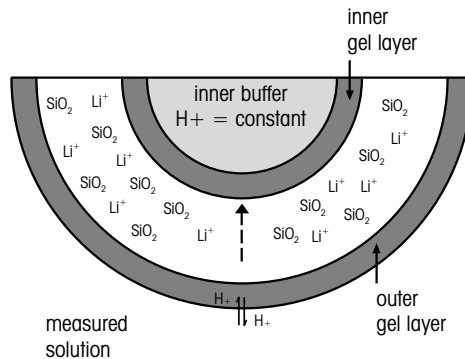


Fig. 20: Cross-section through a glass membrane

A thermodynamic equilibrium of the hydrogen ion arises at the phase boundary between the measuring solution and the outer gel layer. If the activity of the hydrogen ions is different in the two phases, a 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 solution and in the gel layer:

$$E_1 = \frac{2.3 RT}{F} \cdot \log \frac{(a_{H^+})_{\text{solution}}}{(a_{H^+})_{\text{outer gel layer}}}$$

The number of hydrogen ions in the gel layer is given by the silicic acid skeleton of the glass membrane and can be considered a constant and independent of the measuring solution.

The potential in the outer gel layer is transmitted to the inside of the glass membrane by the Li^+ ions found in the glass membrane, where another phase boundary potential arises:

$$E_3 = \frac{2.3 RT}{F} \cdot \log \frac{(a_{H^+})_{\text{inner buffer}}}{(a_{H^+})_{\text{inner gel layer}}}$$

The total membrane potential is equal to the difference of the two phase boundary potentials E_1 and E_3 :

$$E = \frac{2.3 RT}{F} \log \frac{(a_{H^+})_{\text{solution}}}{(a_{H^+})_{\text{outer gel layer}}} \cdot \frac{(a_{H^+})_{\text{inner gel layer}}}{(a_{H^+})_{\text{inner buffer}}}$$

When H^+ activity is identical in the two gel layers (the ideal case) and the H^+ activity of the inner electrolyte is kept constant, the following equation is true:

$$E = \text{constant} + \frac{2.3 RT}{F} \log (a_{H^+})_{\text{solution}}$$

Reference electrode

Not only are the functions of the glass membrane important, but also those of the reference electrode. In order to achieve a potential independent of the measuring solution, the requirements mentioned in section one have to be fulfilled.

Of the different reference electrodes, the silver/silver-chloride electrode has become the most important. Compared to the calomel electrode the silver/silver-chloride electrode is largely hysteresis-free and can be used even at high temperatures.

Another advantage is that the Ag/AgCl electrode has a relatively small temperature coefficient, which is mainly dependent on the chloride concentration of the reference electrolyte.

The junction is a critical part of the measuring chain because of the diffusion potential E_{diff} (see equation). 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 the case. It is, however, possible to keep E_{diff} small and constant.

The migration velocity of ions is determined by their charge and size. The size of an ion is determined by its hydration cover. All ions in aqueous solutions are surrounded by such a cover. Hence the small but highly hydrated lithium ion migrates slower than the much larger but only slightly hydrated potassium ion. Only the hydrogen and the hydroxide ions migrate in accordance with a completely different mechanism. This explains the much higher ion mobility of H^+ and OH^- as compared with all other ions.

Ionic mobilities (in $cm^2s^{-1}V^{-1}$) at 25°C

H^+	36.25×10^{-4}	OH^-	20.64×10^{-4}
Li^+	4.01 "	F^-	5.74 "
Na^+	5.19 "	Cl^-	7.91 "
K^+	7.62 "	NO_3^-	7.41 "
NH_4^+	7.62 "	Acetate	4.24 "

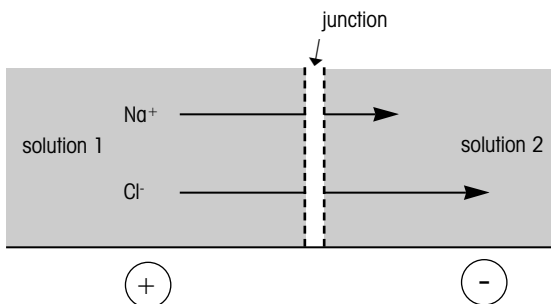


Fig. 21: Build up of a diffusion potential as a result of the difference in ion mobility of Cl^- and Na^+ ions (Cl^- ions are migrating faster than Na^+ ions).

If, for instance, sodium and chloride ions diffuse through a junction from solution 1 into solution 2, a charge separation occurs since Cl^- migrates much faster than Na^+ .

This charge separation causes a diffusion potential which counteracts the migration. This in turn leads to a dynamic equilibrium which may take a long time to come about. This is why the junction is also responsible for the response time of the electrode. So, for example, the response time is short when the junction is highly porous and the electrolyte flow strong.

In principle it would be possible to calculate the exact diffusion potential if the ion activity in the transition layer between the reference electrolyte and the measuring solution were known. Since this is not the case, one has to use an approximation formula such as the Henderson equation.

$$E_{diff} = - \frac{(E_1 - V_1) - (E_2 - V_2)}{(E'_1 + V'_1) - (E'_2 + V'_2)} \frac{RT}{F} \cdot \ln \frac{E'_1 + V'}{E'_2 + V'_2}$$

Where:

$$E_1 = \sum (c^+ \cdot v^+)$$

$$V_1 = \sum (c^- \cdot v^-)$$

$$E'_1 = \sum (c^+ \cdot v^+ \cdot z^+)$$

$$V'_1 = \sum (c^- \cdot v^- \cdot z^-)$$

c = ion concentration

v = ion mobility

z = ion charge

The subscripts 1 and 2 refer to the measuring solution and the reference electrolyte respectively.

The equation shows that the diffusion potential increases when the mobility of the cations and anions is very different. This is especially the case with strongly acidic and basic solutions.

If one of the two solutions is very dilute, the diffusion potential also increases. However, the diffusion potential decreases if the reference electrolyte is a concentrated and equitransferent solution (equal mobility of anions and cations). This is the case with the most commonly used reference electrolytes KCl and KNO_3 solutions. At extreme pH values the diffusion potential is considerable even with ideal reference electrolytes:

Example:

$$\text{KCl sat./1 mol/l HCl} \quad (25^\circ\text{C}) \quad E_{\text{diff}} = + 14.1 \text{ mV} \\ (0.238 \text{ pH units})$$

$$\text{KCl sat./1 mol/l NaOH} \quad (25^\circ\text{C}) \quad E_{\text{diff}} = - 8.6 \text{ mV} \\ (0.145 \text{ pH units})$$

In strongly acidic solutions with small pH deviations the use of a reference electrolyte or a bridge electrolyte with a low pH value is recommended. With high diffusion potentials, the chain potential strongly depends on the stirring velocity. Contaminated junctions may also lead to high diffusion potentials.

Definition of the pH value

According to Sørensen the pH is defined as the negative (base 10) logarithm of the H^+ ion concentration, i.e.:

$$\text{pH} = - \log [\text{H}^+]$$

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

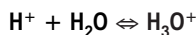
This definition of the pH value is sufficiently accurate only for dilute solutions, since only then are the concentration and activity of the solution equal.

In many cases, however, the activity coefficient is smaller than one (the activity coefficient of the hydrogen ion is not measurable in real solutions). In order to overcome these difficulties, the pH values of a number of buffer solutions were, with the help of theoretically substantiated provisions and precision readings, defined, and thus the conventional pH scale was established. The corresponding work was mainly carried out by Bates at the National Bureau of Standards in the U.S.A., which is why these buffers are also known as NBS buffers.

References:

1. R.G. Bates and E.A. Guggenheim, «Report on the Standardisation of pH and related Terminology», Pure and Appl. Chem. 1 (1960) 163-168
2. R.G. Bates, «The Modern Meaning of pH», (CRC) Critical Reviews in Analytical Chemistry, Jan. 1981, 247-278

It is common to refer to H^+ ions in connection with pH values, although the correct term is the hydronium (oxonium) ion (H_3O^+):



The hydrogen ion normally exists in its associated form:

$$\frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} = \text{constant}$$

Due to the low dissociation degree of water, a_{H_2O} may be considered a constant.

$$a_{H^+} \cdot a_{OH^-} = K_w = 10^{-14} \text{ (mol/L)}$$

whereby K_w is known as the ion product of water.

Correlation of concentration and activity

When $a_{H^+} = a_{OH^-}$ a solution is neutral which corresponds to a pH of 7.

Very soon it was found that it is the activity of, not the concentration of H^+ that is decisive in determining the pH value.

The activity of the hydrogen ion can be defined by its relation to the concentration (molarity $c = \text{mol/L}$; molality $b = \text{mol/kg solvent}$) and to the activity coefficient (γ_{H^+}).

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

In dilute solutions $a_{H^+} = b_{H^+}$

Temperature (T), ion strength (I), dielectric constant, ion charge (z), the size of the ions (in Angstroms), as well as the density (d) of the medium are factors which influence the activity constant.

All these factors link ion activity with ion concentration through two effects. One is the so called salt effect $\gamma_{H^+}^x$.

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

Where: $I = \text{total ionic strength} = \frac{1}{2} \sum c_i z_i^2$

If we assume that both the anion as well as the hydrogen ion are monovalent, z_i will be equal to 1. Thus the molality remains the main factor in calculating the ion strength.

The following example shows the influence of the salt effect on the activity coefficient at the different molalities.

Molality	0.001	0.005	0.01	0.05	0.1
Activity coefficient	0.964	0.935	0.915	0.857	0.829

Table 3

0.01 M HCl solution:

$$\begin{aligned} \text{pH} &= -\log (b_{H^+} \gamma_{H^+}^x) \\ &= -\log (0.01 \times 0.915) \\ &= -\log (9.15 \times 10^{-3}) \\ &= 2.04 \end{aligned}$$

0.01 M HCl solution with 0.09 M KCl

$$\begin{aligned} \text{pH} &= -\log (0.01 \times 0.829) \\ &= -\log (8.29 \times 10^{-3}) \\ &= 2.08 \end{aligned}$$

Hence, 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 H^+ concentration may show different pH values if their ion strengths are different.

The second effect which links activity to concentration is the so called medium effect: $\gamma_{H^+}^m$. This effect shows what influence the medium (solvent etc.) will have on the H^+ ion activity. Here electrostatic and chemical interactions play an important role. For instance, the H^+ activity is 200 times greater in ethanol than in water.

Aqueous standard buffers are generally used to calibrate pH measuring chains. Therefore, it is not possible to find a correlation between the H^+ activity in an aqueous and in a non-aqueous solution.

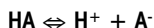
The following equation shows the relationship among activity, concentration, salt effect, and medium effect:

$$a_{\text{H}} = \gamma_{\text{H}^+}^x \cdot \gamma_{\text{H}^+}^m \cdot b_m$$

Conclusion: The more accurately defined the measuring conditions are, the more reproducible the pH values obtained are.

Buffer solutions

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



The anion A^- acts as a base, since it can withdraw protons from the system. The undissociated acid HA, however, supplies the system with protons.

A buffer solution in its equilibrium state has on the one hand enough anions (A^-) to take up the protons added to the system and on the other hand enough dissociated acid available to replace any protons withdrawn from the system.

In other words HA acts as an H^+ donor and A^- as an H^+ acceptor. A buffer solution is at its best when it contains just as many H^+ donors as H^+ acceptors.

The equilibrium constant for a dissociated acid is as follows:

$$K_s = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

or

$$\frac{1}{[\text{H}^+]} = \frac{1}{K_s} \cdot \frac{[\text{A}^-]}{[\text{HA}]}$$

In the case of an incompletely dissociated acid, K_s is not equal to 1. (Where K_s represents the dissociation constant of the acid).

Taking the log of both sides:

$$\log \frac{1}{[\text{H}^+]} = \log \frac{1}{K_s} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

But

$$\log \frac{1}{[\text{H}^+]} = -\log [\text{H}^+] = \text{pH}$$

(from Sørensen equation)

$$\log \frac{1}{K_s} = -\log K_s = \text{p}K_s$$

Hence:

$$\text{pH} = \text{p}K_s + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

This equation is known as the **HENDERSON-HASSELBACH** equation.

The buffer capacity is strongest when the pH value corresponds to the negative log of the dissociation constant, i.e., when:

$$\text{pH} = \text{p}K_s$$

Example:

What pH value does a solution containing 0.1 mol acetic acid and 0.2 mol acetate have? $\text{p}K_s$ value of acetic acid is 4.8

$$\text{pH} = 4.8 + \log \frac{0.2}{0.1} = 4.8 + \log 2$$

$$\text{pH} = 4.8 + 0.3 = 5.1$$

How suitable a solution is as a buffer depends on several factors such as buffer capacity and temperature influences, as well as changes of the pH value due to dilution.

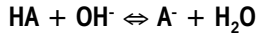
Additionally, it is also important that change in pH value by CO_2 absorption is kept small and that any development of micro-organisms is prevented.

Buffer capacity (β)

The buffer capacity is the ability of a solution to maintain its pH value even after the addition of a strong acid or base.

The buffer capacity of a weak acid or base is limited to $\text{pH} = \text{p}K_s \pm 1$, whereby the greatest buffer capacity is when $\text{pH} = \text{p}K_s$.

If, for example, OH⁻ ions are added to an acetic acid solution (HA), the following equilibrium will appear:



How the pH value depends on the added OH⁻ ions is shown in fig. 22 which represents a titration curve

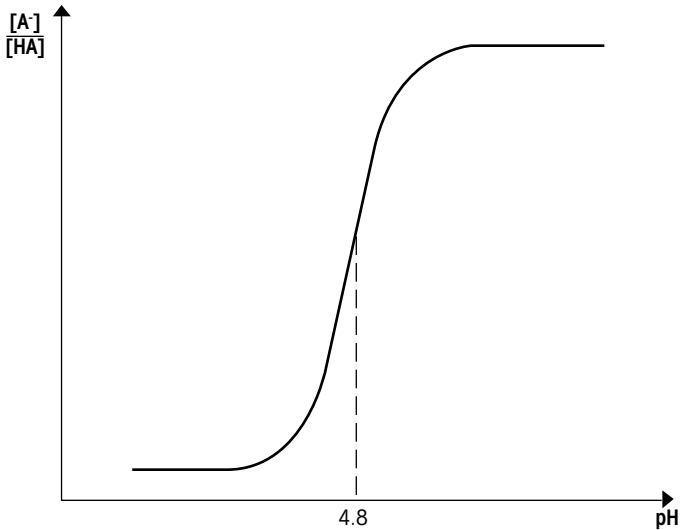


Fig. 22: Titration curve

This curve clearly shows a turning-point at pH 4.8, which corresponds to the pK_s value of acetic acid. At this pH value a relatively large amount of concentrated acid or base is needed in order to change that value.

Dilution value (Δ pH)

The dilution value 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, a negative one that it will decrease with increasing solution.

Standard buffer solution

The buffer solutions of the National Bureau of Standards (NBS) are the basis of the practical pH scale and are accepted by DIN 19266. These should be used as standards for precision measurements and in the manufacture of technical buffer solutions.

Temperature effect $\Delta\text{pH}/\Delta T$

Because the activity of the H^+ ions is dependent on temperature the temperature also influences the pH value.

The temperature coefficient expresses changes of the pH value per $^{\circ}\text{C}$. As shown in table 4 the calcium hydroxide buffer $[\text{Ca}(\text{OH})_2]$, for instance, has a high temperature coefficient of 0.033 pH units per $^{\circ}\text{C}$, i.e., when the temperature increases by 1°C , the pH value decreases by 0.033 pH units.

Composition of the solution (molality)	pH at 25°C	Temperature range ($^{\circ}\text{C}$)	Dilution value ΔpH	Buffer capacity B	Temperature coefficient $\Delta\text{pH}/\Delta T$
primary					
KH Tartrate (sat. at 25°C)	3.557	25 - 95	—	—	—
0.05 M citrate ($\text{KH}_2\text{C}_6\text{H}_5\text{O}_7$)	3.776	0 - 50	+0.024	0.034	-0.0022
0.05 M phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$)	4.008	0 - 95	+0.052	0.016	+0.0012
0.025 M KH_2PO_4 + 0.025 M Na_2HPO_4	6.865	0 - 95	+0.080	0.029	-0.0028
0.008695 M KH_2PO_4 + 0.03043 M Na_2HPO_4	7.413	0 - 50	+0.07	0.16	-0.0028
0.01 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	9.180	0 - 95	+0.01	0.020	-0.0082
0.025 M NaHCO_3 + 0.025 M Na_2CO_3	10.012	0 - 50	+0.079	0.029	-0.0096
secondary					
0.05 M $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	1.679	0 - 95	—	—	—
$\text{Ca}(\text{OH})_2$ (sat. at 25°C)	12.454	0 - 60	-0.28	0.09	-0.033

Table 4: Buffers

Calibration

With a two-point calibration, the pH transmitter is matched to both the zero point and the slope (mV/pH) of the electrode.

A calibration of the zero point and the slope has to be done in order to compensate for any deviations from the ideal values. As mentioned before, these deviations may occur due to a non-ideal behaviour of the different potential sources. A buffer solution with a pH value of 7.0 corresponds to the zero point of most glass electrodes and is especially intended for the zero point calibration. In most cases, buffer solutions of pH 4 or pH 10 (or 9.2) are recommended to adjust the slope.

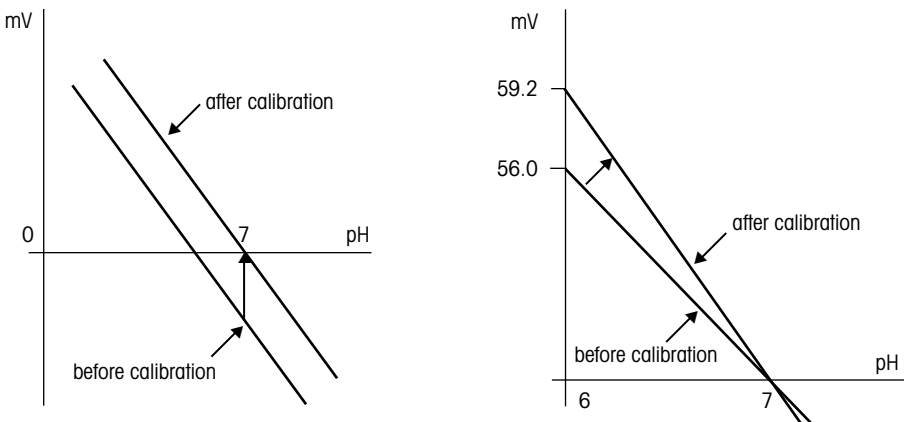


Fig. 23: Zero point compensation (left) and slope compensation at $T=25\text{ }^{\circ}\text{C}$ (right)

Relationship between pH value and temperature

Temperature influences both the individual potentials (E_1 to E_6), as well as the ion activity. This results in two main influences on the slope and the isothermal intersection.

The slope is dependent on the temperature and can be compensated for. The isothermal intersection depends on the behaviour of the individual potentials E_1 to E_6 and is characteristic for every electrode (see fig. 25). An ideal electrode would be present if the calibration lines of different temperatures intersected at the zero point of the electrode (pH 7/0 mV), and if it had a slope according to Nernst, the slope always being proportional to the absolute temperature.

In order to better explain the connection between temperature and slope, we can start with a simplified form of the Nernst equation:

$$E = E_0 + S \log a^{H^+}$$

where $S = \text{slope} = 2.3 RT/F$
 (R and F are constants)

The pH value is, however, defined by Sørensen as $-\log a^{H^+}$, hence:

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

$\Delta pH =$ pH difference between the inner buffer and measured solution

Hence, the slope varies directly with the temperature (Kelvin). This is why the electrode always has to be in a thermal equilibrium with the measured solution (or buffer) in order to obtain a stable pH value.

Temperature compensation

The temperature compensator adjusts for the dependent slope changes described above. The pH meter is equipped with a manual or automatic temperature compensator.

If temperature compensation is not taken into consideration, errors will occur. These will gain in importance with the increasing difference between the fixed and the real temperature. The measuring error also increases the further the pH value of the measured solution is from pH 7 (see fig. 24).

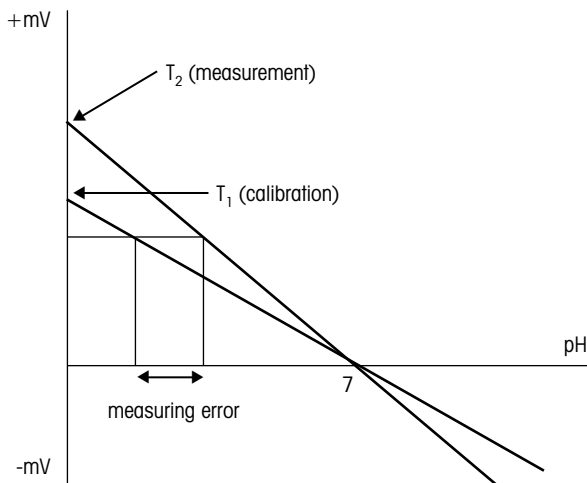


Fig. 24: Temperature compensation

Example: 0.001 mol/L HCl, pH 3

Calibration at T_1	=	25 °C (= 298 K)
Measurement at T_-	=	60 °C (= 333 K)
$E(25\text{ °C})$	=	$E_0 + E_N(25\text{ °C})\text{ pH}$
$E(60\text{ °C})$	=	$E_0 + E_N(60\text{ °C})\text{ pH}$
E_N	=	Nernst potential

Whereby ΔpH is equal to the deviation from pH 7, i.e., in this example, 4 pH units.

Hence:

$$\begin{aligned} \text{Error} &= E(60\text{ °C}) - E(25\text{ °C}) \\ &= E_N(60\text{ °C})\Delta\text{pH} - E_N(25\text{ °C})\Delta\text{pH} \end{aligned}$$

Error in pH units:

$$\begin{aligned} \frac{E(60\text{ °C}) - E(25\text{ °C})}{E_N(25\text{ °C})} &= \Delta\text{pH} \frac{E_N(60\text{ °C}) - E_N(25\text{ °C})}{E_N(25\text{ °C})} \\ &= 0.47\text{ pH units (at } 25\text{ °C)} \end{aligned}$$

Temperature compensation, however, only applies to the function of the electrode and not to the temperature dependent changes of the pH values of the solution. IT CAN NOT BE EMPHASISED ENOUGH THAT IT IS POINTLESS TO DETERMINE A pH VALUE WITHOUT STATING THE TEMPERATURE.

Temperature effects when E_{is} is unequal to 0 mV

In order to fully discuss this error we must look closer at the isothermal intersection E_{is} .

The isothermal intersection E_{is} is the point where the two calibration lines, recorded at different temperatures intersect. In practice this point is seldom at pH 7/0 mV (see fig. 25).

This leads to an error which increases with increasing E_{is} - potential (potential at the isothermal intersection) and the temperature. This error is dependent on the pH value of the measuring solution at definite temperatures.

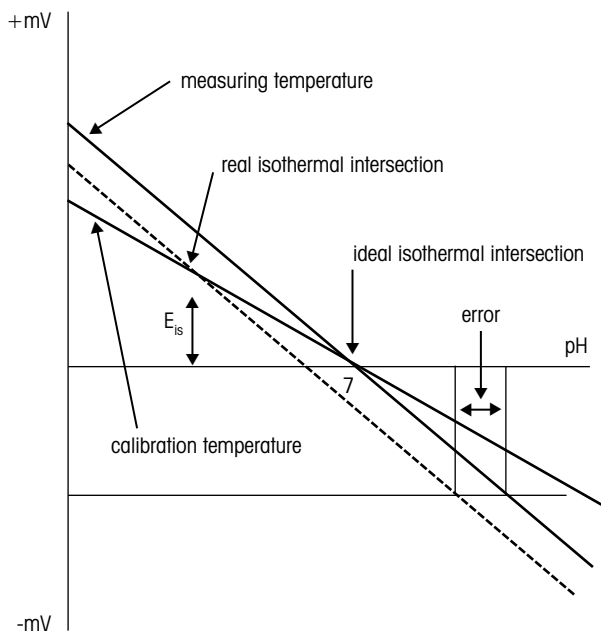


Fig. 25: Isotherm intersection

Example:

0.001 mol/L HCl, pH 3

Calibration at 25 °C

Measuring at 60 °C

$E_{is} = +50$ mV

Slope = 100%

$$\text{Error (in pH units)} = \frac{E_{is}}{E_N(25\text{ }^\circ\text{C})} - \frac{E_{is}}{E_N(60\text{ }^\circ\text{C})} = 0.09 \text{ (@ } 25\text{ }^\circ\text{C)}$$

Further temperature phenomena

In addition to the temperature influences discussed above the response time of the electrode is also influenced by temperature changes.

Temperature coefficient of the measured solution

This phenomenon is not a result of the electrode function or of the interaction between the electrode and the measured solution, but a real pH change which can not easily be compensated for.

As already discussed, the activity of the H^+ ions is temperature dependent. In pure water, the neutral point will shift 1.34 pH units between 0 and 100 °C as a result of the temperature dependent ion product. A similar behaviour is shown by weak acids and bases, since their dissociation constants are also temperature dependent.

The temperature coefficient is determined by two parameters:

- activity coefficient (g)
- acid constant

As a conclusion it can be said that the temperature dependency of the activity constant γ increases the further it is from 1. This is especially the case in concentrated solutions and when ions with high electrical charges are present.

In general, organic acid/base systems show a higher temperature coefficient than inorganic systems. Also alkaline solutions are more temperature dependant than acidic solutions.

This is illustrated by the following example:

Temperature	Phosphate buffer 0.008695mol/l KH_2PO_4 0.03043mol/l Na_2HPO_4	Tris buffer 0.05mol/l Tris HCl 0.01667mol/l Tris
20 °C	pH 7.429	pH 7.840
25 °C	pH 7.413	pH 7.699
30 °C	pH 7.400	pH 7.563
37 °C	pH 7.385	pH 7.382

Tris = Tris-(hydroxymethyl) aminomethane

The above examples show clearly that large temperature coefficients can occur even in nearly neutral solutions.

Phenomena in the case of special measuring solutions

Different problems may occur through disturbances in the measuring system. These problems can either be of electrical or chemical origin.

Alkaline error

The effect called the alkaline error in literature should correctly be called the sodium or lithium error. In practice only these two ions lead to considerable interferences. This effect increases with increasing temperature and pH value ($pH > 9$).

H⁺ ions in the gel layer are partly or completely replaced by alkali ions which leads to a pH value which is too low. Under extreme conditions, i.e., when the H⁺ ion activity can be completely neglected, the glass membrane responds only to sodium ions. This effect can be minimised by using a special pH membrane glass.

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. This effect has been described in literature. As a consequence, an artificially high pH value is registered. The acid error is less disturbing than the alkaline error and is only relevant at very low pH values. Fig. 26 shows the relationship between potential and pH value, taking the acid and alkaline errors into consideration.

Reference: K. Schwabe et al., Z. Elektrochem. 66,304 (1962)

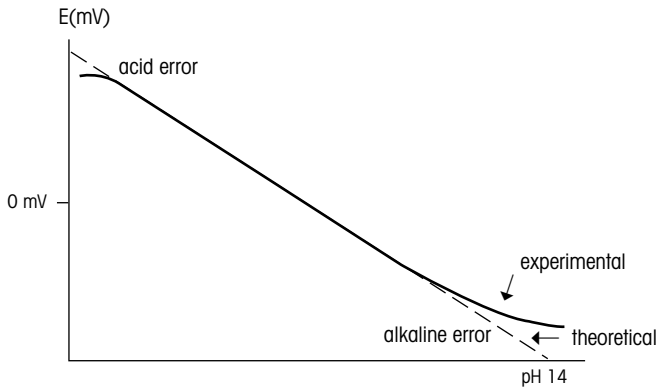
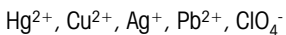


Fig. 26: Relationship between potential and pH value under consideration of the alkaline and acid error respectively

Reactions with the reference electrolyte

Chemical reactions between electrolytes and the measured solution lead to errors. The resulting precipitates clog the pores of the junction and thereby increase the electrical resistance considerably.

The following ions react with KCl to form compounds of low solubility:



Silver chloride may further react with bromide, iodide, cyanide, and especially with sulfide and sulfide compounds such as cystine and cysteine. Contamination due to silver sulfide results in a black coloration of the junction. Contamination of the junction may have as a consequence:

- the response time of the measuring device increases.
- a big and irreproducible diffusion potential develops, which enters into the pH measurement as a direct error.
- the resistance at the junction increases many fold.

In order to prevent such reactions between the electrolytes and the measuring solution either a special electrolyte, which does not react with the above ions, or a bridge electrolyte is used.

Organic media

The conventional pH range of pH 0 to pH 14 is based on the dissociation behaviour of water. However, in some cases the water content of a solution may be increasingly reduced and/or the water is replaced by another solvent. Then, the dissociation equilibrium, i.e., the ion product of the solvent, is relevant and not the one of water. This results in completely different concentration ranges for free, i.e., chemically unbound, H^+ ions. Fig. 27 shows the resulting pH ranges for different solvents.

These difficulties can be partly solved by conditioning the electrode over a rather long period of time (up to several days) in the relevant solvent. Subsequently, the electrode has to be calibrated by adding defined proportions of acid or base. Another method is to calibrate the pH glass electrode with different samples which have a composition corresponding to the different system conditions of the process to be observed. This makes it possible to differentiate these operating conditions during the measurement.

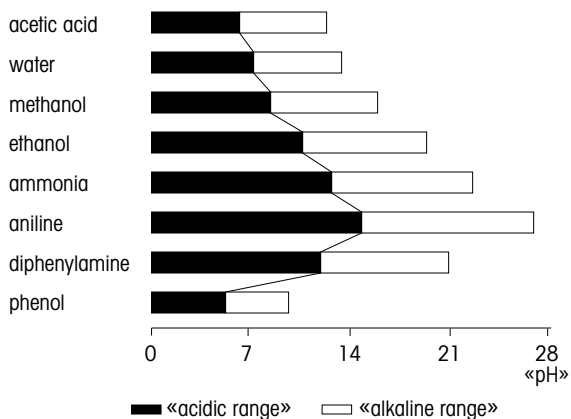


Fig. 27: pH scale in different solvents

Glossary of terms relating to pH

Absolute mV mode

A mode of operation of a pH/mV meter which allows the actual true potential of the electrode to be displayed. In the absolute millivolt mode the calibration control (asymmetry potential control) does not change the readings.

Accuracy

Correctness. The closeness of a measured value to the known "true" value.

Asymmetry potential

The potential across a glass pH electrode membrane when the inside and outside of the membrane are in contact with solutions of identical pH. This term has also been used to define the observed potential differences between identical electrode pairs placed in identical solutions. Differences can occur because of variability in the potentials of the internal reference elements of both the sensing and the reference electrodes, differences in liquid junction potentials, and differences in internal filling solutions. These variations in electrode potential are compensated for by the instrument calibration control (asymmetry potential control).

Automatic temperature compensation (ATC)

Automatic instrumental adjustment of displayed pH to correct for variations in electrode slope due to temperature changes. The output of a thermistor probe regulates the correction factor.

Combination electrode

A sensing electrode and reference electrode housed in one body.

Concentration

The actual amount of a substance in a given volume of solution.

Drift

Slow changes in the potential of the electrode pair maintained in a solution of constant composition and temperature.

Electrolyte

A substance which ionizes in aqueous solution. Weak electrolytes are only slightly dissociated into ions in solution (acetic acid), and strong electrolytes are highly dissociated (HCl, NaCl). Strong electrolytes are good conductors of electricity, and conductance measurements are well correlated with electrolyte strength.

Filling solution

The solution inside a sensing or reference electrode which is replenished periodically. Solutions that are permanently sealed within the electrode (like the buffer inside a pH electrode) are usually called internal reference solutions to differentiate them from filling solutions.

Interference

Any species in the sample solution that causes either a positive or a negative measurement error. Electrode interference - any species, other than the ion being measured, that changes the sensing electrode potential.

Junction potential

The portion of the total observed potential developed between the sensing and reference electrodes that is formed at the liquid/liquid junction between the reference electrode filling solution and the sample solution. For accuracy, the junction potential should be as low and as constant as possible.

Leak rate

The rate at which the reference electrode filling solution enters the sample solution. Low or irregular leak rates may cause variations in the liquid junction potential, resulting in erroneous readings.

Nernst equation

A mathematical description of electrode behaviour.

$$E = E^0 + 2.3 RT/nF \log A$$

Noise

Abrupt, random, small changes in displayed electrode potential, usually due to the pickup of strong static charges. Noise may be caused by air bubbles, poor conductors, or high electrical resistance somewhere in the circuit. Some older pH meters are sensitive to fluctuations in line voltage, and this may appear as noise.

Open circuit

Lack of electrical contact in any part of the measuring circuit (which consists of the sensing electrode, instrument, reference electrode and solutions). An open circuit is characterized by rapid large jumps in displayed potential, followed by an off-scale reading. Frequent large erratic changes in potential indicate an intermittent open circuit.

pH electrode

A specific ion electrode, made of glass, that responds to hydrogen ion activity, over the range 1 M H⁺ (pH 0) to 10⁻¹⁴ M H⁺ (pH 14). Special purpose electrodes are made for very acidic or very alkaline solutions, solutions containing high levels of other cations, high temperature operation, and industrial and medical applications. pH electrodes may be subject to "acid error" in strongly acidic solutions and are also subject to alkaline error caused by response to sodium or other cations in highly basic solutions.

pH/mV meter

An instrument that measures and displays the voltage developed between a sensing electrode and a reference electrode placed in a solution, and which can convert the voltage developed by a pH electrode to a corresponding pH value.

- Analogue pH/mV meter - an instrument that displays voltages, pH units, or other concentration units by means of a needle pointer and scale.
- Digital pH/mV meter - an instrument with digital display of millivolts or pH units. Less operator error is associated with digital instruments since there is no need for interpolation and no risk of confusing scales.

pH unit

A tenfold change in hydrogen ion activity, expressed as the negative logarithm of the hydrogen ion activity. Thus a solution of pH 7 is 10⁻⁷ M in hydrogen ion activity, and a pH 8 solution is 10⁻⁸ M. The lower the solution pH, the more acidic the solution.

Precision

A measure of the reproducibility of a method, when multiple measurements are made on the sample under the same conditions. The observed values may differ from the true values without affecting the precision and reproducibility. See accuracy.

Reference electrode

The half of the electrode pair which provides a constant potential regardless of solution composition.

Relative millivolt mode

An operating mode of a pH/mV meter in which the displayed electrode potential can be changed by means of the calibration (asymmetry potential) control.

Reproducibility

The closeness of replicate measurements on the same sample, using the same measuring technique, under the same conditions. Reproducibility can be limited by many factors, including instrument or electrode stability, loss of the substance being measured during sample operation and contamination.

Response time

The length of time necessary to obtain a stable electrode potential when the electrode is removed from one solution and placed in another of different concentration or temperature. Response time depends on the electrode type, the measuring solution, the magnitude and direction of the concentration change, temperature, and the presence of electrode interferences, if any.

Salt bridge

A technique for isolating the reference element of a reference electrode from the sample solution by use of an intermediate solution containing non-interfering ions. Formerly a U tube filled with saturated KCl (often gelled with agar) was commonly used. In the double junction reference electrode, the outer filling solution serves this purpose.

Slope

The angle between the horizontal axis and the line formed by plotting electrode potentials against ion level on semi-logarithmic graph paper. By analogy, slope has also come to be a measure of electrode response to the ion being detected. Theoretical Nernstian slope, which is temperature dependent, is 59.16 mV at 25 °C for a ten fold change in the activity of a monovalent ion. Less than theoretical slopes (that is, smaller millivolt changes per decade) may be indicative of contamination at the sensing membrane.

Temperature effects

Changes in potential developed between a sensing and reference electrode due to changes in temperature. The slope of a sensing electrode varies with temperature, as does the potential developed by the internal reference element in the reference electrode. In addition, the solubility of salts such as AgCl or HgCl₂ changes with temperature. It is therefore advisable to measure all samples and standardizing solutions at the same temperature.

Troubleshooting

Determining which part of a system is responsible for a problem. In working with electrodes, it must be remembered that the system has six components; sensing electrode, reference electrode, instrument, solution, measuring technique ... and operator.

Zero potential point

The solution concentration at which an electrode pair develops a potential of 0 mV. In many instances, it is also the isopotential point.

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