pH electrodes

Definition:

A specific ion selective electrode, made of glass, that responds to hydrogen ion activity, over the range 1 mol/l H^+ (pH 0) to 10^{-14} mol/l 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.

Reference:

http//www.mt.com/home/products/en/lab/wet/phlab/docs/guideph.pdf (Mettler Toledo's "Guide to pH Measurement")

<u>How are pH values measured?</u>

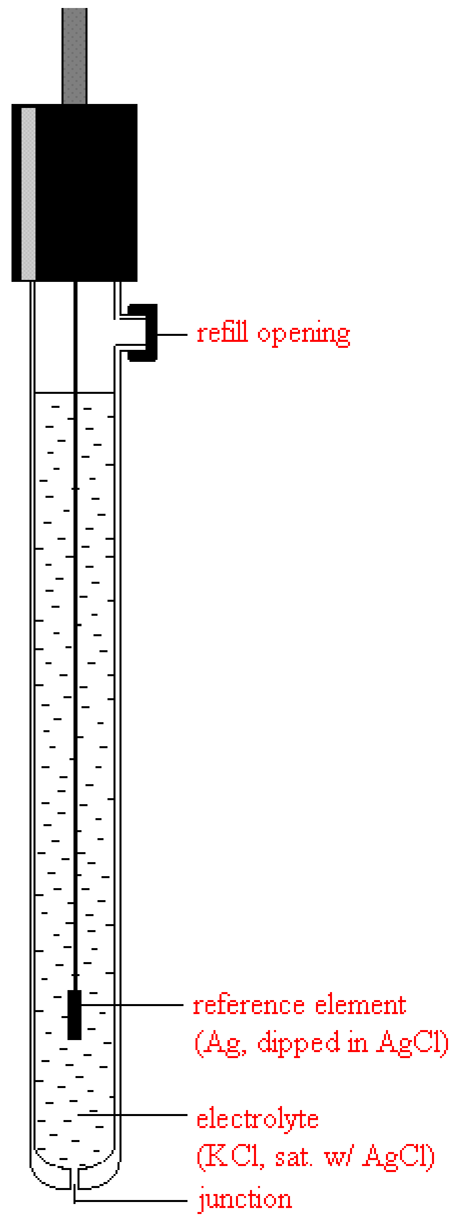
In order to measure a pH value, a **measuring electrode** (pH electrode) and a **reference electrode** are needed. In many cases, a combination electrode, housing both measuring and reference elements, is used.

<u>Reference electrode:</u>

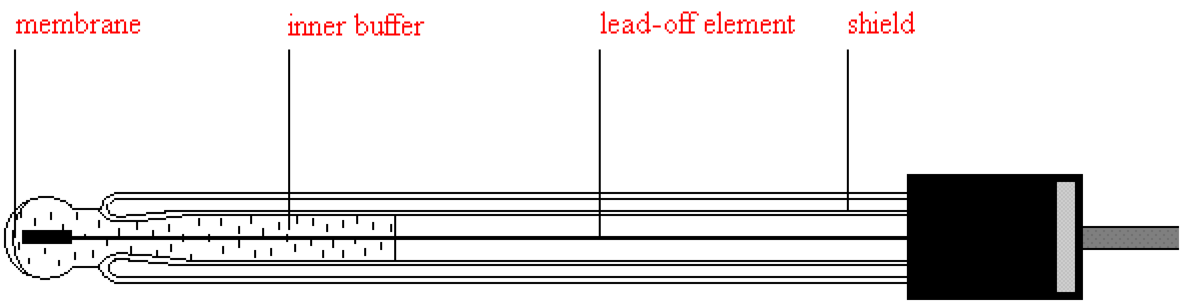
Example:

Silver Chloride electrode

$Ag/AgCl_s,Cl^-_{aq}$



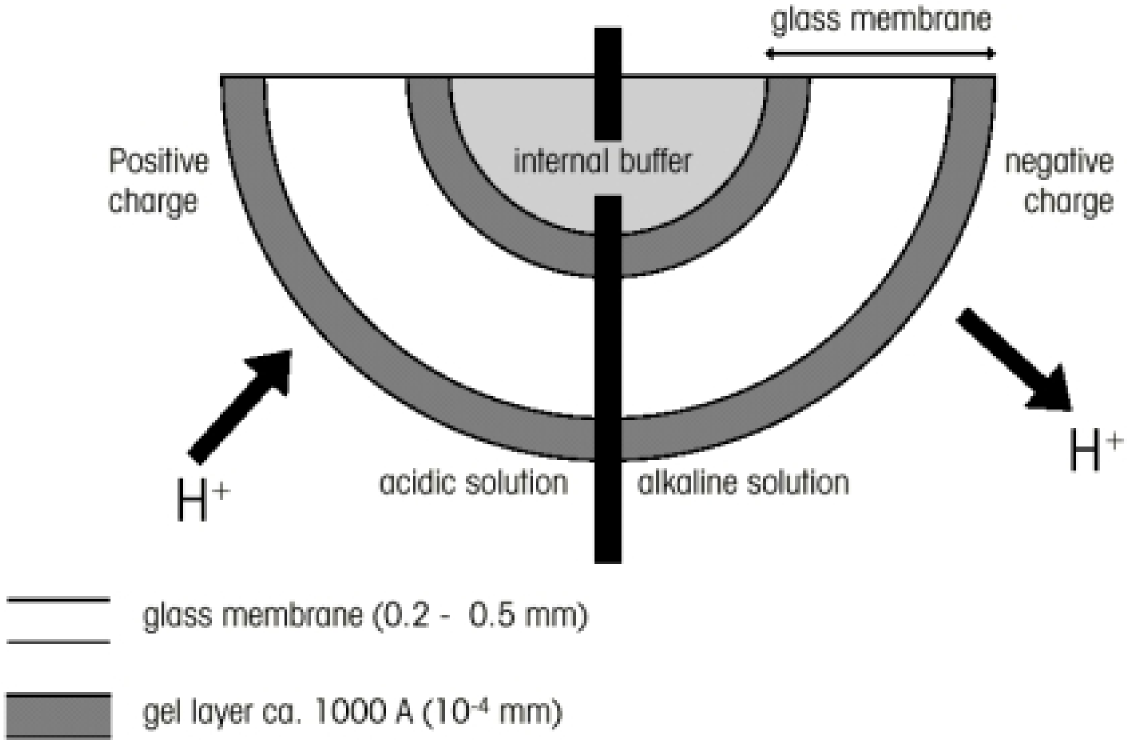
Glass electrode:

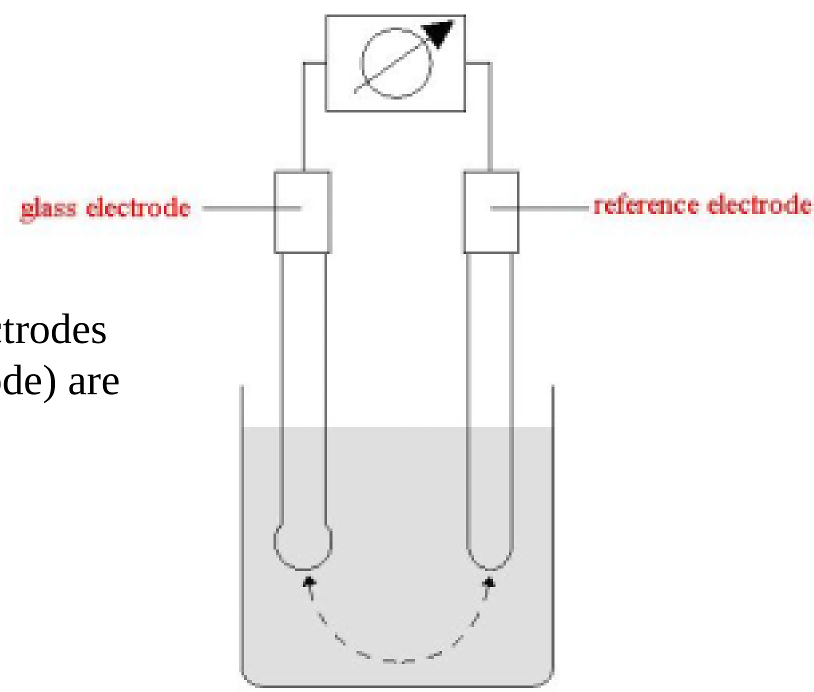


A 'gel layer' develops on the **pH-sensitive glass membrane** when a pH glass electrode comes into contact with an aqueous measuring solution. Such a 'gel layer' arises also on the inside of the glass membrane which is in contact with a defined buffer solution (**the inner buffer**). This buffer solution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

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.

Glass electrode (ctn’d):





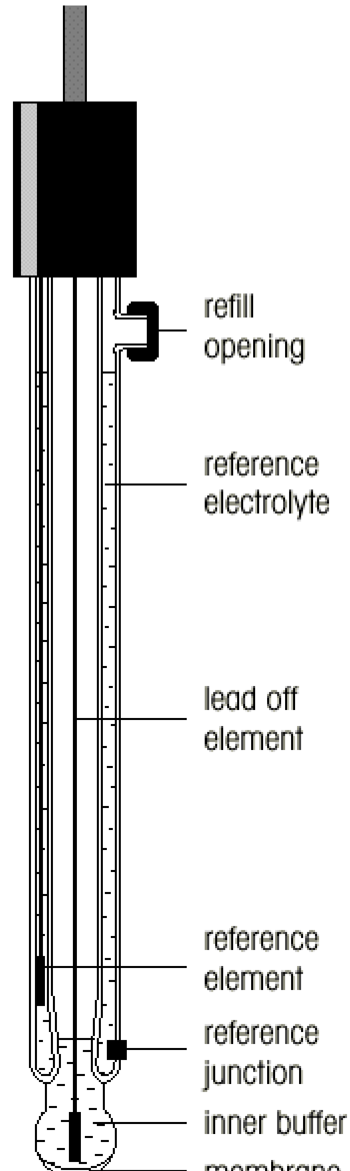
To measure a pH, both electrodes (reference and glass electrode) are connected to a voltmeter:

Combination electrode:

- easier handling than 2 separate electrodes

- today almost exclusively used

  (exception: when the different parts of the electrode are expected to have very different life expectancies is the use of separate electrodes recommended.



Combination electrode:

Overall reaction:

$Ag/AgCl_s,Cl^-_{aq}$,$[H_3O^+]_{glass}$/glass membrane/ test solution$[H_3O^+]_{test}$//$AgCl_s,Cl^-_{aq}$)/Ag

← Glass electrode → ← Ref. Ele.→

Resulting electrode potential:

$$E = E_{ref} – E_{glass} - E_{membrane}$$
$$= E^o_{Ag/AgCl(ref)} - RT/F \bullet \ln Cl^-_{ref} - E^o_{Ag/AgCl(glass)} + RT/F \bullet \ln Cl^-_{glass} - E^o_{membrane} + RT/F \bullet \ln([H_3O^+]_{glass} / [H_3O^+]_{test})$$

The first five terms do not change during the measurements (they are temperature dependent though !) and can be summarised in one constant (Q(T)):

$$E = Q(T) + RT/F \bullet \ln ([H_3O^+]_{glass} / [H_3O^+]_{test})$$

==>

$$E = Q(T) - 59 \text{ mV} \bullet (pH_{test} – pH_{glass}) \qquad (@ 25\ ^oC)$$

The pH_{glass} is also kept constant (usually pH 7) and can be included in Q(T):

$$E = Q(T) - 59 \text{ mV} \bullet pH_{test} \qquad (@ 25\ ^oC)$$

Combination electrode:

The previous equation is used for all practical measurements.

It is a linear equation, so for a calibration (determination of Q(T) and the slope (which is - 59 mV only at 25 ^{o}C) two solutions with known pH are needed.

The potentials of these 2 pH buffer solutions are being measured and the calibration values are set on the pH meter.

Newer pH meters can be calibrated with more than two solutions to account for non-linear behaviour of the glass membrane at very high or very low pHs.

Recent innovations:

- Three-in-one electrodes:
  include temperature sensor for automatic temperature compensation

- ISFET electrodes:
  "electronic electrodes"
  (ISFET stands for Ion Sensitive Field-Effect Transistor, replaces glass membrane by microchip)