

pH electrode

A pH electrode, works the same way as any other ion selective electrode. Here, it is a glass membrane that built-up a potential according to the concentration of H^+ in a solution. This membrane is specific to the hydronium ion (H_3O^+). A pH electrode is made of an ionic conductive glass which is a non crystalline mineral mostly based on silicon oxide.

History and evolution of a very important electrode

In 1906, the first observation of the interaction between H^+ and glass was made by M. Cremer. He notices a potential difference on either side of a glass membrane in acidic solutions. He also concluded that this potential was proportional to the concentration of acid present. Three years later, S. P. L. Sørensen formulated the concept of pH.

$$pH = -\log[H^+] \quad (1)$$

Note: Sørensen chose the letter "p" for "power" since this word starts with "p" in several languages.

	substance	pH
Basic [H ⁺] < [OH ⁻]	Liquid drain	14.3
	NaOH, 0.1 M	12.9
	Household bleach	12.45
	Household ammonia	11.75
	Lime water	10.45
	Milk of magnesia	9.8
	Baking soda	8.25
	Egg white	7.6
	Human blood	7.43 – 7.45
	tears	7.15
neutral	Distilled water at 25 °C	7.00
Acidic [H ⁺] > [OH ⁻]	Milk	6.6
	Saliva	6.3
	Rain	5.7
	Black coffee	4.8
	banana	4.55
	tomatoes	4.05
	Cola, vinegar	2.8
	Lemon juice	2.1
	Gastric juice (stomach)	1.2
	HCl 4 M	-0.27

Why neutral pH is equal to 7.00?

The natural water auto-ionization $H_2O \rightleftharpoons H^+ + OH^-$ $K_w = [H][OH^-] = 1.01 \times 10^{-14}$ at 25 °C

Therefore at 25 °C $[H^+] = 1.00 \times 10^{-7}$ then $pH = -\log(1.00 \times 10^{-7}) = 7.00$

At 37 °C, $K_w = 2.42 \times 10^{-14}$. Therefore, neutral $pH = -\log \sqrt{2.42 \times 10^{-14}} = 6.81$

The same year (1909) the glass electrode was introduced at the Society of Chemistry by F. Haber and Z. Klemensiewicz as a tool to actually measure the pH.

The next important development of the glass-pH electrode was made by T. Kerridge in 1925 when she tried to miniaturized the glass electrode. In this process, she was able to increase the surface area of the platinum electrode used for the potential measurement inside the glass electrode and increase the electrical signal. It was a big improvement since glass is a highly resistive membrane. That is why, a pH electrode is often a very thin glass bulb of less than 0.1 mm thick and spherical to increase the surface area.

In the mid 30', Glen Joseph and Arnold Beckman use the vacuum tube electronic amplifier to increase the weak signal from a glass electrode. Beckman filed a patent in 1934, built the first commercial "acidimeter" and started his own company.

The mechanism associated to the H^+ adsorption on glass is quite complex and was understood in the 1970. Today, a large variety of glass are made to accommodate several type of ions. The selectivity of the membrane can be changed with an appropriate chemical composition. Excess of negatively charged ion sites on the glass, attract cations having the proper charge to size ratio.

Composition %mass					use
SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	Li ₂ O	
70	20	10	-	-	Silicate glass
72	22	6	<1	-	1<pH<9 corning 015 glass
68	27	-	5	-	K ⁺
60	-	-	25	15	Li ⁺
71	11	-	18	-	Na ⁺
52.1	28.8	-	19.1	-	Ag ⁺

Figure 1. Type of soda glasses for potentiometric analysis.

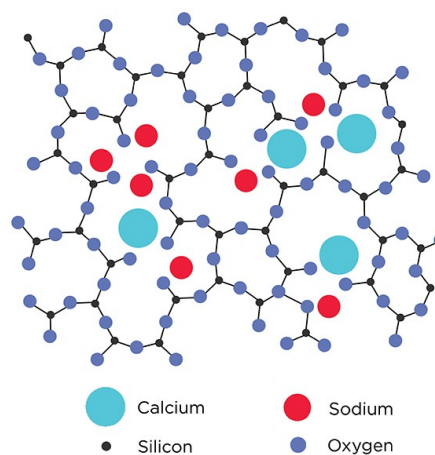


Figure 2. An ionic conductive glass structure.
Source: www.koppglass.com

The glass of a pH electrode (soda glass or borosilicate SiO₂, B₂O₃) is permeable to H^+ and Na^+ therefore, sensitive to both ions.

When the hydronium ion (H_3O^+) is adsorbed on the surface of the electrode (figure 3), it becomes H^+ . This adsorption replaces the Na^+ ion initially present on the surface of the glass. Only Na^+ is allowed to move slowly in the glass ensuring the ionic conductivity.

This combination of H^+ adsorption and Na^+ diffusion-migration is what is actually measured. This results is a potential which corresponds to the concentration of H^+ in the solution-electrode surface at equilibrium.

Consequently, the measurement of the pH requires a certain time for the thermodynamic equilibrium to be established. A pH measurement is not an instantaneous reaction. A time of 30 s to 1 min should be considered for a precise measurement.

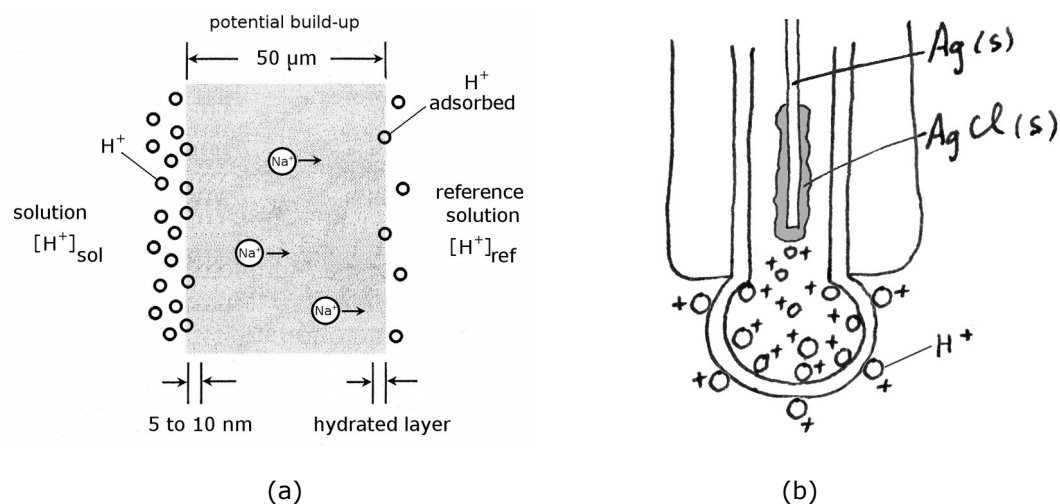


Figure 3. Potential built-up at a glass electrode with H^+ on both sides of the borosilicate glass membrane.
 a. The slow diffusion of the Na^+ in the glass insure the ionic conductivity (very weak however).
 b. schematic representation of the glass membrane of a pH electrode.

The potential of an ion selective membrane is calculated according to the Nikolsky-Eisenman¹ equation. It is based on the ion free energy change associated to the process of ionic solution and absorption. In most cases, without the presence of interfering ions, this equation is simplified:

$$E = \text{constant} + \frac{0.05916V}{z_i} \log(a_{\text{ion}}) \quad \text{at } 25^\circ\text{C} \quad (3)$$

The constant includes all the potentials that are present but fixed which are:

- The difference of potential between the reference electrode and the $Ag/AgCl$ of the glass electrode
- The possible effect of one specific interfering ions (present but constant)
- The presence of any unexpected junction potential (e.g glass frit).

For a pH electrode:

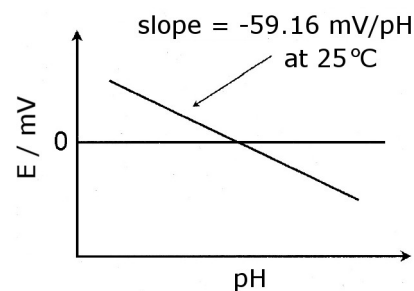
a_{ion} is equivalent to $[H^+]$

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

$z = +1$

Then equation 3 can be written:

$$E = \text{offset} - 0.05916V \times pH \quad \text{at } 25^\circ\text{C} \quad (4)$$



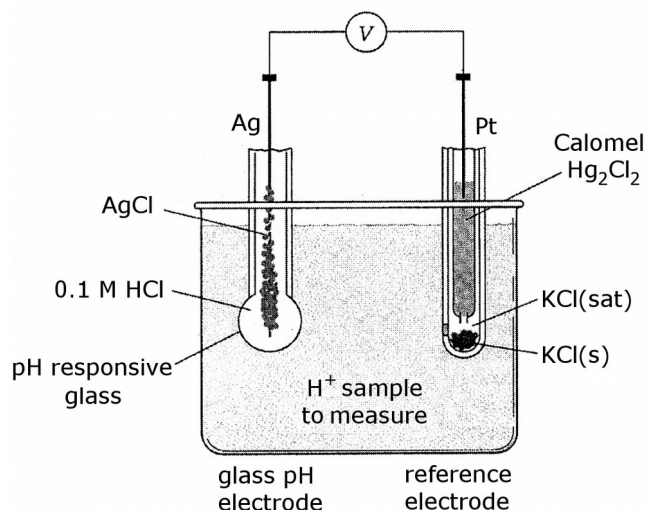
Hence, for practical reason, an ion selective electrode is never an "absolute" potentiometric technique. It relies on a calibration process involving one or several standard solutions.

The slope is -59 mV at 25°C (or $-2.303 RT/F$) when the pH is used instead of the activity

With a calibration solution (pH known), the "offset" value of equation 4 is determined.

1 IUPAC publication. http://publications.iupac.org/analytical_compndium/Cha08sec323.pdf

To measure the potential present on a glass surface, an electronic conductor is required. Just like other selective electrodes, an electrochemical oxidation–reduction system is used. Often, it is two Ag/AgCl electrodes working in opposite direction yielding to a 0.0 V electrochemical potential. Therefore, only the ions present at the glass electrode is accountable for the potential. The figure 4 illustrate a basic setup for a pH measurement (here Ag/AgCl and calomel).


$$\text{Ag(s)}|\text{AgCl(s)}|\text{HCl(aq, } c = 0.1 \text{ mol/L)} || \text{H}^+(\text{aq, } c = \text{unknown}) || \text{KCl(sat)}|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg(l)}|\text{Pt}$$

glass bulb ↑ ↑ *porous junction*

reference electrode

glass electrode

fill hole

reference electrode

Ag conductor

AgCl

reference KCl solution

inner HCl solution

salt bridge frit

AgCl

pH responsive glass



Figure 5. Anatomy of a combined pH glass electrode Figure 6. Commercial combined pH glass electrode
Source: www.metrohm.com

This design is more efficient and practical than having to handle a set of electrode and cable and having to use a large volume of liquid to perform the measurement.

Also, the connection between the two electrode and the pH meter can be made with a coaxial cable which is less sensitive to electrical disturbances.

A short time is always required for this system to reach equilibrium (around 45 s to 1 min). However, the thinner the glass, the faster the response. This is why a pH electrode has a glass thickness often less than 0.1 mm. Consequently, a pH electrode is a **VERY FRAGILE** device.

The offset in equation (4) depends on the concentration of the standard solution. It can have any value as long as it remains constant throughout the measurement. This is why a pH electrode is always calibrated, prior to use.

No current should ever flow through a pH electrode. Static charges can build-up on its surface which is a source of error. Never touch the surface of a pH electrode not even with a tissue.

Sample calculation

When immersed in a buffer solution pH = 4.00 at 25 °C, a glass pH electrode has a potential of 467 mV (relative to a calomel reference electrode)

This same pH electrode has a potential of 395 mV when it is immerse into an unknown solution which is less acidic (known from a pH paper). Calculate the pH of this unknown solution assuming that the electrode follows a Nernstian behavior.

Answer:

$$\text{At } 25\text{ }^{\circ}\text{C} : E = \text{offset} - 0.05916 \text{ V} \times \text{pH}$$

1) Use the buffer pH = 4.00 solution to calculate the offset:

$$0.467 \text{ V} = \text{offset} - (0.05916 \text{ V})(4.00) \Rightarrow \text{offset} = 0.703\text{6} \text{ V}$$

2) Now, calculate the pH of the unknown solution using: $E = 0.703\text{6} \text{ V} - 0.05916 \text{ V} \times \text{pH}$

$$0.395 \text{ V} = 0.703\text{6} \text{ V} - 0.05916 \text{ V} \times \text{pH} \Rightarrow \text{pH} = \frac{0.395 \text{ V} - 0.703\text{6} \text{ V}}{-0.05916 \text{ V}} \Rightarrow \text{pH} = 5.22$$

Note: the indication "less acidic" takes into account that it is impossible to know the polarity of the connections (electrodes) from a single measurement. This information however will be known with the use of two standard solutions.

pH measurement: Basic precautions to take.

ONLY a pH meter can be used to measure the potential of a pH electrode.

A current should never pass through a pH electrode since it is easily affected by any current flow. A pH meter is, in fact, a voltmeter with a very high impedance input, therefore, it has a very low current drain when performing a measurement.

Never touch the glass of a pH electrode

Do not wipe the electrode, not even with a Kimwipes™. The surface can easily be scratched and static electricity could build-up.

Take your time when you are reading the pH.

When performing a pH reading, generally wait from 45 s to 1 min before recording the value. The H^+ ion equilibrium between the glass electrode and the solution requires some time.

The pH reading is never stable.

A pH measurement is a dynamic process. Also the high impedance of the electrode is sensitive to any electromagnetic signals or electric noise (just like the antenna of a radio). In an environment filled with electronic devices, the pH will never be stable.

The temperature should always be recorded and kept constant.

Since the potential read follows the Nernst law, the pH value recorded is sensitive to the temperature. This is why a temperature probe is also included in several pH electrode.

Never store a pH electrode "dry" or in distilled water.

The borosilicate glass needs to be kept hydrated all the times. It should be stored in a KCl aqueous solution. To prevent bacteria and fungus to grow, a buffer solution of pH = 4 with 1/100 KCl added is the best option. Do not store the electrode in distilled water. It will deplete the hydration layer and decrease the life of nonrefillable electrodes.

Store the electrode with its protective cap, vertically and in a box.

The AgCl from both the reference electrode and the pH electrode is light sensitive. Protect these chemical from light by storing the electrode in a box.

For more information about the maintenance of a pH electrode consult the following link:

<https://hannainst.com/ph-electrode-maintenance-calibration-guide>

<https://www.coleparmer.com/tech-article/ph-electrode-care>

pH electrode

Advantages:

- 10^{-9} sensitivity
- The response is logarithmic = wide dynamic range
- Can work in turbid or colored solution
- Response is fairly rapid (<1 min)
- Sample is not destroyed

Drawback:

- Measure the activity rather than the concentration
- Temperature dependent (RT/F)
- frequent calibration is required
- possible interferences (other ions)

The lifetime of a pH electrode vary from a few weeks to several years. It depends of the utilization:

High temperature measurement

Very basic medium

Bad maintenance (dry-out)

Hydrolysis of the glass and degradation

Accuracy

No better than ± 0.02 pH

(Even if it is possible to discriminate between the pH of two similar solutions with ± 0.004 pH)

causes:

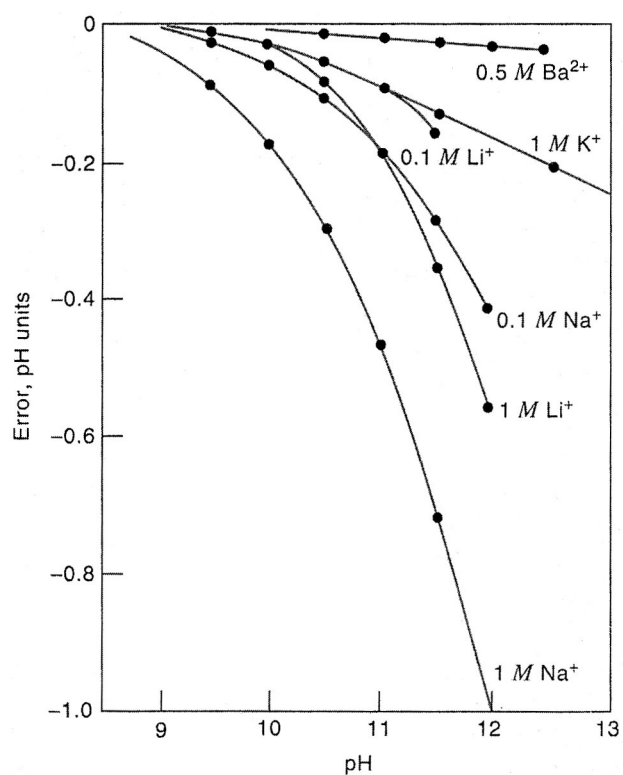
Residual liquid-junction potential (degradation, ion adsorption)

Uncertainty in the standard buffers

For very accurate work, the cell should be standardized at the same temperature as the test solution

Example: pH of blood = 38°C

Presence of some interferent ions to the pH measurement



Error of a glass electrode in strongly alkaline solutions containing various cations.

Also called the sodium error.

Source: L. Meites and L. C. Thomas. *Advance Analytical Chemistry*, McGraw-Hill (1958) New-York