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Education Series
Practical pH: Theory and Use



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Practical pH: Theory and Use

Introduction

Since the Danish chemist S.P.L. Sorensen defined pH in 1909, an enormous development of the theory and practical application of the pH concept has taken place. Today, the pH value is an important determining factor in a majority of chemical processes and the pH meter has, consequently, become the most widely used analytical laboratory instrument. Measurement of pH by means of electronic instrumentation and electrodes holds a key position in the modern laboratory.

Reliable pH measurement requires more than a well functioning pH meter. The electrodes should be selected in accordance with the actual sample(s) and should be in a proper working condition, that is, should be fast and reproducible. Furthermore, the calibration buffers and the calibration procedure are cornerstones if accurate results are to be obtained. The buffers applied should be precision solutions without contamination (CO₂ or microbiological) and the calibration procedure should be correctly performed.

Microprocessor controlled pH meters simplify calibration and operation so that pH measurements can be obtained quickly. Advanced instruments inform the operator about electrode failures or possible operator mistakes. The meter itself is able to check for a properly functioning electrode and correctly perform calibration procedures. A self-check program allows the pH meter to check itself for operational errors. Using NIST buffer solutions rounds out the necessary ingredients for proper and accurate pH measurement.

What is pH?

The Danish scientist S.P.L. Sorensen first proposed the term pH as an abbreviation of "pondus hydrogenii" in 1909 to express very small concentrations of hydrogen ions.

The original definition of pH, is the negative base 10 logarithm of the **hydrogen ion concentration**, or:

$$\text{pH} = - \log_{10}[\text{H}^+]$$

However, since most chemical and biological reactions are governed by the **hydrogen ion activity**, the definition was changed to:

$$\text{pH} = - \log_{10}a_{\text{H}^+}$$

The operational pH definition, which is currently defined using a standard hydrogen electrode setup and buffers standardized in accordance with IUPAC recommendations, is closely related to the definition of pH given above, using the **hydrogen ion activity**.

In any collection of water molecules, a small number of water molecules will dissociate to form $[H^+]$ and $[OH^-]$ ions:



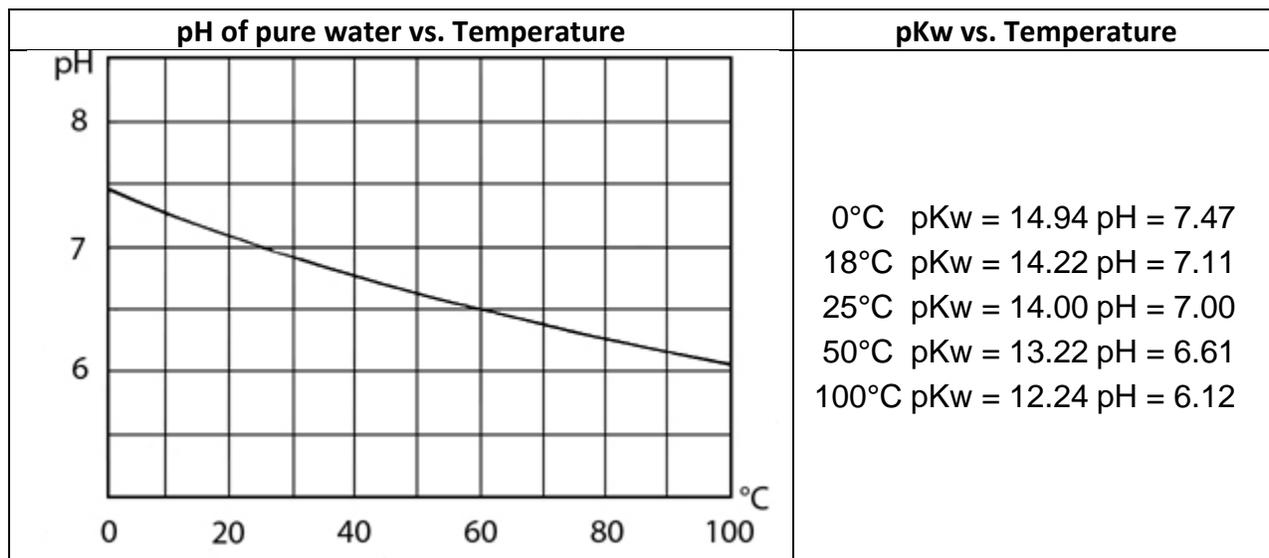
At 25°C (standard temperature), pure water contains 1×10^{-7} moles per liter of hydrogen ions and 1×10^{-7} moles per liter of hydroxide ions.

In any aqueous solution, the concentration of hydrogen ions multiplied by the concentration of hydroxide ions is constant, allowing us to define the dissociation constant for water, K_w :

$$K_w = [H^+] [OH^-] = 10^{-14}$$

where the brackets signify molar concentrations.

The value of K_w (and therefor pH) is temperature dependent:



The pH scale was established to provide a convenient and standardized method of quantifying the acidity or basicity of a particular solution. The range of the pH scale is based on the dissociation constant of water, K_w , defined above.

Since most samples we care about measuring will have less than 1 Molar H^+ or OH^- concentrations, the extremes of the pH scale are established at pH 0 to pH 14. With strong acids or bases, pH values below pH 0 and above pH 14 are possible, but such samples are rarely measured.

When acids and bases are dissolved in water, they alter the relative amounts of H^+ and OH^- ions in solution. If an acid is dissolved in water, it increases the H^+ ion concentration. Because the product $[H^+][OH^-]$ must remain constant, the OH^- ion concentration must therefore decrease. If a base is dissolved in water, the converse happens.

Thus, pH can also be viewed as a simultaneous measurement of both acidity and basicity, since by knowing the concentration of either the H^+ or the OH^- ion, one can determine the other.

pH is a logarithmic function. A change in one pH unit is equal to a ten-fold change in H^+ ion concentration. The table below illustrates the relationship between the H^+ and OH^- ions at different pH values:

HYDROGEN AND HYDROXIDE ION CONCENTRATIONS IN MOLES/LITER AT 25°C		
pH	[H⁺]	[OH⁻]
0	(10 ⁰) 1	0.00000000000001 (10 ⁻¹⁴)
1	(10 ⁻¹) 0.1	0.00000000000001 (10 ⁻¹³)
2	(10 ⁻²) 0.01	0.00000000000001 (10 ⁻¹²)
3	(10 ⁻³) 0.001	0.00000000000001 (10 ⁻¹¹)
4	(10 ⁻⁴) 0.0001	0.00000000000001 (10 ⁻¹⁰)
5	(10 ⁻⁵) 0.00001	0.0000000001 (10 ⁻⁹)
6	(10 ⁻⁶) 0.000001	0.000000001 (10 ⁻⁸)
7	(10 ⁻⁷) 0.0000001	0.00000001 (10 ⁻⁷)
8	(10 ⁻⁸) 0.00000001	0.0000001 (10 ⁻⁶)
9	(10 ⁻⁹) 0.000000001	0.000001 (10 ⁻⁵)
10	(10 ⁻¹⁰) 0.0000000001	0.0001 (10 ⁻⁴)
11	(10 ⁻¹¹) 0.00000000001	0.001 (10 ⁻³)
12	(10 ⁻¹²) 0.000000000001	0.01 (10 ⁻²)
13	(10 ⁻¹³) 0.0000000000001	0.1 (10 ⁻¹)
14	(10 ⁻¹⁴) 0.00000000000001	1 (10 ⁰)

The principle of the potentiometric pH measurement is rooted in Nernst's Law.

Nernst found that when a metal object is immersed into a solution containing ions of the same metal, a potential difference occurs.

Nernst defined this potential difference, E, generated by the exchange of metal ions between the metal and liquid, as:

$$E = E_0 + \left(\frac{RT}{nF} \right) \cdot \ln [M^+]$$

Where:

R = gas constant (R=8.314J/mole·K)

F = Faraday number (F = 96493 C/mole)

n = valency of the metal

[M⁺] = metal ion concentration

T = absolute temperature in Kelvin

E₀ = normal potential

The "normal potential" is the potential difference arising between the metal and solution when the solution contains 1 mole M⁺/liter.

Because the hydrogen ion has similar properties to metal ions (both have a positive charge), Nernst's law can also be applied to a "Hydrogen Electrode" immersed into a solution containing hydrogen ions.

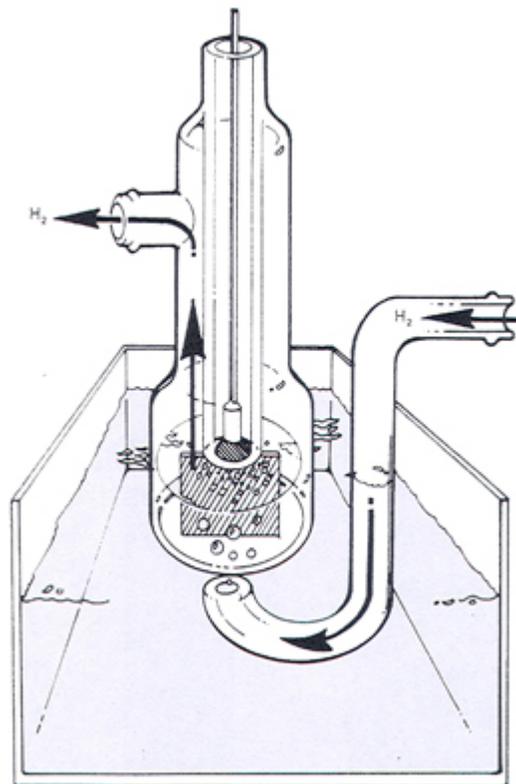
Nernst's original equation can be rewritten as:

$$E = E_0 + \left(\frac{RT}{nF} \right) \cdot \ln [H^+]$$

By definition, the normal potential, E, of the metal "hydrogen" in a 1 normal H⁺ solution is 0 volt at all temperatures. So, we can rewrite the formula as:

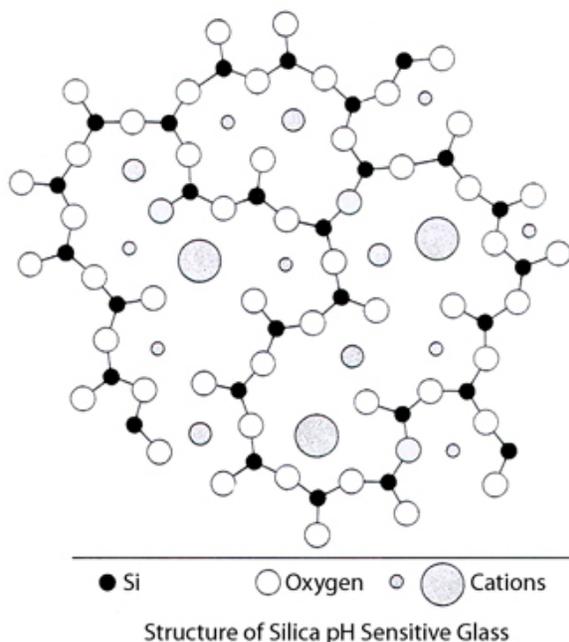
$$E = \left(\frac{RT}{F} \right) \cdot \ln [H^+]$$

The Standard Hydrogen Electrode



A "Hydrogen Electrode" can be made by coating a platinum electrode with a layer of platinum-black and passing a flow of hydrogen gas over it. The platinum-black coating allows the adsorption of hydrogen gas onto the electrode, resulting in a "Hydrogen Electrode".

In 1906, Max Cremer discovered that some types of glass generated a potential difference dependent on the acidic value of the liquid it was immersed in. Together with Fritz Haber, they proved that this potential difference, within a fixed pH range, followed Nernst's law in the same manner as did the "Hydrogen Electrode". They discovered that what made their glass sensors sensitive to changes in pH levels was the formation of what is known in the pH industry as the "gel-layer", or "hydration-layer" of the glass.



As shown in the figure to the left, the structure of pH glass is a network of oxygen atoms held together in irregular chains by silicon atoms. Each silicon atom is associated with four oxygen atoms, and each oxygen is shared by two SiO_4 groups to form a three-dimensional network. The "holes" in this three-dimensional network are occupied by cations (the particular metal cations and their concentrations are typically proprietary formulas), held in place more or less strongly by the electrostatic field of neighboring oxygen ions.

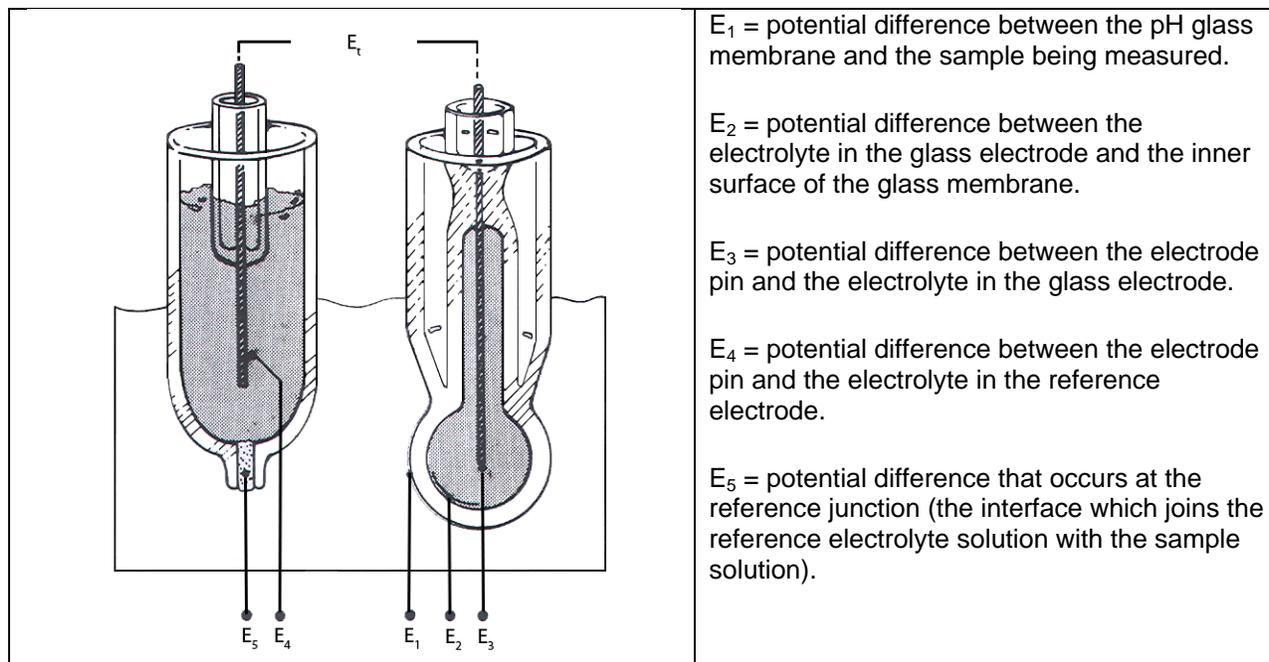
When immersed in an aqueous solution, the surface layers of the pH glass undergo an ion-exchange process, whereby alkali metal ions from the glass go into solution and are replaced by hydrogen ions. This results in both the development of an electrical potential and the buildup of a thin layer containing numerous hydroxyl groups: $\equiv\text{Si-O-Na} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{Na}^+ + \text{OH}^-$ on the surface of the glass membrane. This "gel-layer" or "hydration layer" is the equivalent of the metal in Nernst's theory and is essential for the proper functioning of the pH glass electrode. The formation of this gel-layer continues until the ion exchange equilibria is reached and the electrochemical potential remains constant.

With the equilibrium having been reached, the hydrogen ion concentration/activity outside the glass and inside the gel-layer are equal and no further transport of hydrogen ions occurs. The voltage across the glass membrane is now zero. If the hydrogen ion concentration outside the glass and inside the gel-layer differs from the hydrogen ion concentration in the solution being measured, a transport of hydrogen ions takes place. This movement of ions affects the neutrality of the gel-layer and, consequently, a voltage will develop to prevent further transport of hydrogen ions. The value of this voltage is dependent upon the hydrogen ion concentration in the solution being measured. Because this voltage cannot be measured directly, it is necessary to add a *pH independent reference potential* to the measuring circuit. The addition of this reference potential allows us to measure the potential differences that arise across the glass membrane.

The Electrode Chain

Two electrodes, the pH indicator electrode and the reference electrode, comprise the setup for measuring pH. A combination electrode, which includes the indicator and the reference electrodes built into a single body, is often used for convenience.

A small galvanic cell is produced when the two electrodes are immersed in a solution. The total potential developed is dependent on both electrodes, and is a sum total of several individual potentials. See the diagram below for an explanation of these various potential sources:



The sum total of these potential differences, E_t , is expressed as:

$$E_t = E_1 + E_2 + E_3 + E_4 + E_5$$

We are only interested in E_1 (the potential difference between the pH glass membrane and the sample), so the remaining potentials must be compensated for in such a way as to negate their effect on the true pH measurement. Let us re-examine these potentials:

If the potential difference between the electrolytes and electrode pins in both the pH glass electrode and the reference electrode (respectively) are identical and at the same temperature, the potentials generated by each will be equal but opposite: $E_3 = -E_4$, thereby negating each other. We can therefore simplify our equation:

$$E_t = E_1 + E_2 + E_5$$

With an appropriate selection of reference electrolyte and adequate flowrate through the reference junction, the potential difference, E_5 can be neglected, so that

$$E_t = E_1 + E_2$$

Because E_1 and E_2 are of opposite polarities in the pH measuring loop, our equation becomes:

$$E_t = E_2 - E_1$$

We can keep the potential difference, E_2 constant by filling the glass pH electrode with an electrolyte with excellent buffering properties, leaving us with the only remaining potential difference, E_1 (the potential difference between the glass pH membrane and the sample).

Ideal conditions however, rarely exist in actual practice. For various reasons, a small potential difference can develop, and this potential difference is known as the *asymmetry potential*. The asymmetry potential can be caused by:

- A reference junction potential (E_5 not equal to 0).
- The inner and outer surfaces of the pH glass membrane may vary due to differences in glass texture which can occur during the bulb blowing process ($E_3 + E_4$ not equal to 0).

Fortunately, Asymmetry potentials are compensated for during the calibration process using appropriate buffer solutions.

Only if the potential of the indicator electrode changes in response to varying pH while the potential of the reference electrode remains constant, do ideal measuring conditions exist.

The Nernst equation expresses the measured voltage:

$$E = E_{\text{ind}} - E_{\text{ref}} = E'_T - (R \cdot T/F \cdot \ln a_{\text{H}^+})$$

where

E = measured voltage (mV)

E_{ind} = voltage of indicator electrode (mV)

E_{ref} = voltage of reference electrode (mV)

E'_T = temperature dependent constant (mV)

R = gas constant (8.3144 J/K)

T = absolute temperature (K)

F = Faraday's constant (96485.31 Coulombs)

The formula can be written

$$E = E'_T - (2.303 \cdot R \cdot T/F \cdot \log a_{\text{H}^+})$$

By introducing the pH definition as $\text{pH} = -\log a_{\text{H}^+}$, pH can be expressed at the temperature T as follows:

$$\text{pH}_T = \text{pH}_T^\circ - (E / R' \cdot S \cdot T)$$

where

R' = constant = 0.1984 mV/K

S = sensitivity (since the electrode response may differ from the theoretical response, a correction factor)

pH° = zero pH (the pH value at which the measured potential is zero; changes with temperature, producing another slope; see Figure 1)

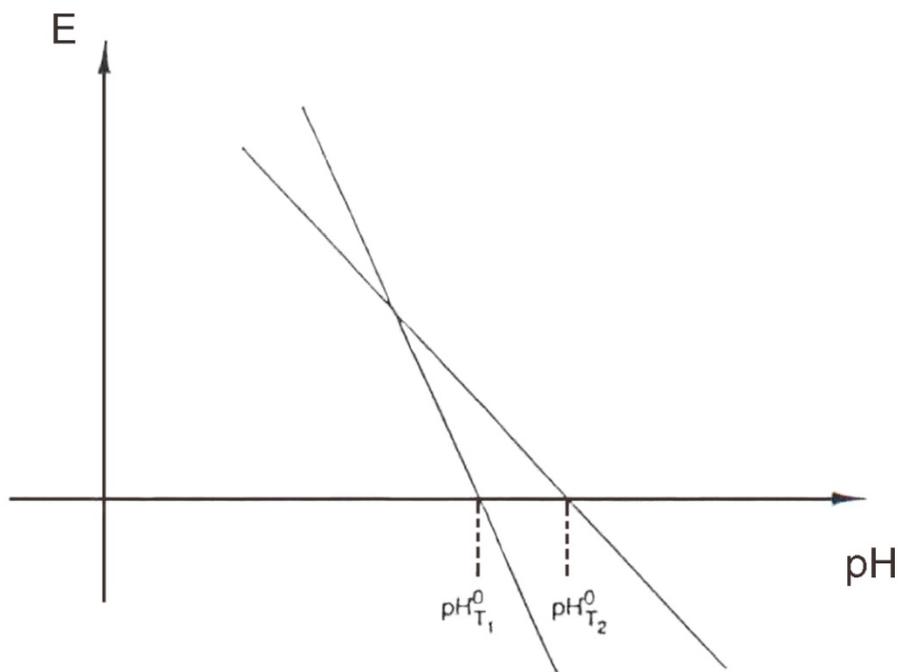
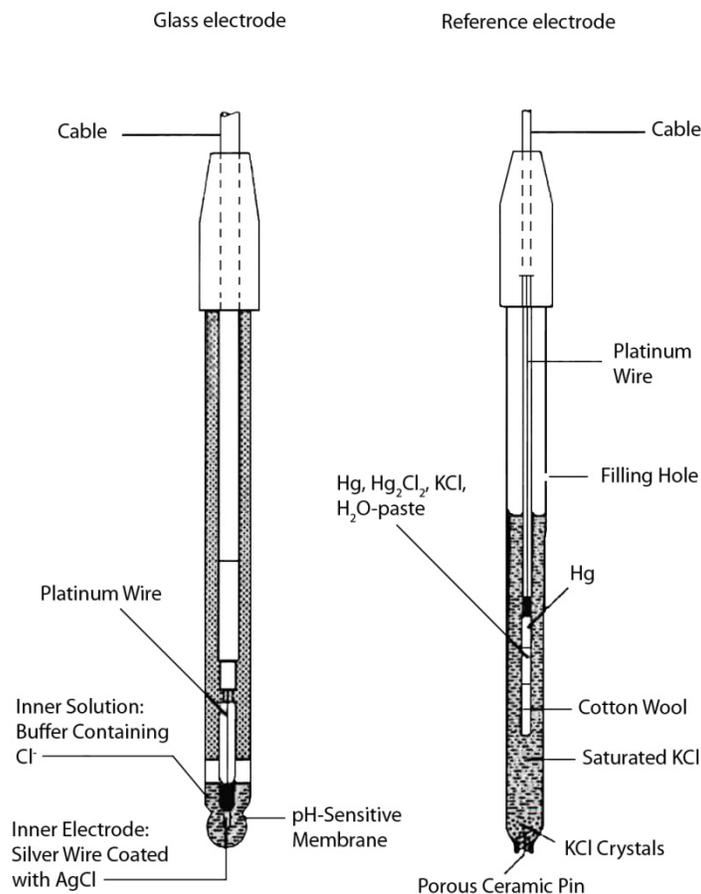


Fig. 1. The mV/pH relation at two different temperatures.

Electrode Construction

There are many ways to construct a glass indicator electrode and a reference electrode. Refer to the figure below for a typical representation of each.

Figure 2. Typical Electrode Constructions.



The potential which will develop for the glass electrode is a function of both the indicator electrode's pH sensitive glass and the composition of the inner solution. The potential of the silver chloride coated silver wire, the inner electrode, depends on the chloride concentration in the inner solution and will remain constant in each electrode.

Response of the electrode may be described as the voltage developed between the inside and the outside of the glass membrane. It is proportional to the pH difference in the sample and in the inner solution. The ion exchange, controlled by the concentration of the H^+ in both solutions, determines the electrode response caused by an exchange at both surfaces of the membrane between the ions of the glass and the H^+ ions of the solution. In addition, owing to the fact that the glass membrane is rarely uniform, an asymmetry potential may develop even if the pH is the same on both sides of the membrane.

The figure above shows a saturated calomel electrode, the reference electrode, consisting of a chamber containing mercury and calomel (Hg_2Cl_2) which are in contact with each other. Contact between the mercury and the calomel is made by a platinum wire while the small internal chamber is surrounded by a solution of saturated KCl. Contact between the saturated KCl and the measured solution, the liquid junction, is made through a porous ceramic pin. The

potential which occurs at this point is constant and is determined by the solubility product of the calomel and the concentration of the KCl solution.

A silver-silver chloride reference electrode is constructed in much the same way. The small internal chamber should be constructed of red glass to prevent photochemical reactions from occurring from exposure to light. A Ag/AgCl reference electrode is used for temperatures that vary from sample to sample and for high temperature measurement.

The potential of the reference electrode should not depend on the sample solution. Ideally, only K^+ and Cl^- ions are transported through the porous pin and move at the same speed. This occurs when the pH range of the samples is in the range of 1 to 13 and when a saturated or 3M KCl internal filling solution is used. A liquid junction potential may occur if there is deviation from this optimal situation.

Liquid junction potentials in different samples obtained with saturated KCl as the internal filling solution are listed in Table 1. Dependence on sample composition and especially on pH is obvious by checking the liquid junction potentials.

Table 1. Liquid junction potentials in different samples.

Sample	Liquid Junction Potential
1M HCl	14.1 mV
0.1M HCl	4.6 mV
0.01M HCl	3.0 mV
0.1M KCl	1.8 mV
pH 1.68 buffer	3.3 mV
pH 4.01 buffer	2.6 mV
pH 4.65 buffer	3.1 mV
pH 7.00 buffer	1.9 mV
pH 10.01 buffer	1.8 mV
0.01M NaOH	2.3 mV
0.1M NaOH	-0.4 mV
1M NaOH	-8.6 mV

Table 2 shows the equivalent conductivity in infinitely dilute solutions of the ions commonly used in internal filling solutions. The lowest liquid junction potential results from equal conductivity of the cation and anion, a measure to their mobility in solution.

**Table 2. Equivalent conductivity of ions
in infinite dilutions ($S \cdot cm^2 / equivalent$) at 25°C.**

Cation	λ	Anion	λ
Li^+	38.7	CH_3COO^-	40.9
Na^+	50.1	ClO_4^-	67.4
K^+	73.5	NO_3^-	71.5
NH_4^+	73.6	Cl^-	76.4
		Br^-	78.1
		$1/2 SO_4^{-2}$	80.0
H^+	349.8	OH^-	198.3

Types of electrodes

Glass Electrodes

Glass electrodes are available in many shapes and lengths to fit a wide variety of applications. Very thin electrodes for measurements in small diameter tubes, spear point electrodes for measurements in meats and cheeses, and flat membrane electrodes for surface measurements are quite common. The composition of the electrode membrane, as well as the shape, size, and type of inner electrode, can vary. The pH sensitive glass composition will determine the electrode's response time and its sensitivity to other ions as well as to H^+ . Sodium ion error or, to a lesser extent, lithium ion error, may enter the picture at high pH values ($> pH 11$). This is normally called the sodium ion or alkaline error. A large concentration of sodium ions and a low concentration of hydrogen ions could cause the absorption of sodium ions to penetrate the surface layer of the glass membrane, resulting in a higher surface ion concentration. A lower pH value will result.

Glass electrodes have two disadvantages: 1) measuring solutions containing particulate can damage the glass membrane and 2) the glass membrane is easily broken. There are alternatives to the glass membrane, though they are used seldom due to other drawbacks, such as limited pH range or long response time. The antimony electrode is used as an alternative, mainly in solutions containing HF. A thin oxide layer formed on the surface of the antimony is sensitive to pH.

Reference Electrodes

A variety of reference electrodes are available. The correct type relates to

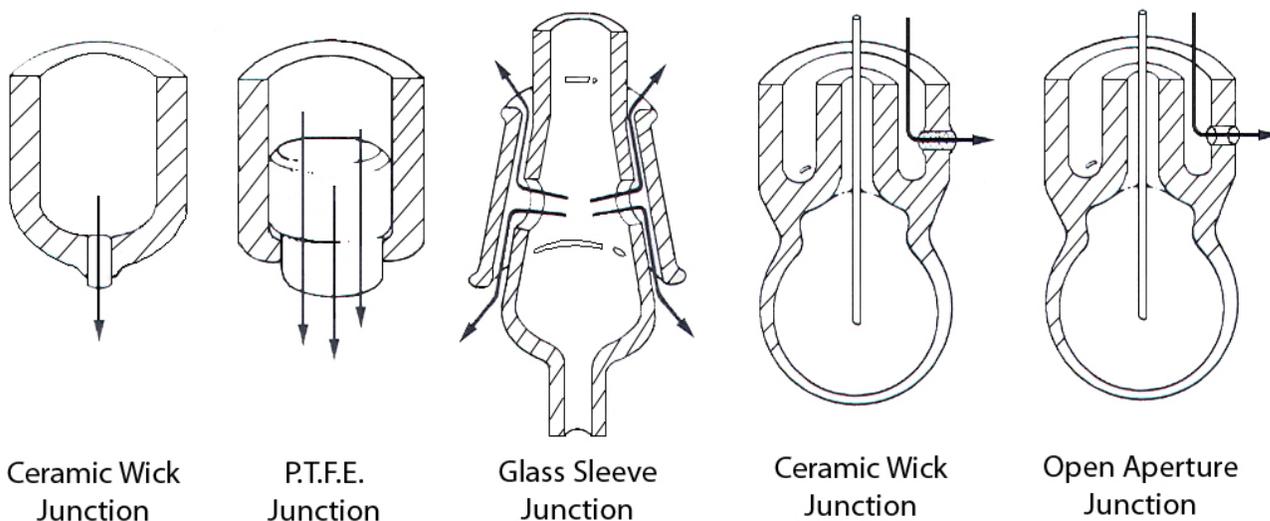
- the physical construction of the liquid junction
- the composition of the internal filling solution
- the electrode's electrochemical composition

Though the most common type of liquid junction is formed by a porous pin, depending on the application, other types may be applicable. Annular ceramic junctions, sleeve junctions, and open liquid junctions are all acceptable alternatives to the porous pin junction, keeping in mind that they all exhibit a higher outflow of internal filling solution. This is very beneficial when measuring in solutions of very high or very low ionic strength. Certain buffers, biological buffers, for example, and viscous solutions require these types of liquid junctions.

Figure 3 shows various different liquid junction types. The typical directional flow of KCl internal filling solution for each is shown.

Figure 3. Various Liquid Junction Constructions.

Arrows indicate direction of electrolyte flow



The internal filling solution should not contain KCl if:

- it will interfere with the measuring solution
- if there is a chance that the liquid junction will clog due to precipitation
- if it is immiscible with the sample

The use of a double junction electrode with a second internal junction not containing KCl or a modified internal filling solution can be used. An electrode utilizing mercurous sulfate and potassium sulfate is one example. Several other combinations can be found in Table 3.

Table 3. Potentials for different reference electrodes.

Type of reference electrode	Salt-bridge solution(s)	Potential vs. standard H ₂ electrode	Potential vs. sat. calomel electrode
Hg/Hg ₂ Cl ₂	sat. KCl	244 mV	0 mV
Ag/AgCl	sat. KCl	200 mV	-44 mV
Hg/Hg ₂ SO ₄	sat. K ₂ SO ₄	640 mV	408 mV
Calomel	sat. LiCl	~200 mV	~ -45 mV
Hg/Hg ₂ Cl ₂	sat. KCl/KNO ₃	244 mV	~ 0 mV

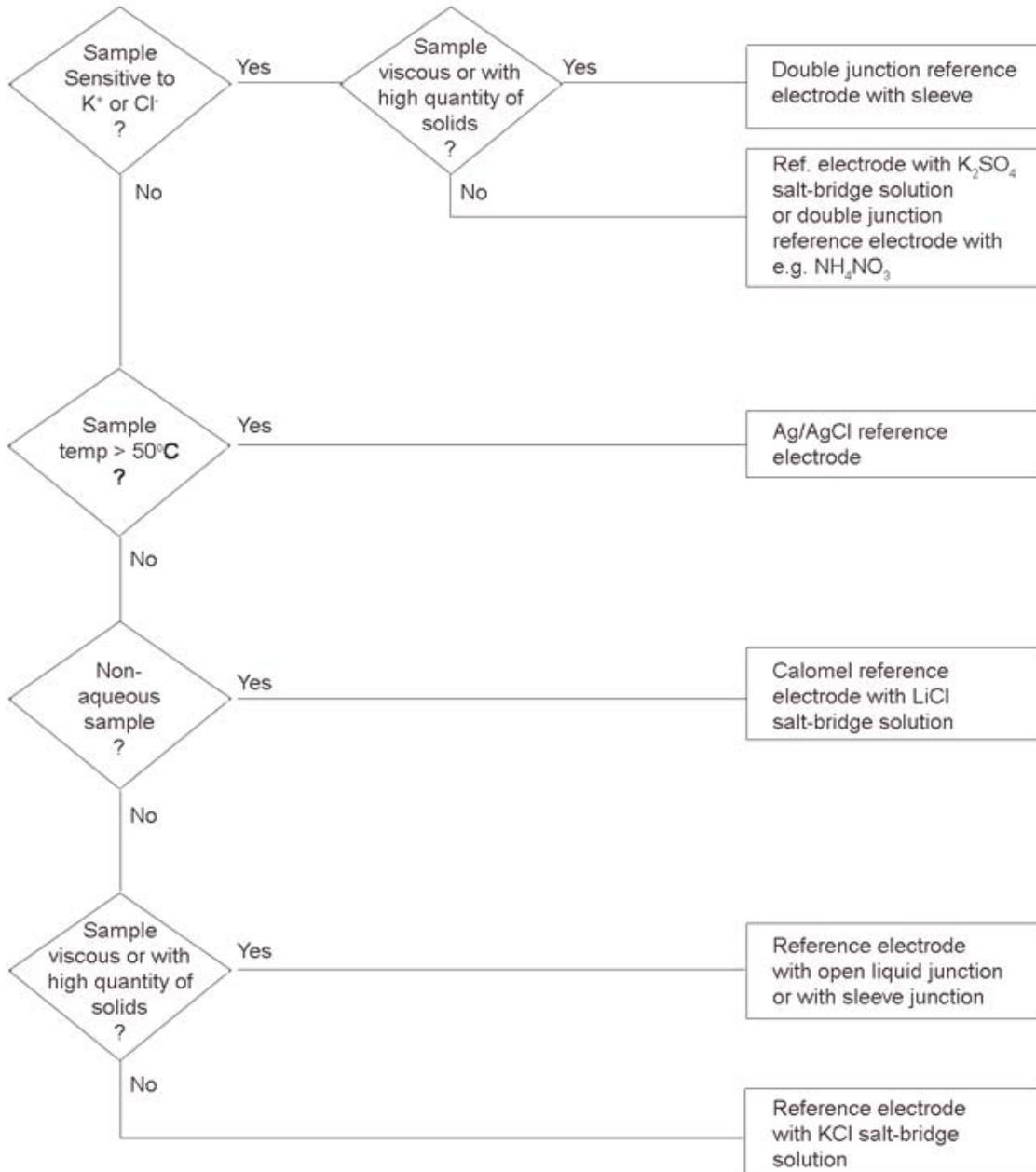
Combination Electrodes

Single stem electrodes, that is, combination electrodes are popular by virtue of their convenience. The indicating electrode and the reference electrode are simply built into the same physical entity. This construction ensures that the two electrodes are at the same temperature during operation.

Combination electrodes with symmetrical electrode chains, that is, identical internal references, are the optimal construction for obtaining temperature equality in the two electrodes. The inner electrode of the glass electrode (Ag/AgCl) is the same type and has the same dimensions as the reference electrode and the internal filling solutions are as identical as possible (saturated KCl).

Which is the correct electrode?

Figure 4. Selection of the correct reference electrode for differing measuring conditions



The correct **physical dimensions** of the electrode are dictated by the sample size and the sample vessel. Electrodes with epoxy bodies and protective cap in place should be used for harsh environment conditions. An electrode with a flat membrane should be used for measurements performed directly on flat surfaces. In short, there is literally an electrode design for almost every possible measuring situation.

High temperature measurements limit your choice of electrodes since only certain electrochemical systems can withstand high temperatures. Calomel electrodes will not withstand temperatures above 60° C, as decomposition of the calomel paste will occur. Certain Ag/AgCl reference electrodes, however, may be used instead. The composition of the electrode also restricts the temperature range in some cases. **Low temperature measurements** requires longer response time for an accurate measurement. Longer response times may also be caused by small or thick membranes and in glass formulations especially suited for measurements in solutions exhibiting alkaline error.

High pH and high salt concentrations require electrodes with alkali-resistant glass membranes. An electrode with standard glass composition should be used in all other cases, as the alkali-resistant glass is more fragile than standard glass.

Emulsions or fatty solutions require the correct type of liquid junction, that is, one that is easily renewed and cleaned. An open liquid junction or sleeve junction electrode is recommended. Though these types of liquid junctions are sometimes recommended for measurements in **non-aqueous solutions**, electrodes containing electrode filling solutions with lithium chloride are usually recommended since LiCl is soluble in many organic media while KCl has a very limited solubility.

If **chloride interference or contamination** is a problem, a reference electrode with a chloride free reference system must be used, that is, an electrode containing Hg/Hg₂SO₄ with K₂SO₄ filling solution, or a reference electrode with a double salt bridge.

Pure water pH measurements or other **solutions exhibiting low ionic strength** may pose measurement problems. An electrode with a fairly high outflow of KCl is necessary to minimize the liquid junction potential, though contamination of the measuring solution will occur more quickly than with other types of liquid junctions. Annular ceramic junction and sleeve junction electrodes will help minimize the outflow of the electrode filling solution, though their junction potentials are less stable.

A **solution high in ionic strength** and some buffer solutions require a high outflow to guarantee that the ionic transport in the junction is still dominated by the K⁺ and the Cl⁻ ions. Open liquid junctions and sleeve junctions are recommended for this type of measuring environment. An open liquid junction with a controlled and small outflow can be used for high precision measurements.

Maintaining the electrode

Maintaining the electrode on a regular basis ensures:

- a faster response
- more reliable measurements
- a longer lifetime

Since the glass electrode and the reference electrode are maintained differently, they will be described separately. A combination electrode is a blend of maintenance procedures from both the glass electrode and the reference electrode instructions.

Several electrode suppliers have maintenance kits containing all necessary items for maintaining glass, reference, and combined electrodes.

Glass Electrode Care

The entire glass membrane must always be clean. Rinsing the membrane with distilled water will often suffice for aqueous solutions. Rinsing the electrode with a mild detergent solution once a week will be beneficial. An alkaline hypochlorite solution can be used to clean electrode membranes subjected to solutions containing fat or proteins.

Between measurements, store the glass electrode in a pH buffer with $\text{pH} < 7$. High temperature measurements, compounded by constant use in strong alkaline solutions or weak solutions of hydrofluoric acid will drastically reduce the lifetime of the electrode, since the glass membrane will slowly dissolve.

Dry storage is recommended if the electrode will **not** be used for two weeks or more. Before use, the electrode should be soaked well.

Trapped air bubbles around the inner reference electrode will produce an unstable reading. Swing the electrode in an arc or tap it gently to remove the bubbles. The electrode may have to be heated gently to approximately 60°C in a water bath if the air bubbles are trapped by KCl crystals.

In order to establish a **stable, hydrated glass membrane**, new or dry-stored electrodes should be soaked overnight in 0.1 M HCl. After overnight soaking, rinsing, soaking in a buffer of $\text{pH} = 4$, and again rinsing, the electrode should be ready for use. If a shorter soaking time is necessary, the electrode should be calibrated frequently to adjust for drifting potentials.

A **sluggish response** for a glass electrode, even after proper maintenance has been performed, may dictate the need for a slight etching of the outer glass layer of the membrane. **The following treatment is only recommended after all other measures have been used to improve response and have failed.** Soak the glass membrane portion of the glass electrode in a 20% ammonium bifluoride solution for one minute, followed by 15 seconds in 6 M hydrochloric acid. (Since hydrofluoric acid can be formed during this procedure, be careful if choosing this method of electrode rejuvenation.) Rinse the electrode well and soak for 24 hours in a pH buffer with $\text{pH} < 7$.

The **proper functioning of the glass electrode depends on the hydration of the glass layer** that takes place on the surface of the pH sensitive glass membrane during soaking and measurement in aqueous solutions. As long as the electrode is frequently rehydrated, accurate measurements in **non-aqueous or partly aqueous solutions** are also possible. This can be accomplished by soaking in a slightly acidic buffer. In non-aqueous solvents completely immiscible with water and before soaking, the electrode should first be rinsed with a solvent which is miscible with both water and the solvent before rinsing with water.

The **electrode cable and the electrode plug must be kept clean and dry** if reliable measurements are to be obtained because of the very small electrode currents which pass through the glass electrode.

A number of factors dictate the **useful lifetime** of the glass electrode membrane and is highly individualistic. High temperatures, frequent measurements in alkaline solutions, repeated etchings, and improper maintenance will reduce the electrode's lifetime, whereas proper maintenance will prolong the useful lifetime. The glass membrane will, however, deteriorate gradually even when stored dry. A standard glass electrode, whether a monoprobe or a combination electrode, will usually last for 12 - 18 months.

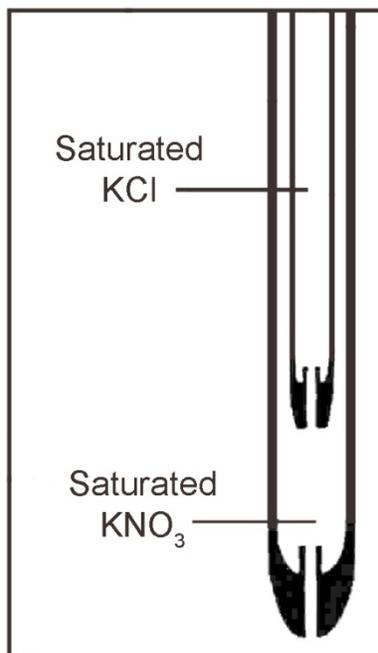
Reference Electrode Care

The reference electrode must also be kept clean. In general, most electrode problems can be traced back to the reference electrode. Cleaning and rinse solutions are the same as for the glass electrode.

The electrode **must always be filled with the salt bridge solution**. For most electrodes, saturated potassium chloride, KCl, is normally used. The presence of **KCl crystals in the salt bridge assures saturation**.

In certain cases, the salt bridge solution may be different than saturated KCl, depending on the special nature of the reference electrode, i.e., the need for a chloride free solution or for non-aqueous solutions. In these instances, potassium sulfate or lithium chloride solutions will be used, respectively. When reference electrodes with a double salt bridge are used, saturated potassium chloride is normally found in the inner salt bridge, while the outer salt bridge contains a suitable salt of high concentration, such as KNO_3 , NH_4NO_3 , or Li-Acetate.

Figure 5. Double junction Reference Electrode



The reference electrode should preferably be stored in a small beaker containing the salt bridge solution for short term storage. For long term storage, the electrode should be rinsed, dried, and stored with the end cap on and the rubber band covering the filling hole in place.

The solution in the salt bridge should always be on a higher level than the solution to be measured, as infiltration of the sample solution may occur in the salt bridge, that is, the direction of flow should always be **from the salt bridge into the sample solution**. If this cannot always be achieved, monthly changing the salt bridge solution should be the norm.

Annular ceramic junctions and porous pin **junctions can occasionally become blocked** due to crystallization of the salt bridge filling solution. Soaking in the salt bridge solution usually remedies the situation, but, on those instance that it doesn't, raising the temperature to the maximum allowable for the reference system will often help. A precipitate of silver chloride or sulfide may clog the porous pin. The gentle use of an abrasive paper, e.g., emery cloth, will remove most blockages. Soaking the porous pin for a few hours in acidic solution of thiourea (1 M thiourea in 0.1 M HCl) will usually do what the abrasive paper sometimes fails to do, that is, chemically clean the blockage.

Trapped air bubbles can also cause malfunctions. These bubbles can be removed by gently tapping the electrode or shaking it downward as one would a clinical thermometer.

The useful lifetime of a reference electrode depends on the maintenance and care given the electrode. The electrode should never be allowed to dry out, the junction should be kept clean, and the salt bridge should always be filled to the level intended by the manufacturer. With proper maintenance, the lifetime for a reference electrode is indefinite, but usually greater than two years.

By providing good maintenance care to the electrodes, proper calibration should be able to be performed easily. If there is a continued problem, the electrodes should be replaced or examined again.

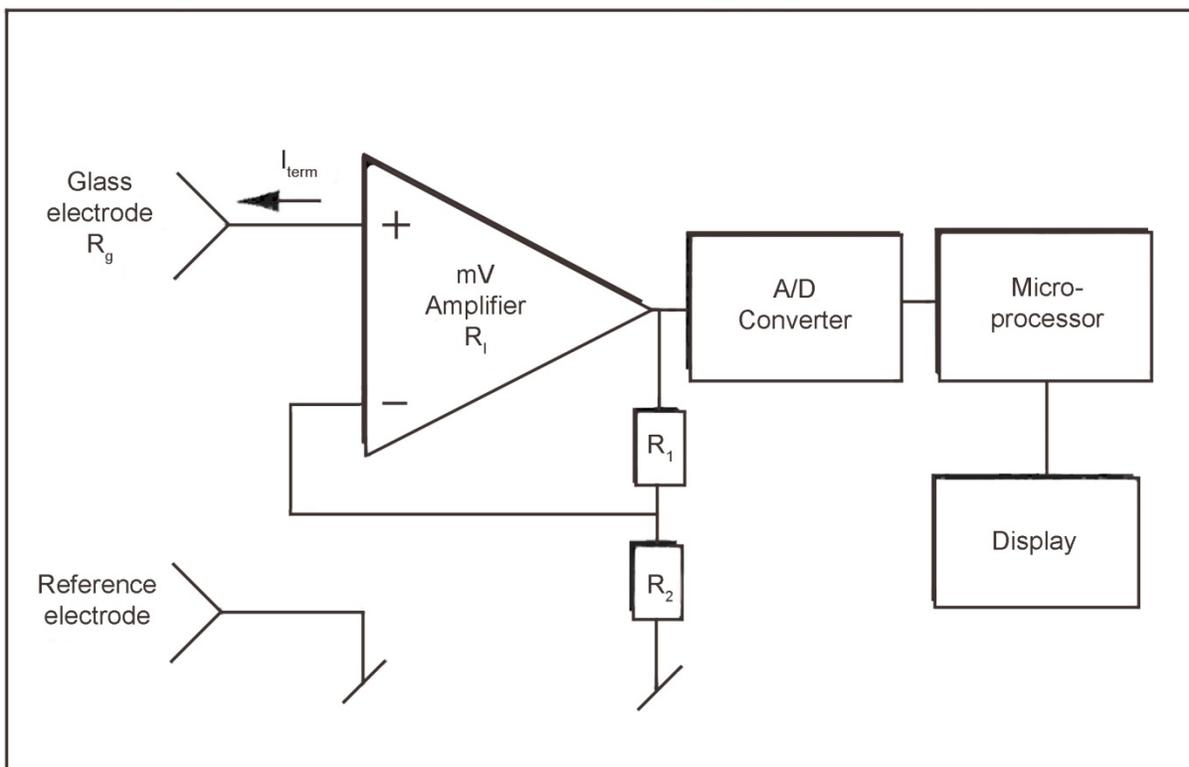
When performing a calibration with two buffers, stability should occur within approximately one minute in each case. The zero point and sensitivity should be written down after each calibration since a large deviation from one calibration to the next indicates a problem.

The pH meter

The function of the pH meter is to measure the potential difference (in mV) between the electrodes and convert it to a pH display.

In Figure 6, we see the construction of a pH meter in a simplified diagram.

Figure 6. Simplified pH Meter Diagram



The input amplifier and the converting circuit must meet certain requirements in order to obtain a correct measurement. A potential difference between the glass electrode and the reference electrode is amplified in the mV amplifier before the A/D converter feeds the signal to the microprocessor for result calculation.

The amplifier's input resistance, R_1 , must be considerably higher than the inner resistance of the typical glass electrode, that is, higher than 10^8 Ohms. It is also important that the amplifier does not send any current through the glass electrode as this will give an error potential and could even damage the electrode. The bias current or so-called terminal current, I_{term} , should therefore be below 10^{-12} A.

When $R_1 > R_g$, $I_{term} = 10^{-12}$ A and $R_g = 10^8$ Ohms, the error introduced can be calculated according to Ohm's Law:

$$V_{error} = 10^{-12} \text{ A} \cdot 10^8 \text{ Ohms} = 10^{-4} \text{ V} = 0.1 \text{ mV}$$

The amplifier and other circuits must have a small temperature coefficient, i.e., the influence of temperature variations must be under control, to attain reliable and consistent results.

The result is displayed in numeric form normally (digital display), though a few pH meters with analogue display are still available.

For an **analogue pH meter**, the zero pH and sensitivity adjustment is carried out using adjustable resistances (knobs) and the amplification factor is under direct manual control. The signal is then sent through an A/D converter. The output is a digital signal for the numeric display.

For a **digital pH meter**, the amplifier works under the same conditions all the time and is directly connected to an A/D converter. A microprocessor based circuit then translates the converter's output and the calculated pH is displayed. A temperature sensor provides both temperature display and a temperature correction. For some microprocessor systems, automatic recognition of calibration buffers and even automatic stability control of the electrode signal is possible.

To avoid interference, the following should be considered:

- To alleviate problems related to noisy electrode signals, proper grounding of all types of pH meters is essential.
- All of the instruments should be connected to the same point if the pH meter is part of a larger measuring system.
- A separate grounding lead must be used if the wall power outlet does not include proper grounding.
- Avoid running the electrode cables parallel to power lines as they may pick up noise.

Buffer solutions

To align the electrodes to the pH meter, a calibration is required. A solution with a precisely known pH with buffering capacity is used for this purpose. Buffering capacity is the ability of the solution to absorb slight additions of acid or alkaline species and still maintain a precisely known pH value.

Pure and stable chemicals are used in buffer solutions. The pH values should be well defined and the liquid junction potential should be the same size as the one for the unknown sample solutions. Two kinds of buffer solutions have been developed: technical buffers with a high buffer capacity and IUPAC / NIST buffers with a lower buffer capacity. The IUPAC / NIST buffers are produced in accordance with the true definition of pH, that is, by using the hydrogen electrode measuring setup, assuring utmost accuracy. The liquid junction potential for these buffers presents no problem in normal, diluted sample solutions.

The buffers in most common usage today have evolved over the years and many of them were originally proposed by the Danish chemist, S.P.L. Sorensen. R.G. Bates, a former employee of the National Bureau of Standards, has researched a number of buffers and his work forms the basis of the current series of IUPAC / NIST buffers.

The buffers' temperature dependency can be expressed using the formula $pH = A/T + B + (C \cdot T) + (D \cdot T^2)$, where T is the temperature on the Absolute temperature scale. The coefficients A, B, C, and D are listed for each buffer.

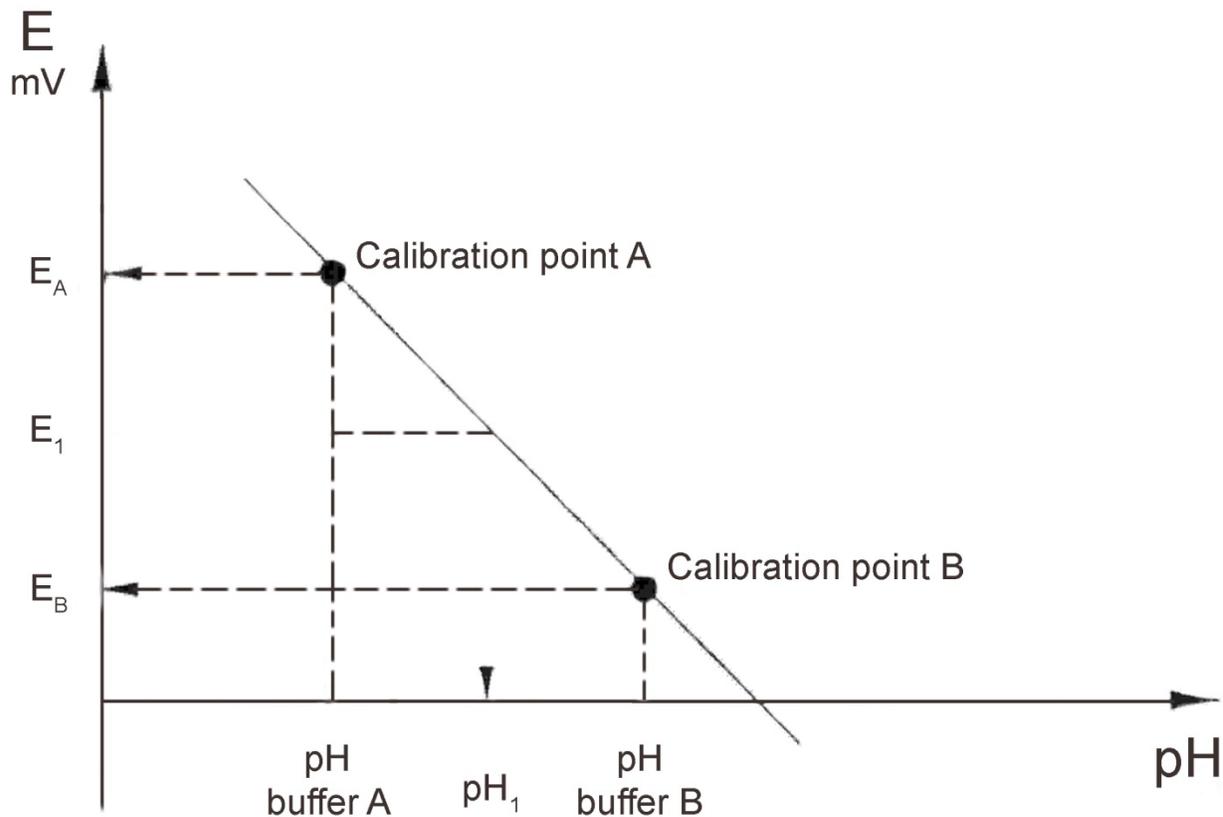
Buffers with high precision have only a limited lifetime, a limited stability. They must be used within a short period of time, governed by how precise the measurements must be. Though alkaline buffers pose the greatest problem because of their tendency to absorb carbon dioxide from the air, a buffer solution in an opened and capped bottle, will last for a limited period of time. Even unopened buffers in thin, plastic bottles have a tendency to absorb CO₂ from the atmosphere. Thick plastic bottles, sealed in cans under a nitrogen atmosphere, have the greatest advantage for maintaining optimal solutions.

High quality buffers contain a small amount of germicide to prevent microbiological growth, since many of the buffers are excellent culture media. Buffers with other additives, including many colored dyes, could disturb the pH value or the stability of the solution. They may have an adverse effect on the liquid junction.

Calibration

Electrodes have slightly different characteristics. Electrodes with different nominal values are produced by different manufacturers. The zero pH and the sensitivity will vary with time. Calibration matches the pH meter to the characteristics of the electrodes being used and continued calibration of the electrode on a regular basis corrects for continually changing characteristics during the lifetime of the electrodes. The most accurate calibration is performed using two different buffer solutions. This enables both pH° (zero pH) and the slope (sensitivity) to be determined.

Figure 7. Calibration Curve



A one-point calibration with only one buffer can be carried out if the last calibration was performed recently or if you are in a hurry. Only the pH° will be determined and the sensitivity previously found will be used.

The sensitivity is independent of temperature and is usually stated as a percentage of the theoretical value. The slope, when expressed as mV/pH, is directly dependent on temperature. The slope (at 25° C) is often used as an alternative to sensitivity in % (100% = 59 mV/pH).

Zero pH (pH°) is generally used to describe electrode characteristics, though the potential at pH 0 or pH 7 at 25° C can also be given.

When performing a calibration, follow a consistent pattern. Use the same stirring speed, the same stability criteria, and the same waiting time. The buffers should be at the same temperature, preferably the temperature of the sample. For the most accurate measurements, the two buffers should bracket the value of the sample solution, that is, for samples between pH 4.0 and 7.0, use of the pH = 4.01 and pH = 7.00 buffers would be advisable. However, sample pH values close to, but outside this range, could be measured using these buffers.

Though there are many varieties of pH meters on the market, for example, those with knobs and dials for adjustment, the simplest and most convenient meters have an auto calibration, that is, buffer recognition, facility. These meters have a full range of buffer values, with corresponding temperature variations, preprogrammed in their memories. Based on definitive buffer recognition, the operator must be sure to use only the preprogrammed buffers, lest the meter be fooled into accepting a false buffer value, for instance, a pH 6.86 instead of a pH 7.00 buffer.

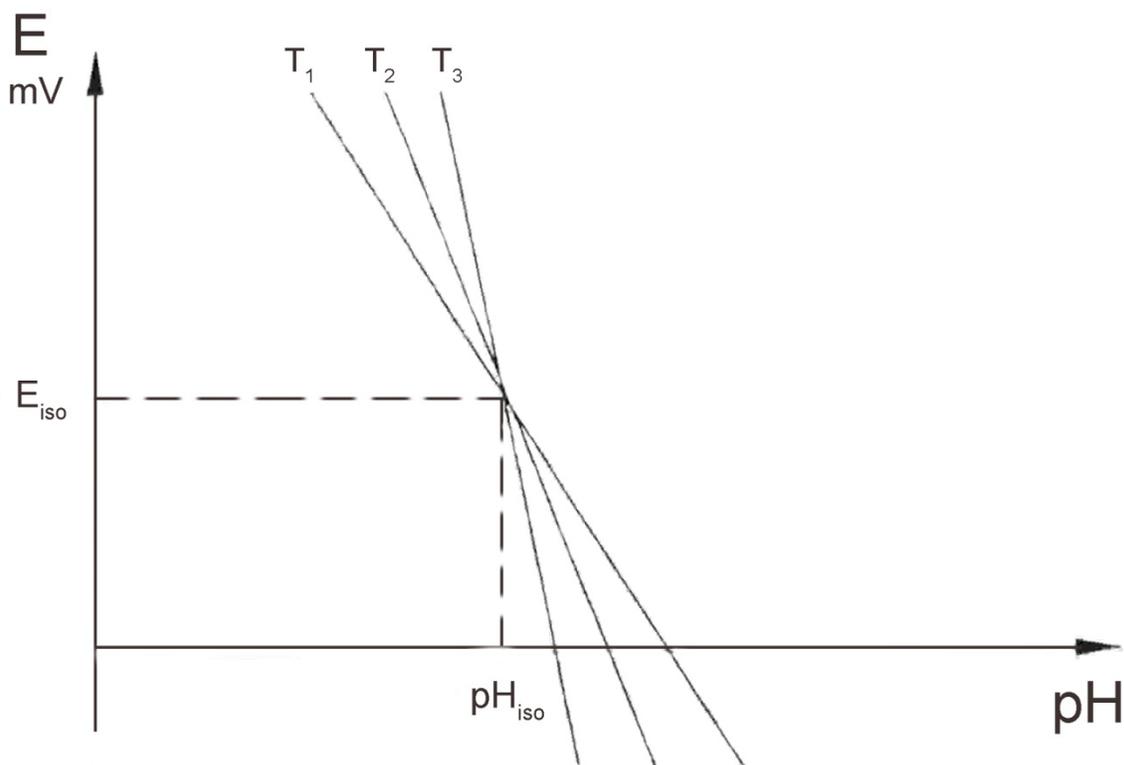
Temperature effects

Temperature influences sample and buffer pH and electrode characteristics. Temperature dependency for all common buffers is known and is usually stated on the buffer bottle or on a separate form sent with the buffers from reputable manufacturers. Temperature has a minimal effect on inorganic acid buffers. It has a significant effect, however, on alkaline buffers and on some organic buffers. Compensation can be made for the influence of temperature on the slope of the electrodes, though no compensation can be made for pH shifts caused by altered reference potentials or a change of the pH in the inner solution in the glass bulb. In addition, almost nothing is known about the influence of temperature on a sample's pH. The temperature of the sample should be recorded along with the pH of the sample.

In summary, electrodes, buffers, and samples should all be at the same temperature. Though some compensation is possible, it is not possible to calculate the pH of a sample measured at one temperature back to the sample pH at another temperature, for example, a reference temperature. A temperature difference, however, of 2 - 5° C will be acceptable in most cases.

When pH vs. mV at a number of different temperatures is plotted for most electrodes, note that the lines intersect at almost the same point.

Figure 8. Definition of iso-pH.
The intersection points do not coincide for isotherms at great variations in temperature.



This point is called the iso-pH or iso potential point. If the pH° and the iso-pH are made to coincide, either by electrical circuitry or calculation, compensation is made for the electrode's temperature dependence and measurements in a fairly large temperature range will be possible. If sample measurement and calibration are performed at two distinct temperatures, errors can be controlled. If the electrodes used have the same electrochemical system as, say, for instance, a glass electrode with Ag/AgCl internal reference and a reference electrode with Ag/AgCl internal reference or a combination electrode, the temperature range allowed is larger than it would be with an unlike electrochemical construction.

The iso-pH calibration is performed by using two buffers at the same temperature and one of the two original buffers (usually the first used) at an elevated or depressed temperature at least 20° C less than or greater than the original temperature. This allows for essentially a three buffer calibration, Buffers A & B at one temperature and Buffer A at a higher or lower temperature than before.

After determining pH° , sensitivity, and iso-pH, the pH can be calculated by using the following equation:

$$pH_T = [pH^\circ \cdot (T_{cal}/T)] - E/(R' \cdot S \cdot T) + [pH_{iso} \cdot (1-T_{cal}/T)]$$

Troubleshooting Guide

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrode, the standards, the sample, and the technique.

Meter

The meter may be checked by following the checkout procedure in the instrument instruction manual.

Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

Electrodes

The electrodes may be checked by using the procedure found in the section entitled **Calibration**.

1. Be sure to use distilled or deionized water when following the procedures given in the **Calibration** section.
2. If the electrode fails to respond as expected, see the section entitled **Maintaining the Electrode**. Repeat the calibration.
3. If the electrode still fails to respond as expected, substitute another electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.
4. If the problem persists, the standards may be of poor quality. Open fresh standards and attempt to calibrate the electrode again.
5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the calibration procedure and be sure to:

- Clean and rinse the electrode thoroughly.
- Prepare the electrode properly.
- Use the proper filling solution.
- Review **Troubleshooting Hints**.

Standards

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard solutions. If in doubt about the credibility of any of the standards, open fresh standards.

Sample

Look for possible contaminants if the electrode works perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts.

Technique

Be sure that the electrode's limit of detection has not been exceeded.

Be sure that the calibration procedure is clearly understood and that Good Laboratory Practice has been followed.

Troubleshooting Hints

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrode(s) not plugged in properly	unplug electrode(s) and reseal
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by redipping electrode
	calibration control not turned far enough	continue turning the calibration control
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by redipping electrode
	wrong reference electrode	use the recommended reference electrode
	meter or stirrer not grounded	ground meter or stirrer
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	Standards contaminated or incorrectly made	use fresh standards