

HACH-Lange Electrochemistry

Liquid Junction

What is it good for - how does it work

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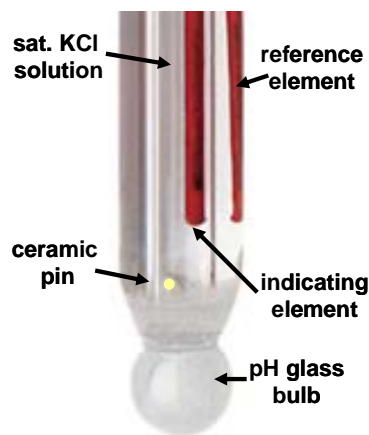
Introduction

Every electrochemical sensor needs a stable reference system to refer to. Whether it is pH or ion selective (ISE) measurement, a reference element is either externally connected or directly built-in, a so called "combined sensor".

The most common reference system is Silver / Silver chloride (Ag/AgCl) in KCl electrolyte solution. The solubility of AgCl is driven by the chloride concentration present in the electrolyte solution. Therefore solutions of 3 molar KCl, 3.5 molar or saturated solutions are available as reference electrolyte. As long as this solution is of constant KCl concentration, e.g. 3 M, the reference element gives a stable and reproducible potential (as function of temperature).

The sample measurement result comes from the potential difference between indicating element vs. reference element. The indicating element is e.g. a pH glass probe or a Platinum probe for ORP measurement.

Figure (1): combined pH probe with ceramic pin as diaphragm



An electrochemical electrode has two parts, which interact when both are in contact to the sample solution. It is obvious that the reference element with KCl solution must not be mixed or diluted with sample solution, otherwise the probe will be damaged.

The liquid junction

In order to maintain the reference element in a stable condition there must be a kind of “separator” between sample and electrolyte solution. This separator should work like a “valve”: only a little liquid can pass ($\sim 10\mu\text{L/h}$). This is called a liquid junction or diaphragm.

If the hydrostatic pressure of the electrolyte solution on the inner side of the diaphragm is higher than of the outer solution (sample), the electrolyte will flow out through the diaphragm. This makes the electrical contact where ions can transport the charge and develop a potential difference between reference and indicating element.

Figure (2): liquid junction (ceramic pin) between electrolyte and sample

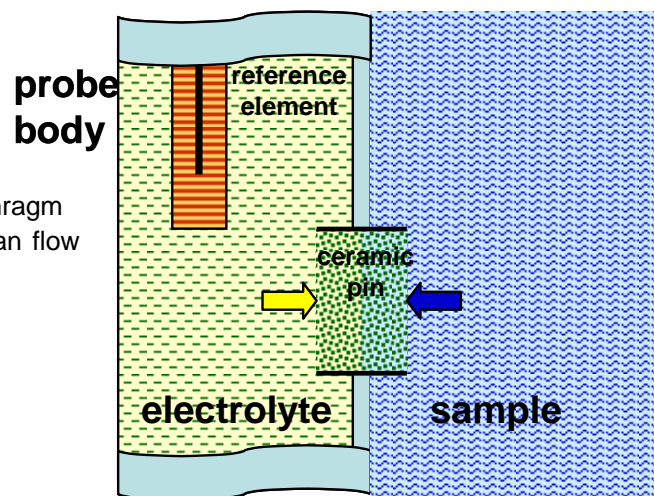
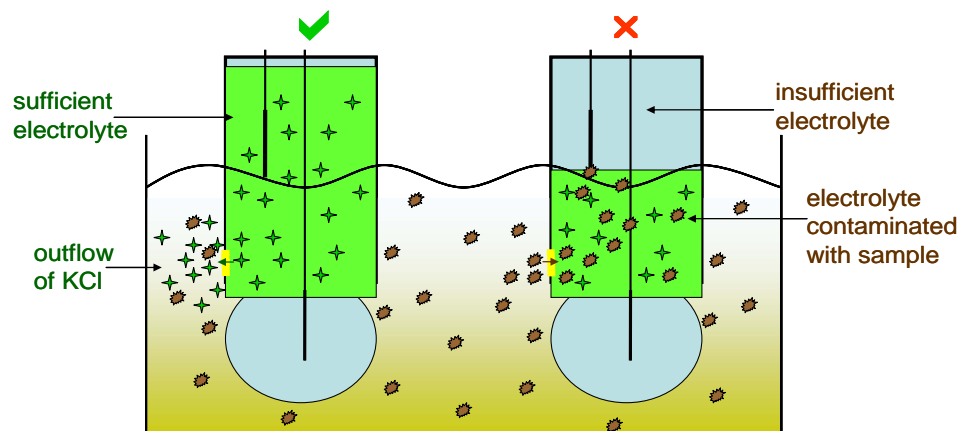


Figure (2) shows the principle how a diaphragm should work. The liquids from both sides can flow through the diaphragm material.

However, what happens when sample goes through into the electrolyte solution is shown in Figure (3).

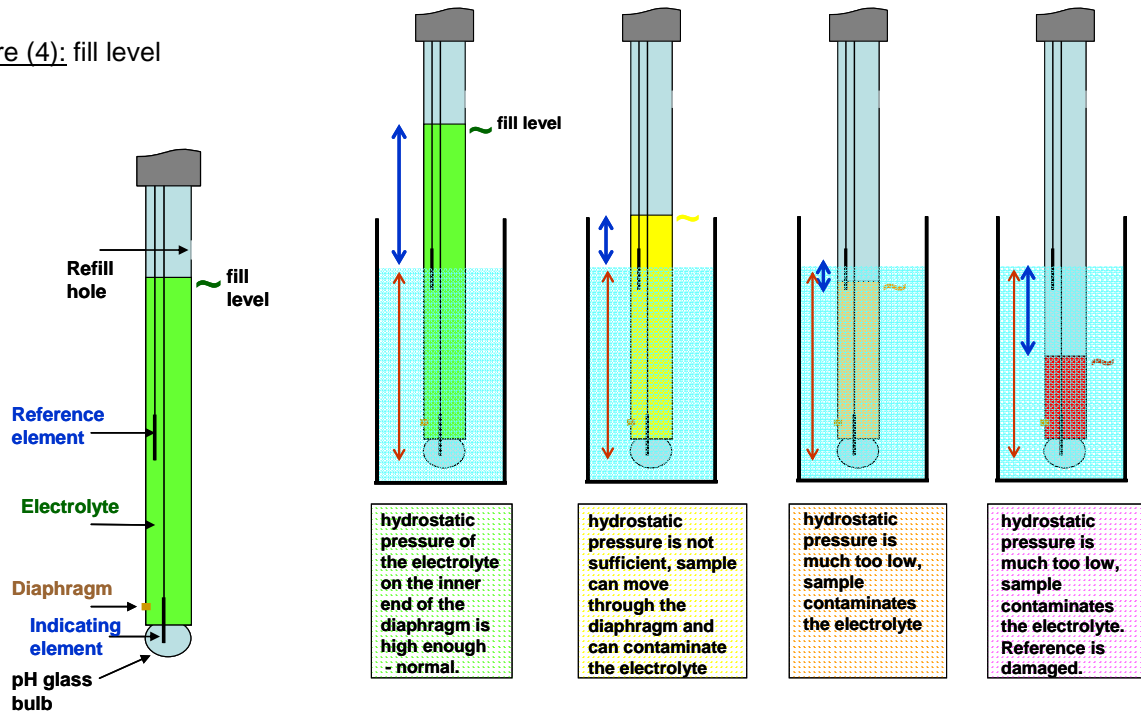
Figure (3): influence of electrolyte fill level on the function of a diaphragm



Electrodes with a liquid filling solution must be regularly checked for sufficient fill level. If the level is too low, the hydrostatic pressure of the electrolyte solution is too low and sample can go into the reference element area.

As mentioned above this may damage the Ag/AgCl reference element or lead to a no longer reproducible potential. Finally the sample measurement is wrong and not reliable.

Figure (4): fill level



Types of diaphragms

There are many different materials and mechanical designs of liquid junctions. Here is an overview of most common types:

open / hole diaphragm

the contact between electrolyte and sample is realized by a gel filled electrode. The gel does not flow out and can directly get in contact with the sample.

Advantage: low maintenance.

Disadvantage: the gel can be contaminated with sample or can dry out when not correct stored in electrolyte



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porous pin diaphragm

one or up to 3 ceramic pins separate the (mainly liquid) electrolyte from the sample. Based on its structure the ceramic pin allows an outflow of approx. 10 $\mu\text{L/h}$.

Advantage: can be used at high temperatures, strong acid or base.

Disadvantage: small particles from the sample can block the way through the ceramic.

**ring diaphragm**

a ring of PTFE or porous glass around the lower end of the tube provides a continuous flow of liquid electrolyte solution into the sample.

Outflow approx. 10-100 $\mu\text{L/h}$.

Advantage: The porous glass is suitable for high temperatures and can even be used in organic solvents.

Disadvantage: almost no.

**Sleeve diaphragm**

For samples of very low conductivity or where the diaphragm may be blocked from viscous samples, a sleeve is the best option.

Outflow approx. 1 ml/h.

Advantage: high electrolyte outflow, easy to clean.

Disadvantage: outflow has to be adjusted manually and may be not reproducible. Electrolyte level can be very low after short time.

**fibre and metal bundle diaphragm**

a bundle of fibre or platinum wires have many little channels which allow a liquid contact between electrolyte and sample.

Outflow < 10 $\mu\text{L/h}$.

Advantage: metal wires withstand high temperatures and are durable in most samples.

Disadvantage: strong oxidizing acids damage the metal bundle.



To understand how a liquid junction works, Figure (5) shows some examples where the inner electrolyte becomes coloured when in contact with sample.

Figure (5): visualization of electrolyte outflow



Liquid junction or diffusion potential

If two solutions of different concentrations and different ion species are in contact, a diffusion potential develops. This potential depends on the individual ion mobility, charge and size.

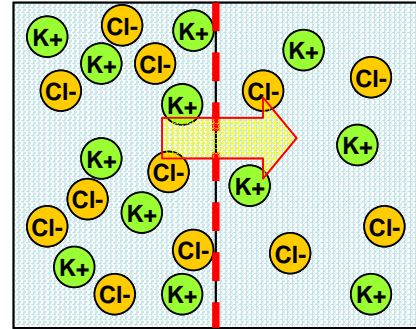
Figure (6): mobility of ions

cation	ion mobility ($\text{cm}^2\text{s}^{-1}\text{V}^{-1}$)	ion radius (pm)
H^+	$36.2 \cdot 10^{-4}$	154
Li^+	$4.0 \cdot 10^{-4}$	68
Na^+	$5.2 \cdot 10^{-4}$	97
K^+	$7.6 \cdot 10^{-4}$	133
NH_4^+	$5.2 \cdot 10^{-4}$	151
Ca^{++}	$6.2 \cdot 10^{-4}$	99

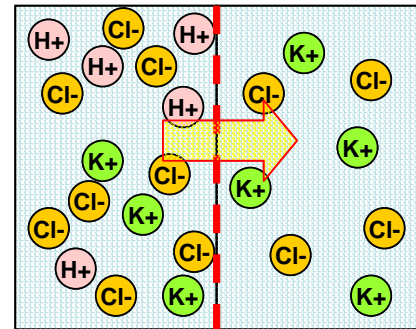
anion	ion mobility ($\text{cm}^2\text{s}^{-1}\text{V}^{-1}$)	covalent radius (pm)
OH^-	$20.6 \cdot 10^{-4}$	98
F^-	$5.7 \cdot 10^{-4}$	133
Cl^-	$7.9 \cdot 10^{-4}$	181
NO_3^-	$7.4 \cdot 10^{-4}$	124
CO_3^{--}	$7.5 \cdot 10^{-4}$?
SO_4^{--}	$8.3 \cdot 10^{-4}$	104

Potassium and Chloride have a similar ion mobility. In case KCl has to move through a barrier like a diaphragm, K^+ and Cl^- will do it in the same velocity. If both ion arrive in parallel on the other side of the barrier, there is almost no liquid junction potential. Because the movement through the barrier is a diffusion, this potential is also called diffusion potential.

If a 3 molar KCl solution is on one side and a tap water sample is on the other side, then the diffusion potential is relatively small. K^+ and Cl^- can move with same velocity.



If other ions are present in the KCl filling solution, which have a different mobility, a diffusion potential can develop.



H^+ ions are much faster than K^+ ions. When ions move through the barrier, Cl^- ions remain the same, but H^+ is much faster, even faster than Cl^- .

Because H^+ ions move much faster, there have more H^+ ions moved through the barrier than Cl^- ion. Consequently this generates a potential difference between inner side and outer side of the barrier (diaphragm).

Figure (7): development of diffusion potential

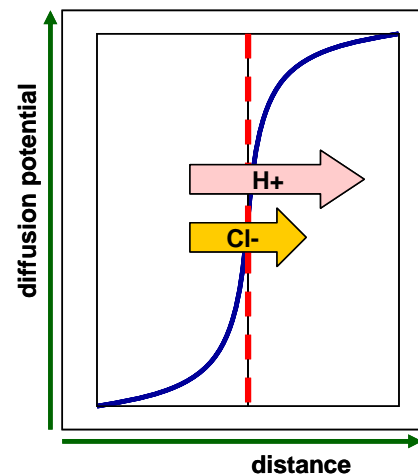






Figure (8): some typical diffusion potentials

solution 1	solution 2	mV
saturated KCl solution	1 M HCl	14
	Buffer 4.01	3
	Buffer 7.00	2
	Buffer 10.01	2
	1 M NaOH	-9

Therefore the potential measured in a sample is the sum of individual potentials, which develop at indicating and reference element and at the liquid junction. The higher the difference between the anions and cations of the reference electrolyte is, the higher is the diffusion potential.

Figure (9): junction overview

Open junction	Ceramic or porous pin	Annular ring	Glass or plastic sleeve
			
NO	electrolyte outflow	HIGH	
NO	maintenance	HIGH	
standard	sample	difficult	

Selecting the right junction

Manufacturers of electrodes recommend their probes for specific applications.

Starting with the sample is often the easiest way to find out the needs for a specific diaphragm.

Field measurements usually demand a robust electrode with plastic housing and a minimum of maintenance. Here an open junction with gel filling is the best choice.

The more the electrode can be contaminated from the sample, the higher is the technical and manual effort for accurate and reliable measurements (e.g. ceramic pin or annular ring). Finally very specific samples require a measurement system, like a sleeve junction, which needs much more attention and maintenance.

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Calculation of the liquid junction potential

Using the “Henderson” equation it is possible to calculate a value representing the junction potential. However, because of a long list of parameters which need to be known to solve the equation, it is not easy to calculate exact values. In some cases certain parameters can be estimated as good as possible and some minor values may be neglected. Finally the result of such a calculation is more an estimation of the influence of the junction potential.

As a rule of thumb one can say that leaving the neutral pH range (pH 7.0) to more acidic (\leq pH 2) or more alkaline (\geq pH 12) area, the value of the junction potential raises and adds to the known acidity or alkaline error.

A very similar effect comes from low conductivity solutions, where the ion concentration difference between inner electrolyte and outer sample solution is very high.

The best way to compensate for those effects is to calibrate with several pH buffer solutions to cover the complete pH range of the sample. If acid samples have to be measured, a calibration with pH buffer 1.67 and pH 4 or pH 7 is recommended. For alkaline samples a calibration with pH 7 or pH 9.18 and 12.45 may be adequate.

In any case the calibration buffers must bracket the sample pH to achieve best results.