

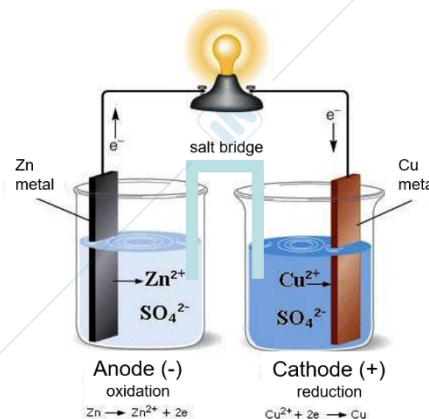
## ELECTROCHEMICAL BIOSENSORS

*In Virtuale there are a couple of videos: one is related to what are the biosensors and the second one is on electrochemical biosensors.*

The lesson before, we have seen that a biosensor is an electrochemical cell and how it is made. There are at least 3 components in cell: 2 electrodes and one electrolyte. These 3 components have different functions:

- The electrodes in metal (or carbon) are **electronic conductors**, which are able to transfer the electrons from the material inside the cell to external space, where we have some loading or something that can use energy (electrons current) to generate some work.

*Why there are two electrodes?* Because electrons exit from one and enter in the other.



- The electrolyte is useful to close the circuit. In the picture we can see a salt bridge (but we can also have a membrane and we will see how it works by transferring the ions). In this case, there is **no transfer of electrons** in the solution, but only of ions. The salt is dissolved in the solvent and usually this salt should be in high concentrations.

We can have different types of salt in solution: a salt mainly related to the electrolyte (like zinc metal and zinc surface) so it's related to the redox couple ( $Zn/Zn^{2+}$ ). But if I want a good transfer of ions, I need also a salt called **support electrolyte** and it is the salt inside the salt bridge. For example, inside the bridge in the picture we can have  $NaNO_3$ , totally different from the other salts, and if I have  $10^{-3}$  M of salt ( $Zn/Zn^{2+}$ ) in the solution in this case  $NaNO_3$  should have a very high concentration (1 M).

A Galvanic cell is when I have a spontaneous process. An Electrolytic cell is when I have to add some energy to have the reaction.

We have seen also the **1<sup>st</sup> Ohm's Law:  $I = E/R$**  that put in relation the current and voltage of the cell, while the parameter in this ratio is the resistance of the cell.

$I$  = current (in ampere, A)

$E$  = voltage (or potential) applied (in volt, V)

$R$  = resistance (in ohm, W)

The **Faraday constant (F)** is the charge carried by 1 mole of electrons. So, for each reaction we can know exactly what is the charge involved.

$$I \text{ (A)} = Q \text{ (Coulomb)} / t \text{ (s)}$$

$$1 e^- = 1,60 \cdot 10^{-19} \text{ C}$$

$$1 \text{ mole of } e^- = 1,60 \cdot 10^{-19} \text{ C} \times 6,023 \cdot 10^{23} \text{ mol}^{-1} = 96485 \text{ C/mol } e^-$$

↑  
Avogadro Number  
 $N_A$

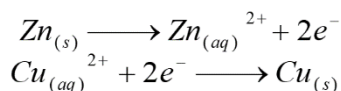
↑  
Faraday constant  
 $F$

C. Arbizzani - Pharmaceutical Biotechnology AA 2022-2023

The **2<sup>nd</sup> Ohm's Law:  $R = \rho L/A$**  put in relation the physical properties of the conductor and we have seen that the reciprocal of the same relation can also be useful for ionic conductors. So instead of resistance we have conductance and instead of resistivity we talk about conductivity, but the concept is more or less the same:

- the meaning of the resistance is an obstacle to the transfer of electrons: if I have high resistance, I have some problems to have the transfer
- the conductance is the opposite: if I have a good conductivity the system works very well

**Anode (oxidation)**  
**Cathode (reduction)**



**Overall reaction**



At the anode there is always the oxidation and at the cathode we have always the reduction. Each half-reaction occurs at a very specific potential, that is very important for predict the potential of a cell. But, unfortunately, it's impossible to know the absolute potential of a single electrode, we can only measure the difference of potential between the electrode and a reference electrode (**standard hydrogen electrode, SHE**). The potential of the SHE is zero, so the voltage of the cell is given by the difference between the potential of the cathode and the potential of the anode  $\rightarrow E = V_c - V_a$

This measurement is made by a voltmeter, an important apparatus with a very high resistance, so for the 1<sup>st</sup> Ohm Law we have a current in the order of nanoampere. Such a low current means that the current is near zero, so it is as the circuit was open. It's not really open, but it is a measure that is very near to the reversibility<sup>1</sup> of the system. On the contrary, if we buy a tester at the supermarket, we cannot do this type of measurement because the resistance is not so high and we will discharge the cell.

To each half-reaction is associated a **standard reduction potential**  $V^\circ$  that indicates the reduction capability of the redox system. This potential is determined by using the SHE as reference.

By looking at this series we know what the most favorite species in usual conditions is. If I take Lithium, I see that in the reduction reaction ( $\text{Li}^+ + 1e^- = \text{Li}$ ) the equilibrium will be shifted toward the  $\text{Li}^+$ , so the Lithium ion is the most stable form for the negative potential. As the same way we can argue that below zero the most favorite species should be the one on the left; while at the positive level we can see that the most favorite species could be  $2\text{F}^-$ , so at the positive value we have to consider that there are stronger oxidizing agents. On the contrary, Lithium is a reducing agent and so it reduces the species and indeed it oxidizes itself.

- $\rightarrow$  Strong oxidants have high  $V^\circ$  values
- $\rightarrow$  High reductants have low  $V^\circ$  values

Half Reaction	Standard Potential (V)
$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	+2.87
$\text{Pb}^{4+} + 2e^- \rightleftharpoons \text{Pb}^{2+}$	+1.67
$\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$\text{Ag}^+ + 1e^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Fe}^{3+} + 1e^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.00
$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-0.13
$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1.66
$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.36
$\text{Li}^+ + 1e^- \rightleftharpoons \text{Li}$	-3.05

↑ stronger oxidizing agent (red arrow)  
↓ stronger reducing agent (blue arrow)

In general, the reduction potential for a half-reaction could be calculated by **Nernst equation**.

The reduction potential  $V$  depends on the activities of the species that take part to the reaction. The **activity** ( $a$ ) is a concept in thermodynamics that is like an effective concentration: if we work a very low concentration the activity is very similar to the concentration, but if we work a high concentration, we need to use an activity coefficient ( $\gamma$ ).

$$V = V^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} \approx V^\circ - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]} \quad * a = \gamma C$$

<sup>1</sup> Reversibility: when we have a process that is very slow

For our purpose we will always use the concentrations of the reduced species and oxidized species simply by changing the  $V_0$ :

$$V = V_0 - \frac{RT}{nF} \ln \frac{a_r}{a_o} = V_0 - \frac{RT}{nF} \ln \frac{\gamma_r C_r}{\gamma_o C_o} = V_0 - \frac{RT}{nF} \ln \frac{\gamma_r}{\gamma_o} - \frac{RT}{nF} \ln \frac{C_r}{C_o}$$

Giving that  $\gamma$  are constants in specific conditions we can call it  $V_0'$ .

The other parameters are:

- T: temperature in Kelvin
- n: number of electrons in the reaction
- F: Faraday constant (96485 C mol<sup>-1</sup>)
- R: gas constant (8,314 J K<sup>-1</sup> mol<sup>-1</sup>)

Another way to write the Nernst equation is by using the decimal logarithm and in which the T is fixed at 298 K (25°C): (*the professor didn't like it so much*)

$$V = V_0' - \frac{0,0592}{n} \log \frac{a_{Red}}{a_{Ox}} \approx V_0' - \frac{0,0592}{n} \log \frac{[Red]}{[Ox]}$$

When can we use the concentration of redox species instead of the activity? Is simply when we have a very low concentration, for example when we have 10<sup>-3</sup> M the concentration and the activity are more or less the same, but if we work with 1 M of species, we measure a voltage, but we have to consider the activity coefficient for calculate it. In fact, the activity coefficients are evaluated by measurements of voltage, because we know the concentration in the solution. With  $\gamma$  we consider the effect of the ion interactions in solution: if we have a diluted solution the ions don't interact so much, but with high concentration ions interact strongly and the behavior is different.

These are some examples of activity coefficients at 25°C (in fact, also the temperature is a parameter that affect the viscosity of the solution): if we have very low concentration the activity is near 1, while if we have high concentration, it's near 0.5.

Coefficients di attività a 25° C (da misure di punti di congelamento)					
m	KCl	K <sub>2</sub> SO <sub>4</sub>	BaCl <sub>2</sub>	Pb(NO <sub>2</sub> ) <sub>2</sub>	CuSO <sub>4</sub>
0.0001	0.982	0.935	0.94	0.965	0.85
0.0005	0.970	0.885	0.89	0.922	0.75
0.005	0.940	0.75	0.77	0.773	0.50
0.01	0.903	0.69	0.72	0.694	0.40
0.05	0.821	0.505	0.568	0.465	0.216
0.1	0.779	0.421	0.501	0.369	0.158
(da misure di forza elettromagnetiche)					
m	LiCl	NaCl	KCl	KBr	KOH
0.001	-	0.966	0.965	-	0.989
0.005	-	0.928	0.926	-	0.954
0.01	0.901	0.903	0.899	-	0.920
0.05	0.819	0.821	0.815	0.816	0.822
0,1	0.779	0.778	0.764	0.765	0.589
0,5	0.725	0.678	0.644	0.653	0.750
1.0	0.757	0.658	0.597	0.612	0.760
2.0	0.919	0.670	0.569	0.589	-
3.0	1.174	0.714	0.571	0.590	1.062

To have these values, the experiments have to build a cell with the Hydrogen reference electrode on the left and on the right the electrode on which we have to measure the standard potential.

The standard potential requires specific conditions: **the activity  $a = 1$** . So, all the values reported in the table are measured when the activity is one.

For example, considering a silver electrode:  $\text{Ag}^+_{(\text{sol})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$

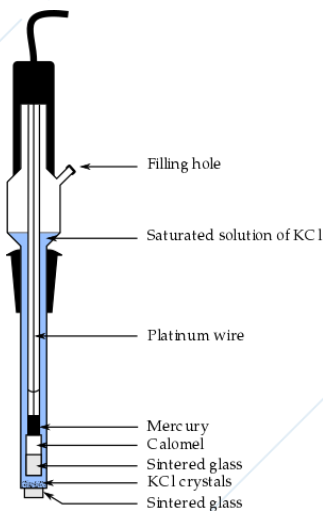
The Nernst equation is:  $V = V_0 - \frac{RT}{nF} \ln \frac{[\text{Ag}]}{[\text{Ag}^+]}$

But the concentrations and the activity of all the solid species is equal one, so we can write:

$$V = V_0 - \frac{RT}{nF} \ln \frac{[\text{Ag}]}{[\text{Ag}^+]} = V_0 - \frac{RT}{nF} \ln \frac{1}{[\text{Ag}^+]} \quad a_{\text{Ag}^+} = 1$$

For this reason, we can say that the concentrations of both species should be equal, but if the concentration for the activity of  $\text{Ag}^+$  is equal to 1, the logarithm is zero and so  $V = V_0$ .

## REFERENCE ELECTRODES



This is another reference electrode because the Hydrogen electrode is not very common in the laboratory due to the high inflammability of Hydrogen gas and its difficulty.

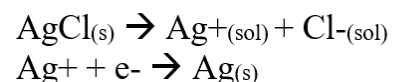
Usually, the most used reference electrodes are:

- the **Saturated calomel electrode (SCE)**
- the **Ag/AgCl electrode** (most used in Biosensors)

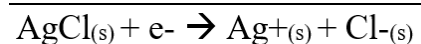
The first type of species of electrodes is when we have one metal and the ion metal in the solution ( $\text{Ag}^+_{(\text{sol})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$ ). Whereas, the SCE and the Ag/AgCl electrode are the second type: a metal with a salt (usually partially or not soluble) and in solution there are the anions of the salt.

For example, in the Ag/AgCl electrode there is:

Silver chloride that is quite insoluble, but there is a metal, so the reaction occurs to the silver.



At this point, if we sum the two reactions (the dissociation and the Faraday reaction) we obtain the total reaction of pure electrode.



If we write the Nernst equation, in this case, we have:

$$V = V_0 - \frac{RT}{nF} \ln \frac{[\text{Cl}^-][\text{Ag}]}{[\text{AgCl}]} = V_0 - \frac{RT}{nF} \ln [\text{Cl}^-]$$

For what we have seen before the  $[\text{Ag}]$  and  $[\text{AgCl}]$  have activity = 1. So, in this case we have the dependence on the anion of the salt.

### REMEMBER!

When you write the Nernst equation in the direction of the reduction always use the MINUS. For facilitating the calculation, we can transform for the properties of logarithm:  $V = V_0 - \frac{RT}{nF} \ln \frac{1}{[\text{Ag}^+]} = V_0 + \frac{RT}{nF} \ln [\text{Ag}^+]$

At this point, we can see that usually we use the solution of KCl, the K ions do not react with the silver, so it is inert and the concentration of the chloride ions determine the potential. It is quite usual to have electrodes, which are to the saturated condition where the concentration of the salt is crucial.

In the **Saturated calomel electrode (SCE)**, the only difference is that the Mercury is liquid and in contact with it there is the calomel  $\text{Hg}_2\text{Cl}_2$  (a not soluble salt).

We can see that if we use the solution 1M, the potential is 0,2680 V, while if we use a saturated solution is 0,2444 V and if we change the salt, we have another different potential because NaCl is more soluble than KCl, so it changes the  $[\text{Cl}^-]$ . In any case, with the electrode we can find exactly the value of the voltage.

$$V^\circ \text{Hg(l)/Hg}_2\text{Cl}_2\text{(s)/Cl}^- = 0,2680 \text{ V KCl 1m}$$

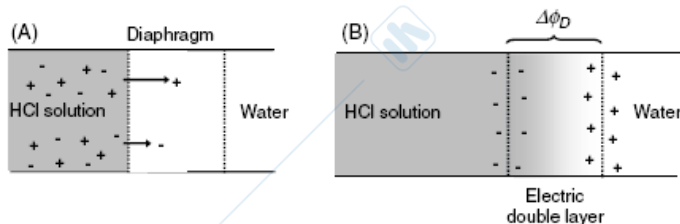
$$V_{\text{ECS, KCl, sat}} = 0,2444 \text{ V}$$

$$V_{\text{ECS, NaCl, sat}} = 0,2360 \text{ V}$$

As said before, we can have a salt bridge or a membrane inside the cell. When we have a membrane, it happens that the ions in one side go in the other side and there is a different distribution of ions concentration. We can have 2 types of interfaces:

- A **permeable interface**, which allows the transfer of ions from one side to the other without any restrictions.
- A **semi-permeable interface** permits only the transfer of certain types of ions

### Permeable interface



The ions from HCl tend to go toward the water, because the ion concentration in water is zero. So we have a diffusion of gradient concentration and ions start to move: the protons are faster than other ions because they can also move with the *Grotthuss mechanism*<sup>2</sup>. After a certain

time, we have a concentration of protons and in the other side a concentrations of  $\text{Cl}^-$ , so it form a *electric double layers*. This double layer produces a potential, called *diffusion potential* or *liquid junction potential* ( $\Delta\phi$ ).

This happens when ions can move without restrictions through the membrane and this is more or less what happens when we have an electrochemical cell. In order to calculate the junction potential, we have to consider the **mass transport of ions across the interface**. As already mentioned, ion transport occurs under the influence of both the **activity gradient** across the interface (diffusion) and the **electric potential gradient** (migration).

This potential is affected by the ions **mobility**<sup>3</sup> ( $\text{m}^2 \text{s}^{-1} \text{V}^{-1}$ ) and thanks to it we can find the **diffusion coefficient** (D) of an ion:

$$D = RTu,$$

where R is the ideal gas constant, u is the mobility and T is the absolute temperature.

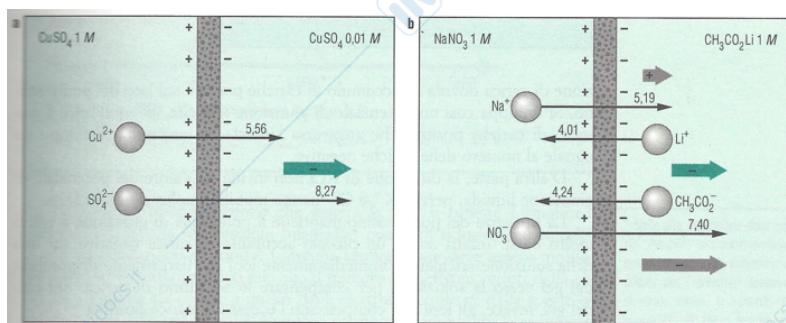
<sup>2</sup> Grotthuss mechanism: protons can attach themselves to water molecules and use this motion

<sup>3</sup> Mobility: The characteristic migration velocity of an ion and is defined as the increase in the ion velocity when crossing the distance between two points at 1m distance from each other and subject to a potential difference of 1V (velocity divided by electric field)

The diffusion coefficient is very important in electrochemistry, because if some species have a low  $D$  the reaction will be slow, because it does not have enough diffusion of species inside the cell.

**The relation between the mobility and the velocity is:  $u \text{ (m}^2/\text{s V)} = v \text{ (m/s)} / E \text{ (V/m)}$**

The electric field is related to the potential because it's the potential divided by the distance of the electrodes.



What's happen when we have the same solution but a different concentration? Of course, we have a movement of all ions from one side to the other for equilibrium and the cation is slower than the anion.

In Figure b, we have 1M of  $\text{NaNO}_3$  and 1M of  $\text{CH}_2\text{CO}_2\text{Li}$ , so we have the same concentration. In this case, all the ions move back and forth across the membrane with different velocity (or mobility) and, at the very end, when we have reached the equilibrium, this equilibrium depends on how fast these ions move.

However, this potential isn't so big and, in some case, it doesn't affect too much the differences of potential measured with electrode in this interface.

In the table below, there are the liquid junction potential at  $25^\circ\text{C}$  (the temperature should be always indicated) and we can see different situations. In one case, when we have the same concentration, we can have a potential near 4 millivolts. But if we increase dramatically one concentration, depending on the ion's mobility, for example the  $\text{KCl}$ 's mobility is slower than  $\text{NaCl}$ , I have to increase the concentration to try to increase the effect of this ion and we can see that the potential is slower (1mV), so it is not so important for our purpose.

**Table 10.2** Liquid junction potentials at  $25^\circ\text{C}$  estimated by Henderson equation

Junction	Potential/mV
0.1 M KCl    0.1 M NaCl	4.4
3.5 M KCl    0.1 M NaCl	-0.2
3.5 M KCl    1.0 M NaCl	1.9
0.1 M KCl    0.1 M HCl	-26.8
3.5 M KCl    0.1 M HCl	-4.2

When we have low concentrations but with the presence of the protons, we have an unbalance because protons have a big mobility and, in this case, we have higher potential.

To sum up, we can work on the concentration if we want to reach a low potential of interface, but sometimes it's not possible because we work with specific system, so we have simply to consider **both** (1:07:30) of this potential.

**Table 10.1** Ion mobility in water at  $25^\circ\text{C}$  in  $\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}$

Cation	Mobility	Anion	Mobility
$\text{H}^+$	$36.25 \times 10^{-8}$	$\text{OH}^-$	$20.5 \times 10^{-8}$
$\text{K}^+$	$7.619 \times 10^{-8}$	$(1/2)\text{SO}_4^{2-}$	$8.27 \times 10^{-8}$
$\text{NH}_4^+$	$7.61 \times 10^{-8}$	$\text{Cl}^-$	$7.912 \times 10^{-8}$
$(1/2)\text{Ca}^{2+}$	$6.166 \times 10^{-8}$	$\text{NO}_3^-$	$7.404 \times 10^{-8}$
$\text{Na}^+$	$5.193 \times 10^{-8}$	$\text{ClO}_4^-$	$7.05 \times 10^{-8}$
$\text{Li}^+$	$4.010 \times 10^{-8}$	$\text{CH}_3\text{COO}^-$	$4.24 \times 10^{-8}$

From Bard, A. J. and Faulkner, L. R. (2001) *Electrochemical Methods: Fundamentals and Applications*. Wiley, New York, p. 68.

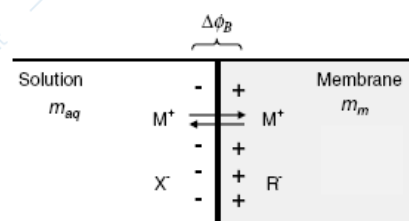
Thus, for a potentiometric sensor with a sensitivity of 59mV, an error of 3mV in the cell voltage brings about an error of 0.05 pX units, that is, a 12% concentration error. This type of error is not absolutely to not consider because it gives us an error on our detection. However, we should see if it acceptable or not: if not we have to decrease this value, while if it is acceptable, we can work.

The effect of the junction potential can be minimized by using a double-junction reference electrode with the electrolyte bridge filled with a solution whose ions have similar mobilities. As the two junction potentials have opposite signs, the overall diffusion potential will be very small.

### Semipermeable interface

The other difference of potential occurs when we have a semipermeable interface, which restricts the transfer of certain types of ions. In this case, the different anions remain on the two sides while only the cations are changing.

This membrane is typical for some electrodes that exchange ions and in some cases the tensions inside this type of electrodes are related to the specific cation or anion. In other cases, there is also some species inside the membrane (*carrier*) that help the transfer from onside to the other. The difference of potential is more or less similar to the one already seen.



Summary slide 53:

We have an equilibrium, and we can calculate a constant of this equilibrium between the concentration of one side and the other and this gives the **boundary potential** of this kind if membrane.

To conclude, we have found a useful equation: the Nernst equation. The most important thing is that the Nernst equation is used only in equilibrium conditions.

At equilibrium, this process is characterized by the partition coefficient  $K_p$ .

$$K_p = \frac{m_m}{m_{aq}}$$

where  $m_{aq}$  and  $m_m$  are the activities of the free metal ions in the solution and in the membrane, respectively. As the partition coefficient is an equilibrium constant, it is correlated with the standard free energy change of transfer  $\Delta G^0$  and with the chemical potentials of the ion in each phase as follows:

$$\ln K_p = -\frac{\Delta G^0}{RT} = \frac{1}{RT} (\mu_{M^+,aq}^0 - \mu_{M^+,m}^0)$$

The boundary potential equation can be derived from the equilibrium condition for the ion transfer between the two phases, which implies equality of electrochemical potentials:

$$\mu_{M^+,aq}^0 + RT \ln m_{aq} + zF\phi_{aq} = \mu_{M^+,m}^0 + RT \ln m_m + zF\phi_m$$

$$\Delta\phi_0 = \phi_m - \phi_{aq} = \frac{RT}{zF} \ln \left( \frac{m_{aq}}{m_m} \right)$$

where  $\Delta\phi_0 = (RT/zF) \ln K_p$  represents the standard boundary potential.

If the metal ion can bind to a ligand to form a complex either in the solution or in the membrane phase, the free ion activity can be obtained from the stability constant of the complex.

## POTENTIOMETRIC BIOSENSORS

Ion sensors are related to the fact that ion carries a charge. So, we have to consider reactions where there is a change in concentration of this ion. The pH is where we have a change in concentration of protons.

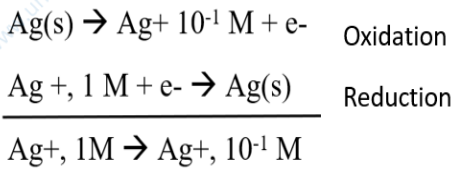
During this measurement we can see what happens at the interface of two phases: one outside the electrode and one inside and in the middle there is a membrane. We have to evaluate the concentrations outside the electrode.

A **concentration cell** means a cell where the two electrodes are the same and the difference between the two compounds is the concentration. We use vertical bars for separate the phases and two vertical bars for the membrane.

For example:  $\text{Ag(s)} \parallel \text{Ag}^+(\text{sol}), 1 \times 10^{-1} \text{ M} \parallel \text{Ag}^+(\text{sol}), 1 \text{ M} \parallel \text{Ag(s)}$

Usually, we consider this the negative electrode (-)

And this the positive electrode (+)



It remains simply the two concentrations, so if we want the Nernst equation of the total cell we can write:

$$E = E_0 - \frac{RT}{nF} \ln \frac{[\text{Ag}^+, 10^{-1} \text{ M}]}{[\text{Ag}^+, 1 \text{ M}]}$$

$E_0 = 0$  because *the electrodes are the same*

But if we want to write the Nernst equation by considering the two different electrodes, I know that  $E = V_{\text{Right}} - V_{\text{Left}}$  and in this case we have to write the equation both in the reduction directions.

$$V_L = V_0 - \frac{RT}{F} \ln \frac{1}{[10^{-1}]}$$

$$V_R = V_0 - \frac{RT}{F} \ln \frac{1}{[1 \text{ M}]}$$

$V_0$  is the same, because  $V_0 = \text{Ag}/\text{Ag}^+$

$$E = -V_0 - \frac{RT}{F} \ln \frac{1}{[1 \text{ M}]} - V_0 + \frac{RT}{F} \ln \frac{1}{[10^{-1}]}$$

$$E = - \frac{RT}{F} \ln \frac{10^{-1}}{[1 \text{ M}]}$$

So, we can evaluate the Nernst equation of our cell simply by obtaining the total reaction of the cell and, in this case, we have to consider the reaction occurring in the cell. Or we can evaluate the potential of our electrode and, in this case, we have to write exactly the reaction in the reduction way.

This is the same situation when we have a membrane, two different concentrations of different salt and the same electrode (so  $E_0$  is not present), where the potential difference through the membrane depends on the difference between the ion activity in the internal solution and in the sample:

$$E_m = - \frac{RT}{nF} \ln \frac{a_1}{a_x} = \frac{RT}{nF} \ln \frac{a_x}{a_1}$$

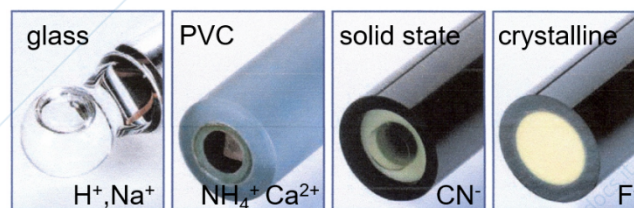


If we know very well  $a_1$ , we can consider it a constant and put it inside the other constants, so we can simplify the equation in this way:

$$E = \text{cost} - \frac{RT}{nF} \ln a_{i,x}$$

We can see that if we measure the potential of the electrode, we have a correlation with the logarithm of activity of species. This is the way potentiometric biosensors work and all these are under equilibrium conditions: no current is flowing in the system.

The Ion selective electrodes (ISE) have several geometry and ISE membranes can be solid glass, polymer, inorganic crystal) and liquid (usually hydrophobic solvents).



There are a lot of electrodes for every kind of ion. In the table below is reported also a range of temperatures in which we can work, the concentration range, the range of ph ecc..

**Pros**

- Linear response in a wide concentration range (1M –10<sup>-6</sup> M)
- Lower concentration limit ca. 10<sup>-7</sup> M.
- Non-destructive analysis, because with this type of electrode we simply measure the potential
- No sample contamination
- Short time response (few seconds)

**Cons**

- Possible electrode contamination (organic molecules, proteins...)
- The response is related to the non-complexed ion activity. Ligands and complexant molecules should be removed from samples before analysis or masked.

Specie	Br-	Ca <sup>++</sup>	Cl-	Cl-	CN-	Cu <sup>++</sup>	F-	F-
<b>Codice</b>	ISE25Br E41M001	ISE25Ca E41M002	ISE25Cl E41M003	ISE/HS25Cl E41M004	ISE25CN E41M005	ISE25Cu E41M006	ISE25F E41M007	ISEC301F E41M007
<b>Conc. range (M)</b>	10 <sup>-6</sup> - 10 <sup>0</sup>	2 x 10 <sup>-6</sup> - 10 <sup>0</sup>	5 x 10 <sup>-5</sup> - 10 <sup>0</sup>	10 <sup>-5</sup> - 10 <sup>0</sup>	5 x 10 <sup>-7</sup> - 10 <sup>-3</sup>	10 <sup>-6</sup> - 10 <sup>0</sup>	5 x 10 <sup>-7</sup> - 10 <sup>0</sup>	5 x 10 <sup>-7</sup> - 10 <sup>0</sup>
<b>Conc. range (ppm)</b>	0.08 - 80.000	0.1 - 40.000	1.8 - 35.000	0.04 - 35000	0.013 - 25	0.06 - 60.000	0.01 - 20.000	0.01 - 20.000
<b>Range di temperatura</b>	0 - 60°C	0 - 50°C	0 - 60°C	0 - 60°C	0 - 60°C	0 - 60°C	0 - 60°C	0 - 50°C
<b>Diametro</b>	12 mm	12 mm	12 mm	12 mm	12 mm	12 mm	12 mm	12 mm
<b>Range pH</b>	2 - 14	4 - 12	2 - 14	2 - 14	9 - 14	0 - 14 (3-7 mis.dir.)	5 - 11 (10 <sup>-1</sup> MF) 5 - 7 (10 <sup>-6</sup> MF)	2 - 12
<b>Tipo di sensore</b>	Stato solido	Membr. PVC	Stato solido	Stato solido	Stato solido	Stato solido	Stato solido	Membr. PVC
<b>Ioni interferenti</b>	I <sup>-</sup> , S <sup>-</sup> , CN <sup>-</sup> , SCN <sup>-</sup>	Zn <sup>++</sup> , Pb <sup>++</sup>	I <sup>-</sup> , CN <sup>-</sup> , Br <sup>-</sup> , SCN <sup>-</sup>	I <sup>-</sup> , CN <sup>-</sup> , Br <sup>-</sup> , SCN <sup>-</sup>	I <sup>-</sup> , Br <sup>-</sup> , S <sup>-</sup>	HgS, Ag <sup>+</sup> , Cl <sup>-</sup>	OH <sup>-</sup>	OH <sup>-</sup>
<b>Elettrodi di riferimento raccomandati</b>	REF 251	REF201/ REF251 REF451	REF251/ REF451 REF601	REF251/ REF451 REF601	REF201/ REF251 REF451	REF201/ REF251 REF451	REF201/ REF251 REF451	REF incorporato A3/AgCl

Specie	I-	K+	Na+	Na <sup>4+</sup>	NO <sub>3</sub> <sup>-</sup>	Pb <sup>++</sup>	S-(Ag+)(*)
<b>Codice</b>	ISE25Br E41M008	ISE25Ca E41M009	ISE25Cl E41M010	ISE/HS25Cl E41M013	ISE25CN E41M014	ISE25Cu E41M015	ISE25F E41M016
<b>Conc. range (M)</b>	10 <sup>-6</sup> - 10 <sup>-1</sup>	2 x 10 <sup>-6</sup> - 10 <sup>0</sup>	2 x 10 <sup>-6</sup> - 10 <sup>0</sup>	3 x 10 <sup>-6</sup> - 10 <sup>0</sup>	3 x 10 <sup>-6</sup> - 10 <sup>0</sup>	10 <sup>-6</sup> - 10 <sup>0</sup>	5 x 10 <sup>-6</sup> - 10 <sup>0</sup>
<b>Conc. range (ppm)</b>	0.13 - 13000	0.08 - 40000	0.04 - 20000	0.06 - 20000	0.2 - 60000	0.2 - 200000	0.02 - 30000
<b>Range di temperatura</b>	0 - 60 °C	0 - 50 °C	0 - 70 °C	0 - 50 °C	0 - 50 °C	0 - 60 °C	0 - 60 °C
<b>Diametro</b>	12 mm	12 mm	12 mm	12 mm	12 mm	12 mm	12 mm
<b>Range pH</b>	2 - 12	2 - 12	5 - 12	3 - 8	3 - 10	3 - 7 (mis.dirette)	1 - 14 (mis.dirette)
<b>Tipo di sensore</b>	Stato solido	Membrana PVC	Vetro	Membrana PVC	Membrana PVC	Stato solido	Stato solido
<b>Ioni interferenti</b>	CN <sup>-</sup> , Hg <sup>++</sup> , Br <sup>-</sup> , SCN <sup>-</sup>	NH <sub>4</sub> <sup>+</sup> , Rb <sup>+</sup>	Li <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Rb <sup>+</sup> , Ag <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup> , Br <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	Hg <sup>++</sup> , Cu <sup>++</sup> , Ag <sup>+</sup>	I cationi in precipitazione formano dei complessi con i solfuri
<b>Elettrodi di riferimento raccomandati</b>	REF201/REF251 REF451	REF251 REF451	REF251 REF451	REF251 REF451	REF201/REF251 REF451	REF251 REF451	REF251 REF451