pH electrode

	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

1906 H. Cremer:

Interaction between H^+(aq) and glass

notice a difference of potential between each side of the glass

1909 S.P.L. Sorensen:

Concept of pH -> **pH = -log[H^+]**

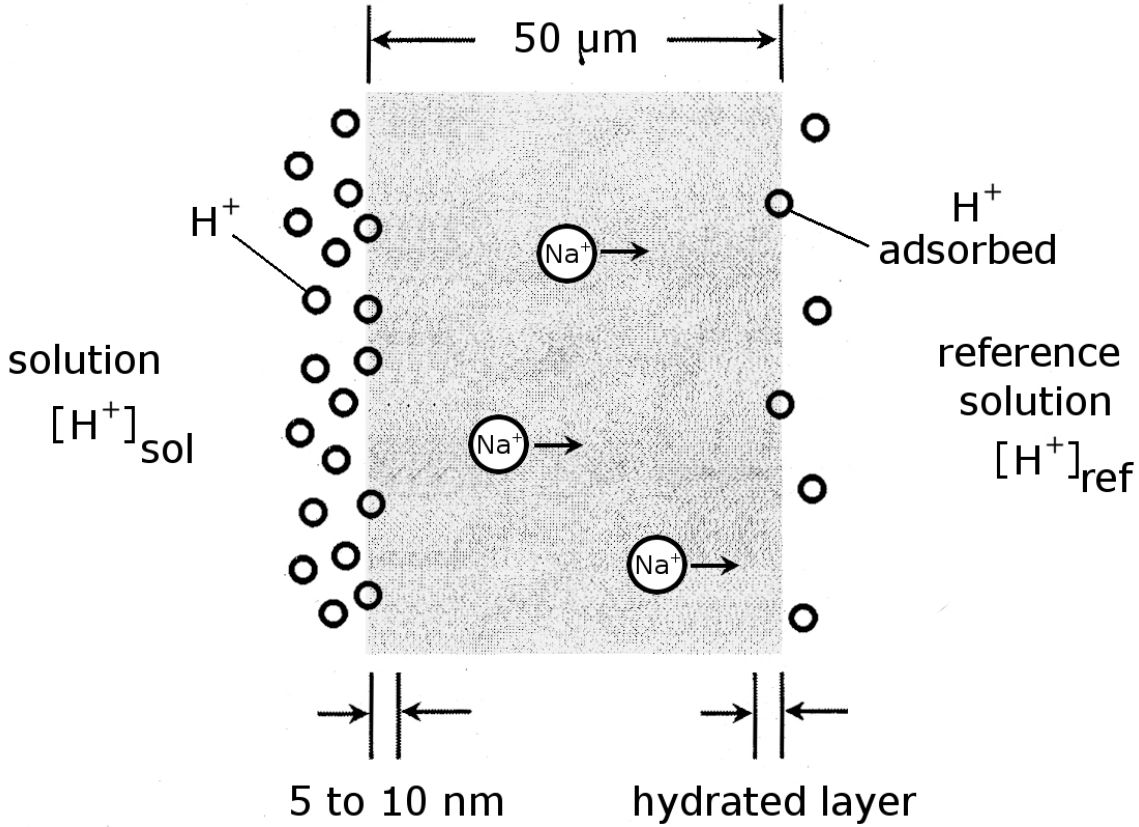
1909 F. Haber and Z. Klemensiewicz:

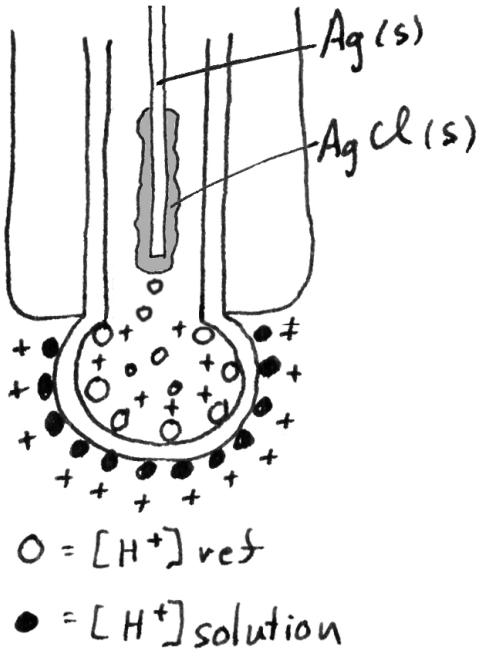
Creation of the glass electrode to measure the pH

1934 G. Joseph and A. Beckman:

Vacuum tube electronic amplifier = First commercial Acidimeter.

Principle





$$\Delta E = 0.05916\,\text{V}\ \log\frac{(a_{\text{sample}})}{(a_{\text{reference}})} \quad \text{at 25 °C}$$

Glass for pH electrodes

Composition %mass					use
SiO_2	Na_2O	CaO	Al_2O_3	Li_2O	
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.

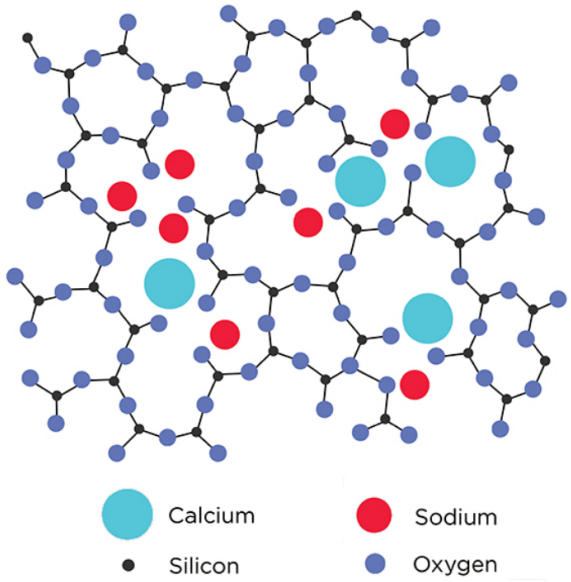


Figure 2. An ionic conductive glass structure.
Source: www.koppglass.com

The glass of a pH electrode (soda glass or borosilicate SiO_2, B_2O_3) is permeable to H^+ and Na^+ therefore, sensitive to both ions. This combination of H^+ adsorption and Na^+ diffusion-migration is what is actually measured.

The results is a potential which corresponds to the concentration of H^+ in the solution-electrode surface at equilibrium.

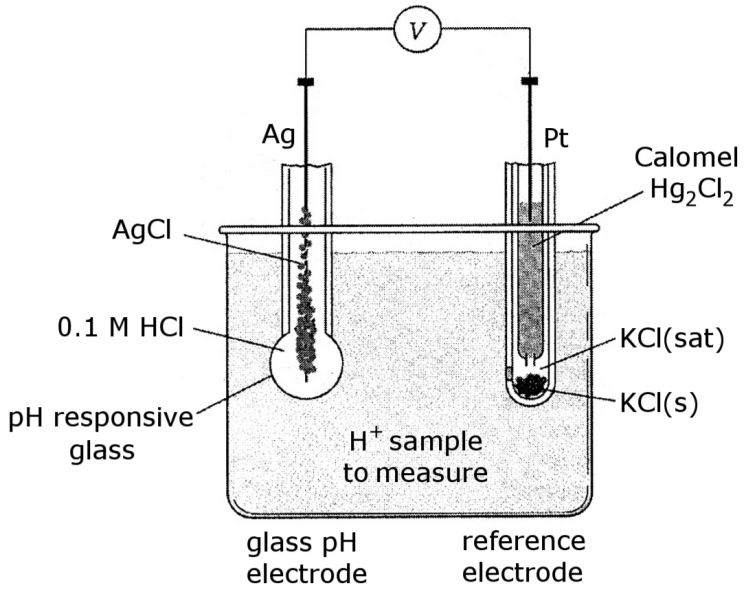


Figure 4. Two electrodes pH measurement with a glass electrode and a calomel reference electrode.

Ag(s)|AgCl(s)|HCl(aq, *c* = 0.1 mol/L) || H^+(aq, *c* = unknown) || KCl(sat)|Hg_2Cl_2(s)|Hg(ℓ)|Pt

glass bulb ⇑ ⇑ *porous junction*

General equation: $E_i = \text{constant} + \frac{0.05916\,V}{z_i}\log(a_i)$ at 25 °C

a_i and **z_i** are the **activity** (concentration) and **charge of the ion**, respectively.

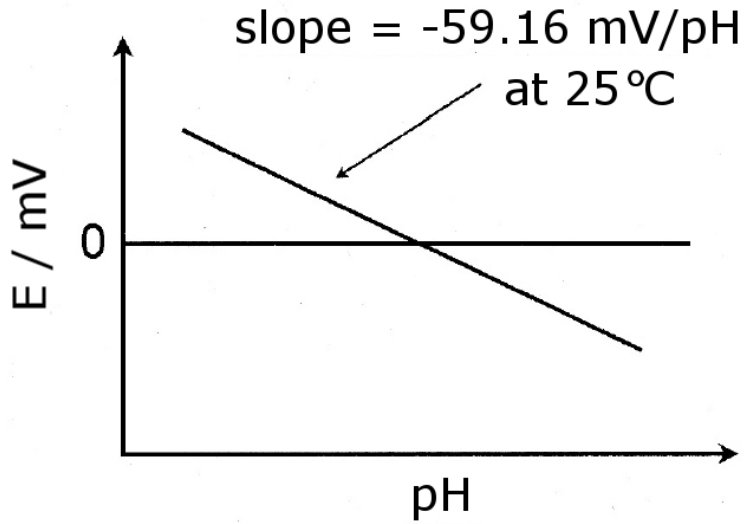
constant: any fixed potential related to the reference system, or junction potential.

For a cation, the potential of the system increases with the concentration.

General equations for pH measurement at 25 °C

$$pH_{sample} = pH_{ref} + \frac{E_{ref} - E_{sample}}{0.05916\ V}$$

E = offset – 0.05916 V × pH



The potential at the pH electrode decreases as the pH increases

(Increase in pH = a_{H+} decreases)

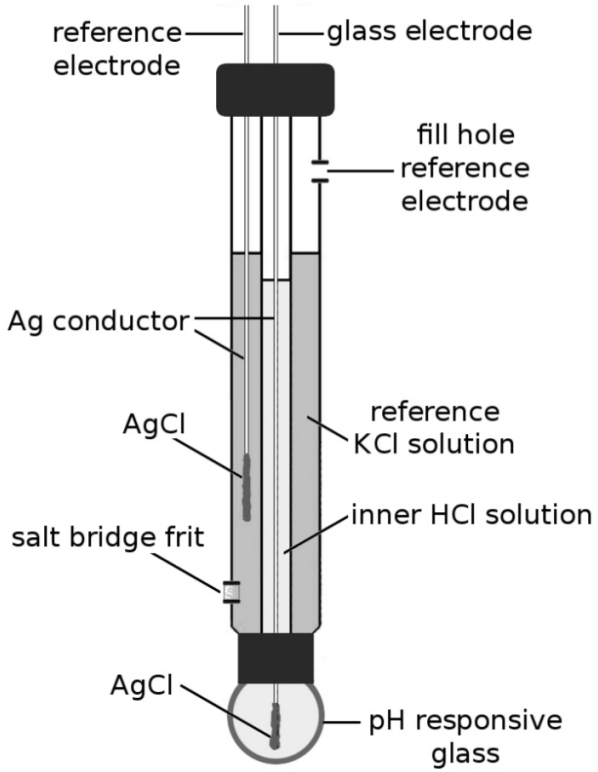


Figure 5. Anatomy of a combined pH glass electrode

Figure 6. Commercial combined pH glass electrode
Source: www.metrohm.com

Knowing that the resistance of the glass electrode membrane is between 10 MΩ to 100MΩ, a 2 electrodes circuit is highly sensitive to any electric activity from the surrounding.

The standard pH electrode is often a combination of two electrodes together (glass + reference electrode) in a single combined electrochemical cell.

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.

$$\text{At } 25\,^{\circ}\text{C}: \quad \mathrm{pH} = \mathrm{pH(ref)} + \frac{E_{\text{ref}} - E_{\text{sample}}}{0.05916\,\text{V}} \quad \text{(Nernstian)}$$

Answer

$$\mathrm{pH} = 4.00 + \frac{0.467\ \text{V} - 0.395\ \text{V}}{0.05916\ \text{V}} \quad => \quad \mathrm{pH} = 5.22$$

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.

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 then the concentration
- Temperature dependent (RT/F)
- frequent calibration is required
- possible interferences (other ions)

Accuracy No better than $^{+}/_{-}$ 0.02 pH

It is possible to discriminate between the pH of two similar solutions with $^{+}/_{-}$ 0.004 pH

causes:

Residual liquid-junction potential, degradation, ion adsorption, quality standard buffers

Lifetime of the electrode

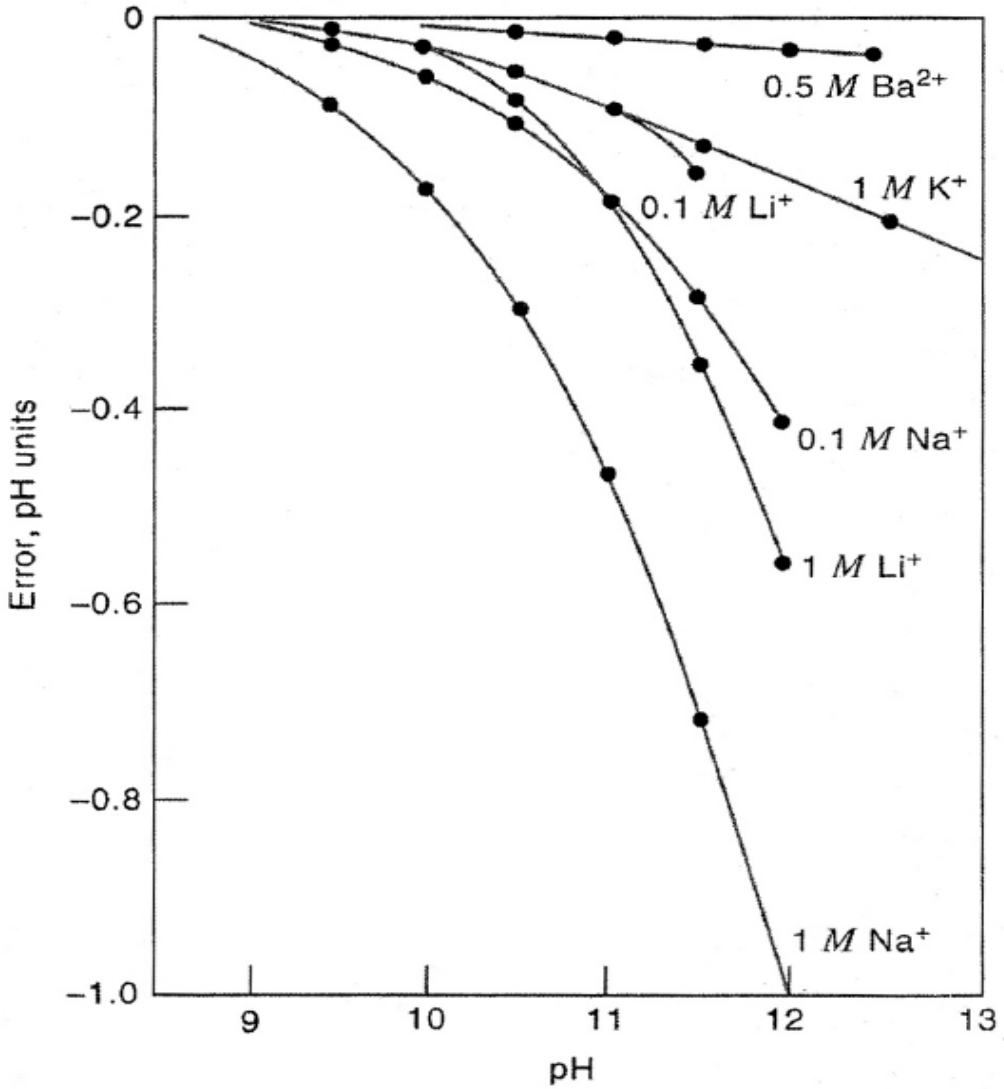
The lifetime of a pH electrode vary from a few weeks to several years. It depends of the utilization:

- High temperature measurement
- Very basic medium
- Bad maintenance (dry-out)
- Hydrolysis of the glass and degradation

Limitations: Interferences

Ex: pH of blood = 38°C

The sodium error



Basic precautions

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

Never touch the glass of a pH electrode

Take your time when you are reading the pH.

The pH reading is never stable.

The temperature should always be recorded and kept constant.

Never store a pH electrode “dry” or in distilled water.

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