4 - CURRENT FLOW: A NON-EQUILIBRIUM PROCESS

The purpose of this chapter is to provide the tools to describe the relationships between voltage and current, in quantitative terms, as a function of time in electrochemical systems.

When a current flows through a system, movements of at least one type of charged species are observed on the macroscopic scale. Consequently the system is in a non-equilibrium state.

4.1 - MASS BALANCES

Once the relationship has been defined between the current and the quantities characterizing mass transport, then one can write mass balances in volume and at the interfaces to describe the electrochemical systems in which a current flows in quantitative terms.

4.1.1 - DEFINITIONS FOR THE MACROSCOPIC QUANTITIES RELATED TO THE CURRENT

Since all elementary charged species have a mass, then by definition the notion of current is related to the notion of overall mass transport.

4.1.1.1 - MOLAR FLUX

Any movement of substance, whether relating to a charged species or not, can be quantified by the amount of substance (mol) flowing through a surface per time unit. This represents the molar flux or flow rate (mol s^{-1}). Here we define an associated local macroscopic quantity: the molar flux density which depends on the position. This value is an average taken around the point in question, and calculated for a large volume when compared to atomic dimensions (greater than tens of nm^3) [1]. The latter is defined in relation to the amount of species i, $\mathrm{d}n_i$, flowing through a surface of elementary area $\mathrm{d}S$ during an elementary time interval $\mathrm{d}t$. It is a vector, $\mathbf{N}_i$, which is collinear with the local velocity of the species in question, and which is oriented in the same direction (see the development below). Its modulus is given by the following equation:

$$\|\mathbf{N}_i\| = \frac{1}{\mathrm{d}S}\,\frac{\mathrm{d}n_i}{\mathrm{d}t}$$

[1] Many authors in the field of electrochemistry wrongly omit the term density when using the term molar flux, whereas it is indeed a matter of molar flux density. This may lead to misunderstanding since the terms flux and flow rate are synonyms in many other scientific domains, yet in this context they have different meanings.

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with: $\mathbf{N}_i$ the molar flux density, with the modulus in [mol m^{-2} s^{-1}]
$\mathrm{d}n_i$ the variation in the amount of species i [mol]
$\mathrm{d}S$ the elementary surface area [m^2]
$\mathrm{d}t$ the elementary time interval [s]

The molar flux density and local velocity vectors are collinear and in the same direction. The proportionality between these two vectors has a physical meaning. The example given below sets out this relationship for a system with unidirectional geometry, whereby one only needs to take into account the spatial variations in one direction [2]. The diagram in figure 4.1 illustrates the volume of this type of system whereby $\boldsymbol{\omega}_i$ is the local velocity of species i, and the surface (S) is chosen with its normal, $\mathbf{n}$, parallel to the velocity vector.

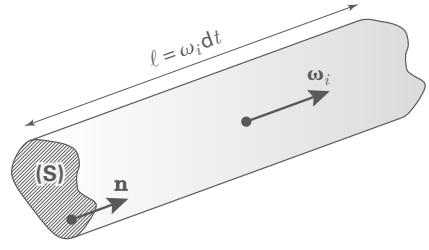

Figure 4.1 - Diagram of an elementary volume dV crossed by species i during a dt time interval

The amount of particles crossing (S) during the time interval $\mathrm{d}t$ is equal to the amount of particles contained in a cylinder volume with a base of area S and a length $\omega_i \mathrm{d}t$:

$$N_i = \frac{1}{S}\frac{\mathrm{d}n_i}{\mathrm{d}t}$$
$$\mathrm{d}n_i = C_i\,\mathrm{d}V = C_i\,\omega_i\,\mathrm{d}t\,S$$

For species i, we end up with the following equation, which can be applied to all geometric configurations:

$$\mathbf{N}_i = C_i \boldsymbol{\omega}_i$$

with: $\mathbf{N}_i$ the molar flux density, with the modulus in [mol m^{-2} s^{-1}]
C_i the local concentration [mol m^{-3}]
$\boldsymbol{\omega}_i$ the local average velocity, with the modulus in [m s^{-1}]

4.1.1.2 - CURRENT DENSITY

The molar flux density of a charged species i is also related to a charge flux density which is most commonly called current density:

$$\mathbf{j}_i = z_i \mathcal{F} \mathbf{N}_i$$

with: $\mathbf{j}_i$ the current density of species i, with the modulus in [A m^{-2}]
$\mathbf{N}_i$ the molar flux density of species i, with the modulus in [mol m^{-2} s^{-1}]
z_i the algebraic charge number of species i
$\mathcal{F}$ the FARADAY constant [C mol^{-1}]

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[2] Unidirectional geometry is the simplest form of geometry. It belongs to the 1D category since the only parameter is the distance from a plane. Other usual 1D systems have cylindrical or spherical geometric forms, where the only spacial parameter is the radius (distance to the cylinder axis or the center of the sphere).

Most often, there are several types of species in movement at a given time: the overall current is created by the movements of all the charge carriers.

The current density is defined as the vectorial sum of the current densities of each charge carrier:

$$\mathbf{j} = \sum_i \mathbf{j}_i = \sum_i z_i \mathscr{F} \mathbf{N}_i$$

When using this definition, one must pay attention to the fact that the current density is a local quantity. Consequently, when writing the sum one should only take into account the species actually present at the point in question. In an electrochemical system, the nature of the charge carriers may vary from one point to another within the device. This frequently occurs in large-sized cells with different species at the anode and the cathode. Yet this is always the case in the area surrounding a metal|electrolyte interface, as shown in the example below.

Let us take the example of a unidirectional system with a planar interface between a copper electrode and an aqueous solution containing copper sulphate. The overall current density vector is the same at all points in space [3] but it is not expressed in the same way in the metallic phase compared to in the solution. In the metal, the only mobile species are electrons, whereas in the solution there are two types of charge carriers, Cu^{2+} and SO_4^{2-} ions. This gives the following equation:

$$\mathbf{j}_{\text{metal}} = \sum_i \mathbf{j}_i = \mathbf{j}_e \qquad \mathbf{j}_{\text{electrolyte}} = \sum_i \mathbf{j}_i = \mathbf{j}_{Cu^{2+}} + \mathbf{j}_{SO_4^{2-}}$$

It would be wrong to indicate that the overall current density equals the vectorial sum of the electron and ion current densities, since these species cannot coexist in the same space zone:

$$\mathbf{j} = \sum_i \mathbf{j}_i = \mathbf{j}_e + \cancel{\mathbf{j}_{Cu^{2+}} + \mathbf{j}_{SO_4^{2-}}}$$

One way of expressing this is to suggest that the observer defining the current value locally is not ubiquitous and cannot see both electrons and ions move around simultaneously.

4.1.1.3 - TRANSPORT NUMBERS

The quantity used to compare the contributions of the various charge carriers to the overall current is the transport number of a given type of charge carrier, defined as the ratio between the overall current and the partial current attributable to the charge carrier. In any geometric situation, the different current density vectors are not necessarily collinear and the general definition of a transport number is as follows:

$$\tilde{t}_i = \frac{I_i}{I} = \frac{\mathbf{j}_i \times \mathbf{j}}{\mathbf{j} \times \mathbf{j}}$$

Transport numbers are local quantities. They have no dimension and may *a priori* be positive or negative. They obey the following equation:

$$\sum_i \tilde{t}_i = 1$$

[3] This property, which applies to unidirectional geometries, is demonstrated in section 4.1.2.

This notion is scarcely used in general cases [4], but is most commonly found exclusively in situations where migration is the only transport phenomenon to be taken into account: the transport numbers are then denoted by t_i, and are positive numbers showing values between 0 and 1 [5].

4.1.2 - VOLUME MASS BALANCE

At the macroscopic level, even without knowing the physical origins of a current [6], several general properties can be outlined pertaining to the current flow through the volume of a conducting medium [7].

A local volume mass balance can be written for each type of species: the local variation of the amount of substance depends on the balance (itself linked to the flux) between the species either leaving or entering the volume and those being created or consumed locally, for example by one or several chemical reactions. This type of mass balance can be done for neutral or charged species [8].

As shown in figure 4.2, the following equation can be written for a unidirectional system, namely one where the local quantities depend exclusively on one spatial dimension, (in other words they are homogeneous in any section perpendicular to the x-axis) and where the $\mathbf{N}$ component on the x-axis is denoted by N_x:

variation	=	species in	–	species out	+	local production
$\mathrm{d}n_i$	=	$N_{x,i}(x)\,S\,\mathrm{d}t$	–	$N_{x,i}(x+\mathrm{d}x)\,S\,\mathrm{d}t$	+	$w_i\,\mathrm{d}V\,\mathrm{d}t$

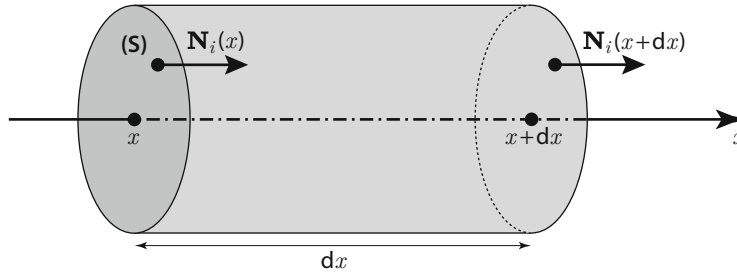

Figure 4.2 - Diagram of a volume with a molar flux of species i flowing through it

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[4] This notion is explained in general terms via an example in appendix A.4.1. It illustrates how in a system where migration and diffusion must be taken into account, the most common transport number, t_i, has no physical meaning whereas the electrochemical transport number, $\tilde{t}_i$, expresses the ratio between the current density of the species in question and the overall current density.

[5] This typical pure migration conditions are described in section 2.2.4.3.

[6] Section 4.2.1 describes the different mass transport processes and how to write the corresponding equations. The main mechanisms involved at the microscopic level are presented in section 4.2.2.

[7] Section 4.1.3 describes what occurs at the interfaces in terms of mass balance.

[8] Expressing mass balances is also an essential tool in chemical engineering, for example with mass or energy balances for open reactors.

By writing that $\mathrm{d}V = S\,\mathrm{d}x$, and using a TAYLOR expansion of the output molar flux density $N_{x,i}(x + \mathrm{d}x)$, one obtain the following equation:

$$\frac{1}{\mathrm{d}V}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \frac{1}{\mathrm{d}x}\left(N_{x,i}(x) - N_{x,i}(x) - \frac{\mathrm{d}N_{x,i}}{\mathrm{d}x}\,\mathrm{d}x\right) + w_i$$

Therefore, the following equation emerges for a species i in a system with unidirectional geometry:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial N_{x,i}}{\partial x} + w_i$$

with: C_i the local concentration of species i [mol m^{-3}]
$N_{x,i}$ the algebraic component on the x-axis of the molar flux density [mol m^{-2} s^{-1}]
w_i the local production rate of species i per unit volume (algebraic) [mol m^{-3} s^{-1}]

Generalising the equation to cover all geometric configurations gives the following[9]:

$$\frac{\partial C_i}{\partial t} = -\ \mathrm{div}\ \mathbf{N}_i + w_i$$

A so-called steady state can be reached in certain conditions, constituting a highly particular and important case from an experimental point of view[10]. One of its specific features notably includes the fact that the various concentrations are not time-dependent. Therefore, the volume mass balance at steady state is written in the following way:

$$\mathrm{div}\ \mathbf{N}_i = w_i$$

Generally speaking, as defined in homogeneous kinetics, the production rate per unit volume and the reaction rates are linked whether the system is at steady state or not. In fact, the rate of a chemical reaction (v in mol m^{-3} s^{-1}) is defined by the following equation:

$$v = \frac{1}{\nu_i}\frac{1}{V}\frac{\mathrm{d}n_i}{\mathrm{d}t}$$

with: V the volume of the system in question [m^3]
ν_i the algebraic stoichiometric number of species i
$\mathrm{d}n_i$ the variation in the amount of species i [mol]
$\mathrm{d}t$ the time interval [s]

$\mathrm{d}n_i/\mathrm{d}t$ represents the production rate of species i by the reaction concerned. When there are several reactions occurring simultaneously (see example below) then this gives the following equation:

$$w_i = \sum_{\text{reactions}} \nu_{i_r}\, v_r$$

---

[9] div is the divergence operator: div $\boldsymbol{X} = \dfrac{\partial X_x}{\partial x} + \dfrac{\partial X_y}{\partial y} + \dfrac{\partial X_z}{\partial z}$.

[10] This equation is often applied in electrochemistry to quasi-steady systems (see section 1.6.4).

If one write the local volume charge balance in the bulk of the conducting medium (that is, located at a distance from the interfaces with the surrounding media) based on the different volume mass balances, then you end up with the following equation:

$$\frac{\partial}{\partial t}\left(\sum_i z_i \mathcal{F} C_i\right) + \text{div}\,\mathbf{j} = 0$$

In fact the overall local charge production balance in the bulk of the solution is always zero.

For example, when certain olefins, R, are reduced in an organic medium, the charge transfer step occurring at the electrode produces an anion radical, which further reacts once in the electrolyte. One of the mechanisms that can be seen here involves three successive reactions in the solution.

After the cathodic electron transfer reaction occurs, producing the radical anion denoted by $R^{\bullet -}$:

$$R + e^- \longrightarrow R^{\bullet -}$$

the anion radical can then be seen to dimerise before two protonation reactions of the dimer formed occur. This is illustrated below with the respective volume reaction rates indicated by v_1, v_2 and v_3:

$$2\,R^{\bullet -} \xrightarrow{v_1} R_2^{2-}$$

$$R_2^{2-} + H^+ \xrightleftharpoons{v_2} R_2H^-$$

$$R_2H^- + H^+ \xrightleftharpoons{v_3} R_2H_2$$

Let us assume that before the olefins are reduced, the only ions contained in the solution are the protons and the nitrate counter-ions.

During the reaction, assuming that the anode and cathode are separated far enough apart to prevent any anodic phenomena from interfering, then the local volume mass balance for the six different species in the solution is as follows:

Volume mass balance	value of $\times z_i \mathcal{F}$
$\frac{\partial[R^{\bullet -}]}{\partial t} = -\,\text{div}\,\mathbf{N}_{R^{\bullet -}} - 2v_1$	$\times -\mathcal{F}$
$\frac{\partial[R_2^{2-}]}{\partial t} = -\,\text{div}\,\mathbf{N}_{R_2^{2-}} + v_1 - v_2$	$\times -2\mathcal{F}$
$\frac{\partial[R_2H^-]}{\partial t} = -\,\text{div}\,\mathbf{N}_{R_2H^-} + v_2 - v_3$	$\times -\mathcal{F}$
$\frac{\partial[H^+]}{\partial t} = -\,\text{div}\,\mathbf{N}_{H^+} - v_2 - v_3$	$\times +\mathcal{F}$
$\frac{\partial[R_2H_2]}{\partial t} = -\,\text{div}\,\mathbf{N}_{R_2H_2} + v_3$	$\times 0$
$\frac{\partial[R]}{\partial t} = -\,\text{div}\,\mathbf{N}_{R}$	$\times 0$
$\frac{\partial[NO_3^-]}{\partial t} = -\,\text{div}\,\mathbf{N}_{NO_3^-}$	$\times -\mathcal{F}$

The overall volume charge balance with the multiplying coefficients indicated above therefore gives the following:

$$\frac{\partial}{\partial t}\left(\sum_i z_i \mathcal{F} C_i\right) = -\operatorname{div}\mathbf{j} + \mathcal{F}\left[+2v_1 - 2(v_1 - v_2) - (v_2 - v_3) - (v_2 + v_3)\right] = -\operatorname{div}\mathbf{j}$$

Electromagnetism has its own equivalent of this property, as shown in the following equation:

$$\frac{\partial \rho_{ch}}{\partial t} + \operatorname{div}\mathbf{j} = 0$$

with: ρ_{ch} the charge density [C m^{-3}]
$\mathbf{j}$ the current density, with the modulus in [A m^{-2}]

By applying these volume mass balances to the conducting media within electrochemical systems, and more generally to electrochemical chains, an important property emerges relating to the current, as demonstrated below. The following equation shows a consequence of the fact that electroneutrality applies throughout the medium on the macroscopic scale in the bulk of any conductor, and after a very short transient state [11]:

$$\sum_i z_i C_i = 0 \quad \text{and thus} \quad \operatorname{div}\mathbf{j} = 0$$

After the transient period, the molar flux perpendicular to the interface between the conductor and the insulating media equals zero. By applying the OSTROGRADSKY theorem [12], it is possible to deduce that the charge flow rate is the same in all sections of the conductor, whether perpendicular to the current density or not, as shown in figure 4.3:

$$\iint_{(S)} \mathbf{j}.\mathbf{n}\,dS - \iint_{(S')} \mathbf{j}'.\mathbf{n}'\,dS + 0 = 0$$

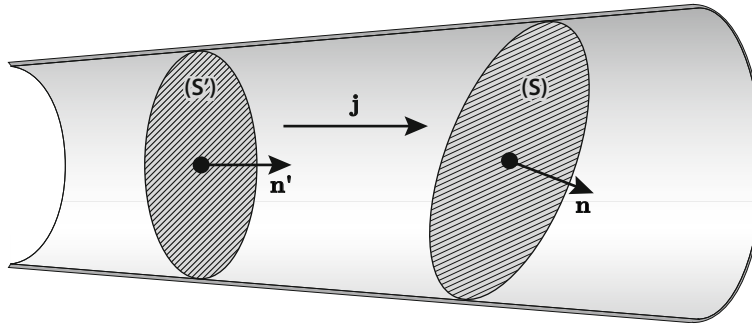

Figure 4.3 - Diagram of a conductor volume with a current flowing through it

Note that in the particular case of unidirectional geometry, the current density vector is the same at all points inside an electrochemical chain:

$$\operatorname{div}\mathbf{j} = \frac{\partial j}{\partial x} = 0 \quad \Rightarrow \quad \mathbf{j} = \text{Cst}$$

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[11] This question is addressed in section 3.1.1.1: the order of magnitude of the time needed for electroneutrality to be established in an electrolyte is one nanosecond.

[12] $\oiint \mathbf{j}.\mathbf{n}\,dS = \iiint \operatorname{div}\mathbf{j}\,dV$

Therefore, because electroneutrality prevails throughout the conducting material's volume, the current can be clearly defined (except for the sign) since it is the same in all sections. This particular property relating to the current in a conducting medium can be extended to an electrochemical cell:

$$I = \iint_{(S)} \mathbf{j} \,.\, \mathbf{n} \, \mathrm{d}S = \iint_{(S')} \mathbf{j'} \,.\, \mathbf{n'} \, \mathrm{d}S$$

Remember that the current sign depends on the orientation of the normal to the interface. The common convention used by electrochemists involves orientating the normal from the metal towards the electrolyte. This implies that the current is positive at the interface with an anode and negative at a cathode interface [13].

4.1.3 - INTERFACIAL MASS BALANCE

4.1.3.1 - GENERAL CASE

In order to write the mass balance for the species i at the interface level, one needs to consider a small volume with a very low width of $2\,\delta x$, which includes the interfacial zone. This volume's limiting surfaces are respectively situated in the two extreme phases, denoted by α and β in figure 4.4 which illustrates a system with unidirectional geometry.

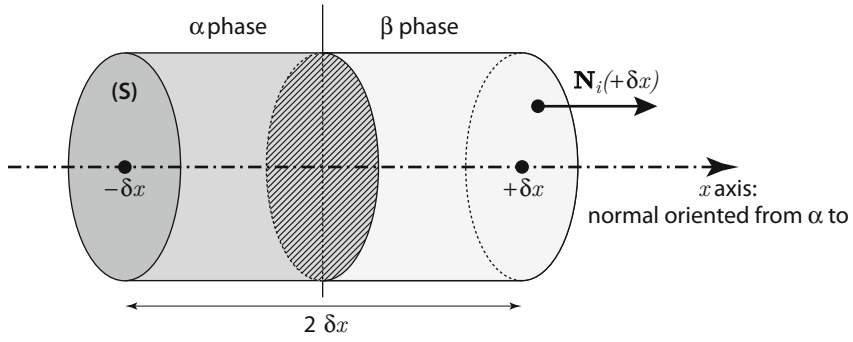

Figure 4.4 - Diagram of an interface with a molar flux flowing through in unidirectional geometry

$N_{n,i}$ is the component of the molar flux density of species i in the direction normal to the surface at the point being studied. Therefore, $N_{n,i} = \mathbf{N}_i \times \mathbf{n}$. $N_{n,i}$ is a scalar quantity. By convention, the normal is oriented from phase α to phase β [14]. We will use w_{S_i} to symbolize the algebraic production rate of species i per unit area. This species is produced or consumed locally by heterogeneous chemical reactions occurring in the interfacial zone. Γ_i is the surface concentration of species i, in mol m^{-2} [15], namely the

[13] *This sign convention, illustrated in figures 1.5 and 1.7, is described in more detail in section 1.4.1.3.*

[14] *The opposite convention could also be chosen but the signs of the ensuing expressions would then be different.*

[15] *This notion is complex and a more detailed presentation would need to go beyond the scope of this document. In particular, in order to describe the thermodynamics of interfaces one would need to refer to the notion of surface excess as defined by the GIBBS model. We can still say that Γ_i is the integral of the volume concentration over a distance equal to the thickness of the interfacial zone*

amount of substance per unit surface in a small volume with a width of 2 δx defining the interfacial zone.

In unidirectional geometry, the variation $\mathrm{d}n_i$ of the amount of species i in the volume 2 $S\,\delta x$ between t and t + dt can be expressed as:

variation	=	in	−	out	+	local production
$\mathrm{d}n_i$	=	$N_{n,i}(-\delta x)\,S\,\mathrm{d}t$	−	$N_{n,i}(+\delta x)\,S\,\mathrm{d}t$	+	$w_{S_i}\,S\,\mathrm{d}t$
	=	$\mathrm{d}\Gamma_i\,S$				

One therefore has: $$N_{n,i_\beta}(+\delta x) - N_{n,i_\alpha}(-\delta x) = -\frac{\mathrm{d}\Gamma_i}{\mathrm{d}t} + w_{S_i}$$

The following equation applies to unidirectional geometry when the thickness tends towards zero:

$$(N_{n,i})_{\langle\langle x=0\rangle\rangle_\beta} - (N_{n,i})_{\langle\langle x=0\rangle\rangle_\alpha} = -\frac{\mathrm{d}\Gamma_i}{\mathrm{d}t} + w_{S_i}$$

Generalising the equation to cover all geometric configurations gives the following[16]:

$$(N_{n,i})_{interface_\beta} - (N_{n,i})_{interface_\alpha} = -\frac{\partial\Gamma_i}{\partial t} + w_{S_i}$$

with : Γ_i the surface concentration of species i [mol m^{-2}]
$N_{n,i}$ the normal component of the molar flux density of species i [mol m^{-2} s^{-1}]
w_{S_i} the production rate of species i per unit area (algebraic) [mol m^{-2} s^{-1}]

Keep in mind that the signs indicated above take into account the precise definition of the orientation of the normal to the interface, namely from phase α to phase β.

The notation "$x = 0$" is meant to emphasise that it is not a mathematical notation corresponding to a surface. It refers to an interfacial zone. In particular, the passage to the limit corresponds to a very small but non-zero value for δx. However, in order to simplify the equations throughout the rest of the document we will simply write $x = 0$ for the quantities related to the interface in unidirectional geometry. Similarly, again to simplify the equations in what follows, we will no longer indicate the index n as a reminder that equations are written for the normal components of flux and current densities.

As in the case of homogeneous reactions in volume mass balances there is a link between the production rate per unit area and the heterogeneous reaction rates:

$$w_{S_i} = \sum_{\text{reactions}} \nu_{i_r}\, v_{S_r}$$

where ν_{i_r} is the algebraic stoichiometric number of species i in reaction r.

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along the normal to the surface. Based on this definition, the value of Γ_i depends on the choice of δx. However it can be shown that its time variation, which is the important quantity relating to equations which is outlined in this document, does not depend on δx.

[16] In particular, when the geometry is not unidirectional, the surface concentration Γ_i is not necessarily identical at all points on the surface and becomes a function of several variables (time and space). The term needed in the interfacial mass balance is therefore a partial derivative: $\partial\Gamma_i/\partial t$, instead of $\mathrm{d}\Gamma_i/\mathrm{d}t$ in unidirectional geometry.

The interfacial mass balances can be illustrated for instance by a system with a phase transfer reaction between an aqueous solution containing potassium chloride and a solution containing crown-ether (ligand L) in an organic solvent (figure 4.5).

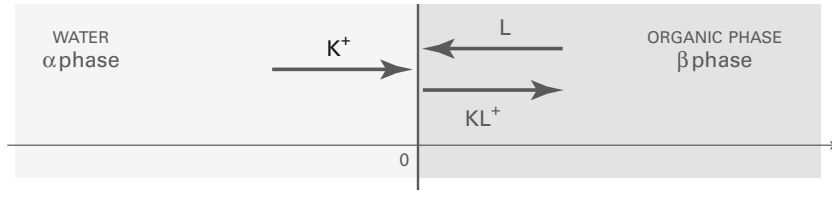

Figure 4.5 - Diagram of a phase transfer reaction

Here we have chosen to orient the x-axis in the direction from the water phase towards the organic solvent (phase α : water and phase β : organic phase). Let v_S be the rate of the following surface reaction:

$$L + K^+ \longrightarrow KL^+$$

At steady state, the variation in the surface concentration is zero and the local mass balance at the interface is expressed as follows:

$$(N_i)_{x=0_\beta} - (N_i)_{x=0_\alpha} = w_{S_i}$$

Taking into account that K^+ ions are not mobile in phase β, whereas the L and KL^+ species are not mobile in phase α, we can write the following:

$$(N_L)_{x=0_\beta} - \cancel{(N_L)_{x=0_\alpha}} = w_{S_L} = -v_S$$

$$(N_{KL^+})_{x=0_\beta} - \cancel{(N_{KL^+})_{x=0_\alpha}} = w_{S_{KL^+}} = v_S$$

$$\cancel{(N_{K^+})_{x=0_\beta}} - (N_{K^+})_{x=0_\alpha} = w_{S_{K^+}} = -v_S$$

hence $$(N_{KL^+})_{x=0_\beta} = (N_{K^+})_{x=0_\alpha} = -(N_L)_{x=0_\beta} = v_S$$

This correlates with the directions for the molar flux densities as those indicated in figure 4.5: N_{K+} and N_{KL+} have the same positive direction whereas N_L has the opposite direction.

4.1.3.2 - ADSORBED SPECIES

The same reasoning can be applied to a species adsorbed at the interface. This type of species is not mobile in either of the two phases (the adsorbed species may possibly be mobile along the interface). The fluxes normal to the surfaces are therefore zero, which in turn simplifies the general equation outlined above. The local interfacial mass balance for a species i adsorbed at the interface is:

$$\frac{\partial \Gamma_i}{\partial t} = w_{S_i}$$

In particular, at steady state the production rate of an adsorbed species is zero since its surface concentration is time-independent.

4.1.3.3 - ELECTROCHEMICAL INTERFACES

This section is restricted on describing the electrochemical interfaces between a metal and an electrolyte. Remember that there are no free mobile electrons in an electrolyte

and no mobile ions in a metal. Respecting the sign conventions commonly shared by electrochemists[17], the normal to the interface is oriented towards the medium containing mobile ions, namely from the metal to the electrolyte (figure 4.6):

Figure 4.6 - Diagram of an electrochemical interface

The following equation applies to a species i which is mobile in the electrolyte:

$$(N_i)_{\text{interface}} = -\frac{\partial \Gamma_i}{\partial t} + w_{S_i}$$

Note that this algebraic equation is only valid for a species that is mobile in the electrolyte and if the normal to the interface is oriented from the metal to the electrolyte.

The equation reveals two terms, and therefore any molar flux can be formally divided into the sum of two terms:

- a term called faradic (current, flux)[18]

$$(N_i^{\text{farad}})_{\text{interface}} = w_{S_i}$$

- a term called capacitive[[19] (or pseudo-capacitive for a neutral species)

$$(N_i^{\text{capac}})_{\text{interface}} = -\frac{\partial \Gamma_i}{\partial t}$$

At a reactive electrochemical interface, charge movements simultaneously bring into play a reorganisation of the double layer alongside the heterogeneous redox reaction itself. In simple cases, for example where no specific adsorption occurs[20] and when a supporting electrolyte is present, this step of formally splitting the molar flux densities or current densities into a faradic term and a capacitive term has a physical meaning. In fact, the two phenomena then correspond to different ion movements:

- the local mass balance for the ions of the supporting electrolyte is:

$$(N_i)_{\text{interface}} = -\frac{\partial \Gamma_i}{\partial t}$$

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[17] Stating that the current at the anode is positive involves orientating the normal to the interface from the metal to the electrolyte, as outlined in section 1.4.1.3.

[18] The reason why this term is chosen is because the corresponding molar flux correlates with the FARADAY law, which is outlined in its integrated form in section 2.2.2.2, and demonstrated in section 4.1.4.

[19] This term is chosen because most of the time the corresponding molar flux is related to movements which are required for the reorganisation of the double layer, which has a structure similar to that of a capacitor.

[20] See section 2.2.1.2 for a brief presentation of adsorption phenomena. A distinction is made between accumulation (linked, for example, to the double layer reorganisation) and specific adsorption when a bond to the interface is involved.

The fraction of the current resulting from the movements of the supporting electrolyte ions is therefore exclusively capacitive;

- the local mass balance for electroactive ions is:

$$(N_i)_{\text{interface}} = w_{S_i}$$

The fraction of the current resulting from the electroactive ions is therefore exclusively faradic, namely produced by the interfacial redox reaction.

4.1.4 - A DEMONSTRATION OF FARADAY'S LAW

FARADAY's law, which has already been applied in this work in its integrated form (see section 2.2.2.2), can be demonstrated based on the interfacial mass balances.

In simple cases where there are no specifically adsorbed species at the electrochemical interface, the various flux densities of the electroactive species at this interface are all proportional to each other. This link looks like a mass balance taking into account the stoichiometric numbers as in any chemical reaction. Therefore, the amount of charge flowing through the system, for instance *via* the current density, can then be linked to the mass balance.

For example, let us look at a unidirectional electrochemical system with an interfacial oxidation reaction involving species that are mobile in the electrolyte. When the metal is chosen as phase α and the electrolyte as phase β, the reaction at the interface is written as follows:

$$\underset{\beta}{|\nu_{\text{Red}}|\,\text{Red}} \longrightarrow \underset{\beta}{|\nu_{\text{Ox}}|\,\text{Ox}} + \underset{\alpha}{|\nu_{\text{e}}|\,\text{e}^-}$$

Remember that in the laws of physical chemistry, stoichiometric numbers are algebraic coefficients. The general equation that is obtained as a result can equally be applied to a half-reaction occurring either in the direction of oxidation ($\nu_{\text{e}} = +n$) or reduction ($\nu_{\text{e}} = -n$) [21] provided that the reaction rate is also taken in algebraic terms following the direction of the redox reaction.

As for mobile species in the electrolyte (phase β) and for electrons in the metal (phase α), the local mass balance relating to the faradic part can be written as follows:

$$(N_i^{\text{farad}})_{\text{interface}_\beta} - \cancel{(N_i^{\text{farad}})_{\text{interface}_\alpha}} = + w_{S_i}$$

$$\cancel{(N_{\text{e}}^{\text{farad}})_{\text{interface}_\beta}} - (N_{\text{e}}^{\text{farad}})_{\text{interface}_\alpha} = + w_{S_{\text{e}}}$$

The production rates (denoted by w_{S_i} and $w_{S_{\text{e}}}$) are linked to the rate of the redox reaction (denoted by v_S):

$$w_{S_i} = \nu_i \; v_S$$

$$w_{S_{\text{e}}} = \nu_{\text{e}} \; v_S$$

---

[21] n is the (positive) number of electrons exchanged in the redox half-reaction in question (see section 2.1.2.1).

Finally one obtains:

$$(N_i^{\text{farad}})_{\text{interface}} = \nu_i \; v_S$$

$$(N_{\text{e}}^{\text{farad}})_{\text{interface}} = -\nu_{\text{e}} \; v_S$$

As for any mobile species in the electrolyte which are involved in the overall redox half-reaction, the following reaction emerges:

$$\frac{1}{\nu_i}(N_i^{\text{farad}})_{\text{interface}} = -\frac{1}{\nu_{\text{e}}}(N_{\text{e}}^{\text{farad}})_{\text{interface}}$$

The only mobile species in the metal is the electron, hence one has:

$$\mathbf{j} = \mathbf{j}_{\text{e}} = -\mathscr{F}\,\mathbf{N}_{\text{e}}$$

When a species i is mobile in the electrolyte, then FARADAY's law can be seen presented in the following equations:

$$j^{farad} = \mathscr{F}\frac{\nu_e}{\nu_i}(N_i^{farad})_{interface} \quad \textit{or} \quad (N_i^{farad})_{interface} = \frac{\nu_i}{\nu_e\,\mathscr{F}}\,j^{farad}$$

with:

j^{farad}	the faradic current density modulus	[A m^{-2}]
$\mathscr{F}$	the FARADAY constant	[C mol^{-1}]
ν_i	the algebraic stoichiometric number of species i	
$(N_i^{\text{farad}})_{\text{interface}}$	the molar faradic flux density at the interface	[mol m^{-2} s^{-1}]

Remember that this equation stands in algebraic terms as long as the sign convention chosen is fully respected. The interfacial mass balance is written with the normal oriented from the metal to the electrolyte. As already outlined, this boils down to considering the currents through the anode to be positive and those through the cathode to be negative. Moreover, this equation only applies to species i that are mobile in the electrolyte.

It is easy to build the integrated version of FARADAY's law (presented in section 2.2.2.2) simply by introducing the definition of the molar flux density:

$$N_i^{\text{farad}} = \frac{1}{S}\frac{\mathrm{d}n_i}{\mathrm{d}t}$$

One then has:

$$\mathrm{d}n_i^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathscr{F}}\,j^{\text{farad}}\,S\,\mathrm{d}t$$

FARADAY's law can be found again in its integrated form by making up the integral between time t and time $t+\Delta t$:

$$\Delta n_i^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathscr{F}}\,Q^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathscr{F}}\int_t^{t+\Delta t} I^{\text{farad}}(t)\,\mathrm{d}t$$

The diagram in figure 4.7 shows a ferric ion being reduced at the platinum electrode interface, in a system with unidirectional geometry. The aqueous solution contains Fe^{2+}, Fe^{3+}, K^+ and NO_3^- ions (KNO_3 being the supporting electrolyte).

FARADAY's law is presented in the following terms:

$$j^{\text{farad}} = \mathscr{F}(N_{\text{Fe}^{3+}}^{\text{farad}})_{x=0} = -\mathscr{F}(N_{\text{Fe}^{2+}}^{\text{farad}})_{x=0}$$

This result can be reached through two different methods, one expressing the current density in the metal (as above), the other one in the electrolyte. The first one is faster but the second one makes it easier for one to understand all of these equations. One can also note that this mathematical development illustrates the qualitative link which can be inferred from figure 4.7: the molar flux densities of the two electroactive species have opposite directions.

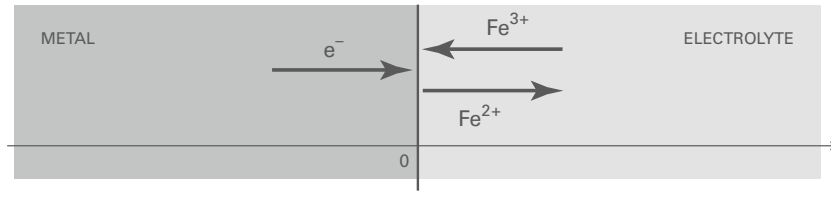


Figure 4.7 - Diagram of an interface with reduction reaction

Let us consider below the half-reaction with its actual direction of advancement (in this case reduction), with its rate denoted by v_S:

$$e^- + Fe^{3+} \longrightarrow Fe^{2+}$$

Remember that the reduction direction is chosen, therefore the following values emerge:

$$\nu_{Fe^{2+}} = +1 \quad \nu_{Fe^{3+}} = -1 \quad \nu_e = -n = -1$$

The following results are given by the interfacial mass balance for each species in the system (applying the same reasoning as previously in this section):

$$(N^{\text{farad}}_{Fe^{3+}})_{x=0} = -(N^{\text{farad}}_{Fe^{2+}})_{x=0} = -v_S$$
$$(N^{\text{farad}}_{e})_{x=0} = v_S$$
$$(N^{\text{farad}}_{NO_3^-})_{x=0} = (N^{\text{farad}}_{K^+})_{x=0} = 0$$

By definition, the overall faradic current density at any point in space is:

$$\mathbf{j} = \sum_i \mathbf{j}_i = \sum_i z_i \mathcal{F} \mathbf{N}_i$$

- when applied to the metal where only electrons are mobile, the following equation emerges:

$$j^{\text{farad}} = -\mathcal{F}(N^{\text{farad}}_{e})_{x=0} = -\mathcal{F} v_S$$

- when applied to the electrolyte where all the ions must be taken into account, this equation emerges:

$$j^{\text{farad}} = \mathcal{F}\left(3N^{\text{farad}}_{Fe^{3+}} + 2N^{\text{farad}}_{Fe^{2+}} + N^{\text{farad}}_{K^+} - N^{\text{farad}}_{NO_3^-}\right)_{x=0}$$
$$= \mathcal{F}(-3v_S + 2v_S + 0 - 0) = -\mathcal{F} v_S$$

FARADAY's law is obtained in both cases in the following way:

$$j^{\text{farad}} = -\mathcal{F} v_S = \mathcal{F}(N^{\text{farad}}_{Fe^{3+}})_{x=0} = -\mathcal{F}(N^{\text{farad}}_{Fe^{2+}})_{x=0}$$

If several reactions occur at an interface, the same type of reasoning demonstrates that faradic currents are additive.

Take the same example as above, but this time with a non-deaerated solution. Two simultaneous reduction reactions occur: for Fe^{3+} ions and for dissolved dioxygen:

$$e^- + Fe^{3+} \longrightarrow Fe^{2+} \qquad v_{S_1}$$
$$4e^- + 2H_2O + O_2 \longrightarrow 4OH^- \qquad v_{S_2}$$

The interfacial mass balance for each of the system's charged species gives the following results (applying the same reasoning as previously in this section):

$$(N^{\text{farad}}_{Fe^{3+}})_{x=0} = -\,(N^{\text{farad}}_{Fe^{2+}})_{x=0} = -\,v_{S_1}$$

$$(N^{\text{farad}}_{OH^-})_{x=0} = 4\,v_{S_2}$$

$$(N^{\text{farad}}_{e})_{x=0} = v_{S_1} + 4\,v_{S_2}$$

$$(N^{\text{farad}}_{NO_3^-})_{x=0} = (N^{\text{farad}}_{K^+})_{x=0} = 0$$

For the first half-reaction you can write:

$$j_1^{\text{farad}} = \mathcal{F}(N^{\text{farad}}_{Fe^{3+}})_{x=0} = -\,\mathcal{F}(N^{\text{farad}}_{Fe^{2+}})_{x=0}$$

If the second half-reaction occurred alone, you would have:

$$j_2^{\text{farad}} = -\,\mathcal{F}(N^{\text{farad}}_{OH^-})_{x=0}$$

Therefore, when both half-reactions occur simultaneously, you end up with:

$$j^{\text{farad}} = -\,\mathcal{F}(N^{\text{farad}}_{e})_{x=0} = -\,\mathcal{F}(N^{\text{farad}}_{Fe^{2+}})_{x=0} - \mathcal{F}(N^{\text{farad}}_{OH^-})_{x=0}$$

namely:

$$j^{\text{farad}} = j_1^{\text{farad}} + j_2^{\text{farad}}$$

If one aims to establish the mass balance in a macroscopic volume of electrolyte in an electrochemical system, then one must take into account all the factors behind the variations. FARADAY's law only deals with variations due to an electrochemical reaction, as shown in the first example. Yet other examples can present more complicated scenarios:

- throughout the whole electrolyte volume, the balance of the anodic and cathodic reactions must be taken into account;
- when the electrolyte is circulating, as in many cases in industry, there also occurs a variation in the amount of substance, which is due to the forced convection.

4.2 - CURRENT FLOW IN A MONOPHASIC CONDUCTOR

The shape of the current-potential curves and, more generally speaking, the relationships (I, U, t) in an electrochemical system involve the kinetics of both the interfacial phenomena (in particular, charge transfers at reactive interfaces) and the mass transport inside the conducting volumes.

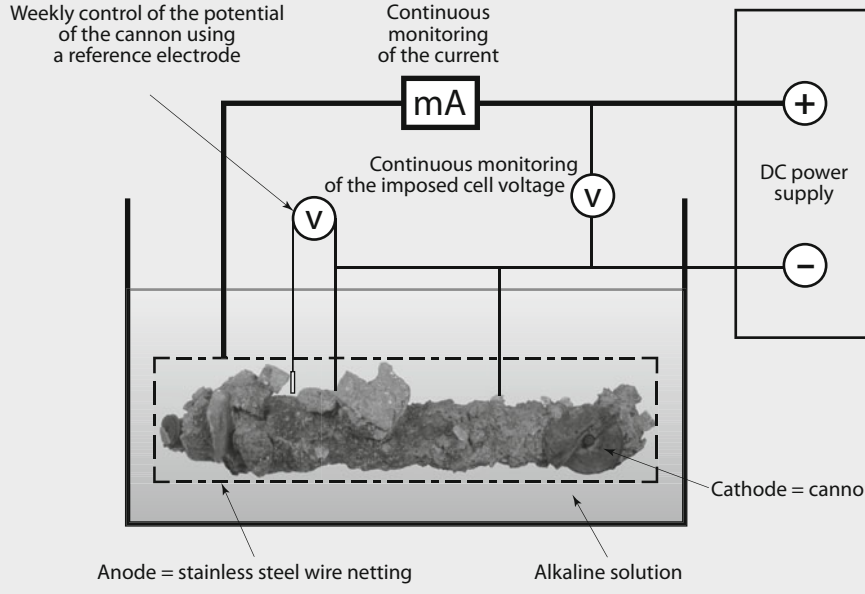
The latter phenomenon will be described first, in the context of a current flowing through the conducting media, before returning to phenomena linked to the current flowing through the interfaces [22]. Therefore, in this section we intend firstly to describe in more details the mass transport phenomena in the particular case of charged species.

[22] Section 4.3 deals with this particular aspect found in phenomena related to current flow.

CONSERVATION OF ARCHAEOLOGICAL ARTEFACTS

Document written with the kind collaboration of E. GUILMINOT, research engineer at the Arc'Antique Laboratory in Nantes, France

Given the long periods that iron or copper artefacts remain buried under the earth or sea, it is inevitable that over time they should alter state due to the build-up of corrosion. In most cases, the corrosion process goes through chloride-containing phases. Following an archaeological excavation, these artefacts, which are known as 'active' undergo a process whereby the corrosion is reactivated, and accelerated, causing the irreversible loss of the original surface detail where the history of the artefact is engraved (inscriptions, adornments, but also deterioration marks). In the case of ferrous artefacts, damage may be more serious and lead to the partial or entire loss of the object itself. Therefore as soon as these artefacts arrive in the preservation and restoration workshops, they undergo immediate stabilizing treatment.



The principle of the stabilizing treatment of a metallic artefact (cannon) by electrolysis
(from a diagram kindly provided by E. GUILMINOT - Laboratoire Arc'Antique)

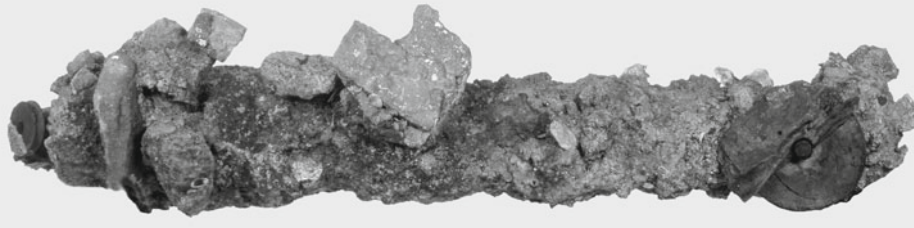
As a rule, when the iron artefacts emerge from long periods in sea water, they are covered with concretions or gangue (a mixture of calcite, quartz and marine organisms) which hide their original surface. The first step in treatment is to remove these concretions, which can be done using electrochemistry.

The artefact is therefore submitted to a cathodic polarisation whereby it is encased in an anodically polarised stainless steel cage, which is built to mould its shape. The cathodic potential must be carefully monitored because if the resulting hydrogen bubbling effect is too strong, it may cause cracks in the artefact. This soft cathodic treatment is meant to embrittle the gangue and thus make its removal significantly easier.

The second goal of this electrochemical treatment is to extract the chloride ions from the artefact towards the electrolyte. This removal process is an essential step to prevent the artefact from rapidly corroding again when re-exposed to air. The chloride concentration in the electrolyte is measured periodically during the operation. The electrolytic treatment process is considered complete once the chloride concentration of the electrolyte has reached sufficiently low levels.

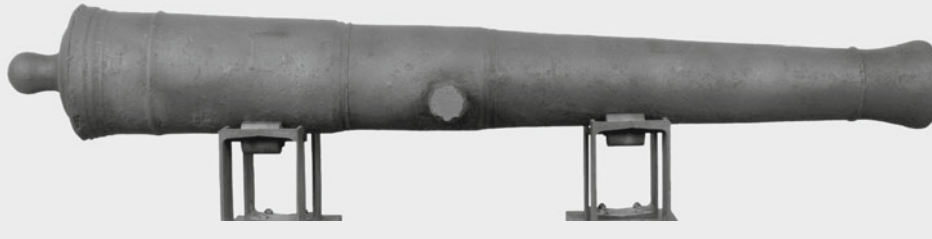
When artefacts emerge from marine environments, the quantity of chlorides that need to be extracted can be very high: it can reach up to several kilograms of chlorides for one ton of cast iron. The baths must be regularly renewed as soon as the solution becomes saturated with chlorides.

The question of how long the treatment should last depends on the quality and origin of the artefact. If you take large size artefacts emerging from submarine environments, the average duration is from 6 months to one year for cuprous substances, 1.5 to 2 years for wrought iron and 2 to 3 years for cast iron. However, in order to stabilize certain highly damaged cast iron cannons, over 5 years of treatment are required.



State before treatment *(photo J.G. AUBERT - Laboratoire Arc'Antique)*

The benefit of electrolysis treatment is that the artefact can be cleaned in a uniform fashion, without seeing its original surface harmed. It can ' let the artefact tell its own tale ' by revealing surface inscriptions such as the maker's name or stamp, which is the primary element used for authenticating and identifying artefacts.



Post-treatment state *(photo J.G. AUBERT - Laboratoire Arc'Antique).*
Cannon surfaced from the wreck of the ALCIDE dating from the beginning of the eighteenth century, exhibited in the town of Carantec in France

4.2.1 - CONDUCTION PHENOMENA: A MACROSCOPIC APPROACH

4.2.1.1 - DIFFERENT DRIVING FORCES FOR TRANSPORT

Here let us return to the classification for the various driving forces behind mass transport:

- migration relates to charged species moving under the influence of an electric field;
- diffusion relates to neutral or charged species moving under the influence of a chemical potential gradient. For example, if two solutions, in the same solvent and containing a neutral species with two different concentrations, are put in contact with each other then the system tends towards an equilibrium state: it forms a homogeneous solution with an intermediate concentration. Before reaching this equilibrium state, the system passes through various non-equilibrium states, where species can be seen to move spontaneously from the more concentrated solution to the less concentrated one. Unlike the phenomenon of migration, diffusion operates with both neutral and charged species.

  Although diffusion is mostly associated with a concentration gradient, it should be noted that this phenomenon is in fact created by a chemical potential gradient. These two gradients are not identical: one can have an activity gradient without a concentration gradient. For instance, this is the case when two solutions containing the same solute in the same solvent are put in contact, whereby the solute is the only electrolyte on one side, and it is mixed with a supporting electrolyte on the other side. Initially, there is a gradient of ionic strength which results in a gradient of activity, although no concentration gradient exists.

  Both of these preceding phenomena can be grouped together using the concept of electrochemical potential:

$$\widetilde{\mu}_i = \mu_i + z_i \mathcal{F} \varphi$$

  The electrochemical potential gradient is therefore the driving force for both diffusion and migration, which are generally coupled together;
- convection relates to the overall movement of a medium when it is fluid. It can occur naturally, for instance when influenced by gravitational forces (density gradients) or uncontrolled vibrations. This natural convection, which is particularly pronounced in the case of large systems, can also be the root cause of many observations made during experiments with smaller devices, such as in analytical chemistry. In addition, in numerous experiments one uses an external device to maintain the fluid in a forced convection movement (for example with a rotating disc electrode, RDE). There is no convection in solid-state materials.

The fact of there being a temperature gradient may bring about indirect consequences on mass transport phenomena. First of all, it generally creates a chemical potential gradient and therefore gives rise to diffusion phenomena. It also entails a density gradient in the medium and consequently a natural convection movement. Moreover, one can observe a coupling of the thermal flux and the molar fluxes (see the thermodynamics of linear irreversible processes in the next section). This is what happens with the SORET effect, also called thermal diffusion, which is when mass transport is seen to occur following a temperature gradient, yet without any concentration gradient.

4.2.1.2 - THERMODYNAMICS OF LINEAR IRREVERSIBLE PROCESSES

By definition, from a thermodynamic point of view, mass transport phenomena (and especially charge transport) are irreversible processes. Here, a linear relationship can be envisaged between flux and force, yet this linearity is called into question if ever the forces applied are too strong. For instance, when mass transport occurs *via* migration, one can see a deviation from the linear behaviour when the electric field applied is either very intense [23] or when it has a very high frequency [24].

When there are several different fluxes and forces brought into play in a system, then the thermodynamics of linear irreversible processes postulates that there is a matrix relationship between the different fluxes and forces (with a symmetrical matrix: ONSAGER relations). The non-zero non-diagonal terms in the matrix signify that a coupling of the phenomena is taking place.

In the case studied here, the fluxes and forces that need to be taken into account are vector quantities, and the molar fluxes in question are relative to the mean motion of the medium. The molar flux densities of each type of species (including the solvent if applicable), $\mathbf{N}_i^{\text{rel}}$, and the heat flux density, $\mathbf{N}_T$, are created out of the gradients of electrochemical potential, $\widetilde{\mu}_i$, for each type of species, and the temperature gradient. For general cases the following equations are written:

$$\mathbf{N}_i^{\text{rel}} = -\sum_k L_{ik}\ \mathbf{grad}\,\widetilde{\mu}_k - L_{iT}\ \mathbf{grad}\,T$$

$$\mathbf{N}_T = -\sum_k L_{Tk}\ \mathbf{grad}\,\widetilde{\mu}_k - L_{TT}\ \mathbf{grad}\,T$$

As of now, the description will be confined to systems with no temperature gradient, and containing only diagonal terms in the equations:

$$\mathbf{N}_i^{\text{rel}} = -L_{ii}\ \mathbf{grad}\,\widetilde{\mu}_i$$

It should be noted that although this form for writing the equations may appear simple, since each flux density is directly proportional to a single force, it nonetheless covers implicit couplings in so far as there are migration terms (which involve the same electric field) and as electroneutrality applies. As for this notion of electroneutrality, if it is introduced into ONSAGER relations (resulting in coupling the concentrations) then all the previous equations can be rewritten to remove the potential. As a result, the electrochemical potentials of ions are replaced by terms which are based on the chemical potential of electrolytes. The latter can be measured in an experiment, unlike electrochemical potentials which are essentially theoretical concepts, which are highly useful from an educational point of view.

The example given below illustrates the coupling between the molar flux densities by means of electroneutrality. It is outlined here, although the mathematical equations that one would need to firstly understand the various components of the molar flux density will be addressed only in the next two

[23] For an electrolytic solution this phenomenon is known as the WIEN effect.

[24] This phenomenon is known as the FALKENHAGEN effect.

paragraphs (see sections 4.2.1.3 and 4). Here we are focusing on the current flow in a unidirectional system withaqueous solution containing a 1-1 electrolyte, such as a solution of hydrogen chloride. Convection is being disregarded in this example, and solely the diffusion and migration of the different species are taken into account.

Since there are only two types of ions present, the electroneutrality in the medium means that the concentrations in the cation (H^+) and the anion (Cl^-) are equal at any point in the electrolyte volume. A concentration profile can exist, but it must be the same for both ions. Let us consider that C symbolizes this unique concentration. The molar flux densities of both types of ions are given in the following simplified form (see section 4.2.1.4):

$$\begin{cases} N_+ = -D_+ \dfrac{\partial C}{\partial x} - u_+ C \dfrac{\partial \varphi}{\partial x} \\ N_- = -D_- \dfrac{\partial C}{\partial x} + u_- C \dfrac{\partial \varphi}{\partial x} \end{cases}$$

Here, D_+ and D_-, the respective diffusion coefficients of H^+ and Cl^-, as well as u_+ and u_- their electric mobility values (see definition in section 4.2.1.4), are considered as being independent of the concentration and therefore of x. As a consequence, they are considered as constants in the equations. If we consider the volume mass balance of these species [25], then two different equations emerge to define the concentration variations with time:

$$\begin{cases} \dfrac{\partial C}{\partial t} = -\dfrac{\partial N_+}{\partial x} = D_+ \dfrac{\partial^2 C}{\partial x^2} + u_+ \dfrac{\partial}{\partial x}\left(C \dfrac{\partial \varphi}{\partial x} \right) \\ \dfrac{\partial C}{\partial t} = -\dfrac{\partial N_-}{\partial x} = D_- \dfrac{\partial^2 C}{\partial x^2} - u_- \dfrac{\partial}{\partial x}\left(C \dfrac{\partial \varphi}{\partial x} \right) \end{cases}$$

The migration term, once extracted from the first equation, then replaced in the second equation, is therefore removed to obtain the following simple equation:

$$\frac{\partial C}{\partial t} = \frac{u_- D_+ + u_+ D_-}{u_- + u_+} \frac{\partial^2 C}{\partial x^2} = D_\pm \frac{\partial^2 C}{\partial x^2}$$

The concentration field looks like it applies to a pure diffusion phenomenon (without migration) for a species (here HCl) with a mean diffusion coefficient, $D_\pm$.

However, strictly speaking it is not identical to the diffusion of a neutral molecule because in the H^+ and Cl^- case, an electric potential field is created in relation to the concentration profile.

The following equation shows the link that can be found between both fields at any time:

$$\frac{\partial}{\partial x}\left(C \frac{\partial \varphi}{\partial x} \right) = -\frac{D_+ - D_-}{u_- + u_+} \frac{\partial^2 C}{\partial x^2}$$

As explained later, if one wishes to fully describe the system in even greater detail, then one would need to include the boundary conditions [26].

[25] The volume mass balances are described in section 4.1.2. The system in question here has a unidirectional geometry and no chemical reaction in its volume.

[26] The fluxes at the electrochemical interfaces must be written. Various examples are given in section 4.3. In addition, an example similar to that described here, with a 1-1 electrolyte and no supporting electrolyte, is described in thorough detail in appendix A.4.1. The steady-state potential profile in the electrolyte is presented, and there is a section specifically addressing the question of whether electroneutrality applies or not.

4.2.1.3 - LINK BETWEEN MIGRATION AND DIFFUSION

In the previous description using electrochemical potentials, it is assumed that movements by migration and diffusion have identical mechanisms at the microscopic level. This hypothesis may lead to errors if ever the charge carriers are not sufficiently well identified, which is especially the case when large quantities of neutral ion pairs are involved. In fact, in this instance, the ion pairs play a part in the diffusion without contributing to migration.

The equation which presents molar flux densities as a function of the electrochemical potential implies that the proportionality coefficient for the driving forces is identical in the case of both migration and diffusion.

Another way of expressing this relationship between migration and diffusion is to use the concept of electrochemical mobility (or absolute mobility, $\widetilde{u}_i$). This is the modulus of the steady-state relative velocity of the charged species when it is submitted to a unit force per mole. Let us consider a charged species moving by diffusion and migration with a $\boldsymbol{\omega}_i^{\text{rel}}$ velocity relative to the average motion of the fluid which has a $\boldsymbol{\omega}_{\text{medium}}$ velocity. Following the definition for electrochemical mobility, and applying the convention previously used in section 3.1 for the electrochemical potential (i.e., using the molar quantity), one obtains the following equation:

$$\boldsymbol{\omega}_i^{\text{rel}} = - \widetilde{u}_i \ \mathbf{grad}\, \widetilde{\mu}_i$$

The electrochemical mobility unit is therefore mol s kg^{-1} or mol m^2 s^{-1} J^{-1}. Thanks to the link between molar flux density and local velocity described in section 4.1.1.1, one ends up with the same proportionality link between flux and force (thermodynamics of linear irreversible processes) as seen previously:

$$\mathbf{N}_i^{\text{rel}} = - C_i \ \widetilde{u}_i \ \mathbf{grad}\, \widetilde{\mu}_i$$

One can separate the two terms of diffusion and migration by expanding the expression of electrochemical potential:

$$\begin{aligned} \mathbf{N}_i^{\text{rel}} &= - C_i \ \widetilde{u}_i \ \mathbf{grad}\, \mu_i - C_i \ \widetilde{u}_i \ z_i \ \mathcal{F} \ \mathbf{grad}\, \varphi \\ &= - C_i \ \widetilde{u}_i \ \mathrm{R}T \ \mathbf{grad}\, (\ln a_i) + C_i \ \widetilde{u}_i \ z_i \ \mathcal{F} \ \mathbf{E} \end{aligned}$$

As will be discussed later, this equation underlines the interdependence of the coefficients for the migration and diffusion terms. Bear in mind that just because there is a connection made between the proportionality factors in the migration and diffusion components it does not mean that the corresponding molar flux densities are collinear and in the same direction. There is *a priori* no connection between the respective forces (related to the gradients of electric potential or of activity). For example, one may come across cases where the migration and diffusion currents for a species i share the same direction, and other cases where the directions are opposite [27].

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[27] Section 4.3.1.5 gives examples describing various situations. One can even imagine situations where migration and diffusion currents are not collinear.

4.2.1.4 - EXPRESSING MOLAR FLUX AND CURRENT DENSITIES

If convection is involved, the medium moves with a mean velocity denoted by $\boldsymbol{\omega}_{\text{medium}}$ and the relative molar flux density is:

$$\mathbf{N}_i^{\text{rel}} = C_i\,(\boldsymbol{\omega}_i - \boldsymbol{\omega}_{\text{medium}}) = -\,C_i\;\widetilde{u}_i\;\mathbf{grad}\,\widetilde{\mu}_i$$

Writing the definition of current densities gives:

$$\begin{aligned}\mathbf{j}_i &= z_i\;\mathscr{F}\,\mathbf{N}_i = z_i\;\mathscr{F}\,C_i\,\boldsymbol{\omega}_i = z_i\;\mathscr{F}\,(\mathbf{N}_i^{\text{rel}} + C_i\,\boldsymbol{\omega}_{\text{medium}})\\ &= -\,C_i\;z_i\;\mathscr{F}\,\widetilde{u}_i\;\mathrm{R}T\;\mathbf{grad}\,(\ln a_i) + C_i\;\widetilde{u}_i\;z_i^2\;\mathscr{F}^2\,\mathbf{E} + C_i\;z_i\;\mathscr{F}\,\boldsymbol{\omega}_{\text{medium}}\end{aligned}$$

The common expression for current density does not involve electrochemical mobility but rather:

- the molar conductivity for the migration term

$$\lambda_i = z_i^2\;\mathscr{F}^2\,\widetilde{u}_i$$

with the molar conductivity λ_i expressed in S m^2 mol^{-1} (or S cm^2 mol^{-1}).

There are also expressions using the electric mobility, u_i, which is the steady-state relative velocity of a charge species submitted to a unit electric field, namely 1 V m^{-1}. Its SI unit is therefore m^2 s^{-1} V^{-1}. Simple equations can be found linking the electrochemical and electrical mobility, and the molar conductivity of a given species:

$$u_i = |z_i|\;\mathscr{F}\,\widetilde{u}_i \qquad \text{and} \qquad \lambda_i = \mathscr{F}\,|z_i|\;u_i$$

with : u_i the electric mobility [m^2 s^{-1} V^{-1}]
z_i the algebraic charge number of species i
$\mathscr{F}$ the FARADAY constant [C mol^{-1}]
$\widetilde{u}_i$ the electrochemical mobility [mol s kg^{-1} or mol m^2 s^{-1} J^{-1}]
λ_i the molar conductivity of species i [S m^2 mol^{-1}]

- the diffusion coefficient for the diffusion term with

$$D_i = \widetilde{u}_i\;\mathrm{R}T$$

with the diffusion coefficient D_i expressed in m^2 s^{-1} (or cm^2 s^{-1}).

This latter is known as the NERNST-EINSTEIN equation[28]. It can also be written involving the electric mobility:

$$\frac{\boldsymbol{u_i}}{\boldsymbol{D_i}} = |\boldsymbol{z_i}|\;\frac{\mathscr{F}}{\boldsymbol{RT}}$$

The current density of species i is then expressed as follows:

$$\mathbf{j}_i = \underbrace{-\,D_i\;z_i\;\mathscr{F}\,C_i\;\mathbf{grad}\,(\ln a_i)}_{\mathbf{j}_{i\,\text{diffusion}}} + \underbrace{\lambda_i\;C_i\;\mathbf{E}}_{\mathbf{j}_{i\,\text{migration}}} + \underbrace{C_i\;z_i\;\mathscr{F}\,\boldsymbol{\omega}_{\text{medium}}}_{\mathbf{j}_{i\,\text{convection}}}$$

---

[28] Some authors call this the EINSTEIN equation, preferring to save the term 'NERNST-EINSTEIN equation' to describe the link between the molar conductivity at infinite dilution and the diffusion coefficients of an electrolyte $A_{p_+}B_{p_-}$:

$$\Lambda^0 = (p_+\;D_+\;{z_+}^2 + p_-\;D_-\;z_-^2)\,\frac{\mathscr{F}^2}{\mathrm{R}T}$$

with the connection between migration and diffusion (see previous section) also expressed by the following equation:

$$\lambda_i = D_i \; z_i^2 \; \frac{\mathscr{F}^2}{\mathsf{R}T}$$

To sum up,

- in an ideal conducting medium, such as an electrolyte solution at infinite dilution, the activities are assumed as being equal to the concentrations and in addition the molar conductivity at infinite dilution, λ_i^0, and the diffusion coefficient at infinite dilution, D_i^0, can be used. One therefore obtains the following simplified equation for the various components of the current density of species i:

$$\mathbf{j}_i^0 = \underbrace{- \; D_i^0 \; z_i \; \mathscr{F} \; \mathbf{grad} \, C_i}_{\mathbf{j}^0_{i\,\text{diffusion}}} + \underbrace{\lambda_i^0 \; C_i \; \mathbf{E}}_{\mathbf{j}^0_{i\,\text{migration}}} + \underbrace{C_i \; z_i \; \mathscr{F} \; \boldsymbol{\omega}_{\text{medium}}}_{\mathbf{j}^0_{i\,\text{convection}}}$$

with the following equation: $\lambda_i^0 = D_i^0 \; z_i^2 \; \dfrac{\mathscr{F}^2}{\mathsf{R}T}$

Moreover we can equally write the molar flux density as a function of D_i^0, λ_i^0, $\widetilde{u}_i^0$ or u_i^0:

$$\begin{aligned}
\mathbf{N}_i^0 &= - \quad D_i^0 \; \mathbf{grad} \, C_i \quad + \quad z_i \; \frac{\mathscr{F}}{\mathsf{R}T} \, D_i^0 \; C_i \; \mathbf{E} \quad + \quad C_i \; \boldsymbol{\omega}_{\text{medium}} \\
\mathbf{N}_i^0 &= - \quad \frac{\lambda_i^0}{z_i^2} \, \frac{\mathsf{R}T}{\mathscr{F}^2} \, \mathbf{grad} \, C_i \quad + \quad \frac{\lambda_i^0}{z_i \; \mathscr{F}} \; C_i \; \mathbf{E} \quad + \quad C_i \; \boldsymbol{\omega}_{\text{medium}} \\
\mathbf{N}_i^0 &= - \quad \widetilde{u}_i^0 \; \mathsf{R}T \; \mathbf{grad} \, C_i \quad + \quad z_i \; \mathscr{F} \; \widetilde{u}_i^0 \; C_i \; \mathbf{E} \quad + \quad C_i \; \boldsymbol{\omega}_{\text{medium}} \\
\mathbf{N}_i^0 &= - \quad \underbrace{\frac{u_i^0}{|z_i|} \, \frac{\mathsf{R}T}{\mathscr{F}} \, \mathbf{grad} \, C_i}_{\mathbf{N}^0_{i\,\text{diffusion}}} \quad + \quad \underbrace{\frac{z_i}{|z_i|} \, u_i^0 \; C_i \; \mathbf{E}}_{\mathbf{N}^0_{i\,\text{migration}}} \quad + \quad \underbrace{C_i \; \boldsymbol{\omega}_{\text{medium}}}_{\mathbf{N}^0_{i\,\text{convection}}}
\end{aligned}$$

- for any conducting medium, such as a concentrated electrolyte solution, the activity coefficients, γ_i, cannot be ignored. As well as $\widetilde{u}_i$, λ_i and D_i, they depend *a priori* on the concentrations of all the other species, even if there is no coupling between the fluxes of the different species, in terms of the thermodynamics of irreversible processes. Since one rarely has an accurate idea of the link between activity and concentrations, it is difficult to measure the diffusion coefficient in an experiment. In this case, an apparent diffusion coefficient D_i^{app} can then be introduced, which depends on the concentrations of all the other species. By introducing $a_i = \gamma_i \, C_i$ into the general equation for diffusion current density, the following emerges:

$$\mathbf{j}_{i\,\text{diffusion}} = - \; D_i \; z_i \; \mathscr{F} \; C_i \; \mathbf{grad} \, (\ln a_i)$$

hence:

$$\begin{aligned}
\mathbf{j}_{i\,\text{diffusion}} &= - \; z_i \; \mathscr{F} \; C_i \; D_i \; \mathbf{grad} \, (\ln \gamma_i + \ln C_i) \\
&= - \; z_i \; \mathscr{F} \; C_i \; D_i \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i} \right) \mathbf{grad} \, (\ln C_i)
\end{aligned}$$

and finally:
$$\mathbf{j}_{i\,\text{diffusion}} = -\, z_i\, \mathcal{F}\, \underbrace{D_i \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln C_i}\right)}_{D_i^{\text{app}}} \mathbf{grad}\, C_i$$

It should be noted that the apparent diffusion coefficient, D_i^{app}, which depends on the various species concentrations by means of the activity coefficient, does not follow the equation involving λ_i derived from the NERNST-EINSTEIN equation:

$$D_i^{\text{app}}\; {z_i}^2\, \frac{\mathcal{F}^2}{\mathsf{R}T} \neq D_i\; {z_i}^2\, \frac{\mathcal{F}^2}{\mathsf{R}T} = \lambda_i$$

Finally, one ends up with very general equations:

$$\mathbf{N}_i = \underbrace{-\, D_i^{app}\, \mathbf{grad}\, C_i}_{\mathbf{N}_{i\,diffusion}} + \underbrace{\frac{z_i}{|z_i|}\, u_i\, C_i\, \mathbf{E}}_{\mathbf{N}_{i\,migration}} + \underbrace{C_i\, \boldsymbol{\omega}_{medium}}_{\mathbf{N}_{i\,convection}}$$

$$\mathbf{j}_i = \underbrace{-\, z_i\, \mathcal{F}\, D_i^{app}\, \mathbf{grad}\, C_i}_{\mathbf{j}_{i\,diffusion}} + \underbrace{\lambda_i\, C_i\, \mathbf{E}}_{\mathbf{j}_{i\,migration}} + \underbrace{C_i\, z_i\, \mathcal{F}\, \boldsymbol{\omega}_{medium}}_{\mathbf{j}_{i\,convection}}$$

In order to simplify the notations, we will only use the symbol D_i, even if the system in question is not ideal. This is therefore an assimilation of D_i^{app} and D_i. However, we must keep in mind that in general cases these equations commonly comprise the three different types of driving forces for the moving species, yet the proportionality coefficients are not interconnected in any simple way. In addition, in an experiment it is not possible to ascertain the distribution between the migration and diffusion terms for a charged species. Only a hypothesis such as the NERNST-EINSTEIN equation can lead to a quantitative distribution between these two terms [29]. Even if such a hypothesis is made frequently, one must be aware that it does not strictly apply in a non-ideal medium.

4.2.1.5 - GENERAL EQUATIONS IN A MONOPHASIC CONDUCTOR

If one can describe the concentration profiles for all species and the potential profile at any time and at any point, i.e., the functions $C_i(x, y, z, t)$ and $\varphi(x, y, z, t)$, then it is possible to use the above equations to describe the time evolution of the current through a conductor.

Remember that this section is not focused on interfaces but on the volumes of the conducting media. We will not attempt at first to describe the boundary conditions [30]. At this stage the voltage in question is therefore the potential difference across the conductor outside the interfacial zones, in other words, what is usually called the ohmic drop.

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[29] Later in this section we give an example showing how migration and diffusion are distributed with different proportions in the anion and cation fluxes. An additional example is outlined in appendix A.4.1. In both cases the NERNST-EINSTEIN equation is supposed to apply.

[30] Section 4.2.3 addresses this issue.

In most electrochemical systems, except for poor conducting media [31], one can assume that electroneutrality applies on a macroscopic scale in the zone located away from the interfaces. The mathematical description of the system therefore combines the electroneutrality and the various volume mass balances of each species with the equations for the molar flux densities in the framework of the thermodynamics of linear irreversible processes. The result is the following system with $(n+1)$ differential equations for $(n+1)$ unknowns (n concentrations and the potential):

$$\forall i \begin{cases} \dfrac{\partial C_i}{\partial t} = - \text{ div } \mathbf{N}_i + w_i \\ \sum\limits_i z_i \ C_i = 0 \end{cases}$$

with:

$$\forall i \begin{cases} \mathbf{N}_i = - \ D_i \ \textbf{grad}\, C_i - \dfrac{|z_i|}{z_i} u_i \ C_i \ \textbf{grad}\, \varphi + C_i \ \boldsymbol{\omega}_{\text{medium}} \\ w_i = f(C_j) \qquad \text{homogeneous kinetic laws} \end{cases}$$

In order to give a full description of the system and establish the (I, U, t) relationships, one also needs to take into account its geometry, the initial state and the boundary conditions, i.e., the equations at all the boundaries, including the electrochemical interfaces.

In all systems, one of the impacts of electroneutrality in the conducting volumes ($\sum\limits_i z_i C_i = 0$) is that the overall convection current density is always zero, resulting in the following equation:

$$\mathbf{j} = \underbrace{- \mathcal{F} \sum_i z_i \ D_i \ \textbf{grad}\, C_i}_{\mathbf{j}_{\text{diffusion}}} \ \underbrace{- \sum_i \lambda_i \ C_i \ \textbf{grad}\, \varphi}_{\mathbf{j}_{\text{migration}}} + \underbrace{\mathcal{F} \ \boldsymbol{\omega}_{\text{medium}} \cancel{\sum_i z_i C_i}}_{\mathbf{j}_{\text{convection}}}$$

One can also observe that if the diffusion coefficients are considered as sufficiently close to each other, then the overall diffusion current density vanishes as shown below:

if $$\forall i \qquad D_i \approx D$$

then $$\mathbf{j}_{\text{diffusion}} \approx - \mathcal{F} \ D \sum_i z_i \ \textbf{grad}\, C_i \approx - \mathcal{F} \ D \ \textbf{grad} \left(\cancel{\sum_i z_i C_i} \right) = 0$$

hence $$\mathbf{j}_{\text{migration}} \approx \mathbf{j}$$

Although this approximation is often faulty in numerical terms, it is nonetheless used quite frequently in electrochemistry. An example where such an approximation cannot be accepted is discussed in detail below.

To give a particularly important example of these volume equations, take the case where diffusion is the only mass transport mode of a given species at a given point in space,

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[31] Section 3.1.1.1 addresses this aspect. If electroneutrality does not apply, then the corresponding equation must be replaced by a more general equation: one of the MAXWELL equations if there are significant magnetic phenomena involved, or merely the POISSON equation. This may occur in poor conducting media or if the time scale considered is too short for electroneutrality to be restored (this may happen if high local ion depletion occurs in the medium).

and where there is no local volume mass source such as a homogeneous chemical reaction. These conditions are frequently come across in electrochemistry, and indeed they will be addressed in detail in the forthcoming sections (see sections 4.3 and 4.4). The corresponding equation is known as the second FICK law [32], and is written as follows:

$$\frac{\partial C_i}{\partial t} = D_i \, \nabla^2 C_i$$

or in a system with unidirectional geometry:

$$\frac{\partial C_i}{\partial t} = D_i \, \frac{\partial^2 C_i}{\partial x^2}$$

The example given here is rather complex compared to the situations typically described in electrochemistry text books, in particular because there is no supporting electrolyte and the diffusion coefficients are significantly different. However, using an example involving simple calculations can illustrate some of the consequences which emerge as a result of the differences in diffusion coefficients. Sections 4.3 and 4.4 should be read before returning to the details of this calculation.

- ***Presentation of the system studied***

  Let us consider the electrolysis of a deaerated aqueous solution containing highly concentrated hydrogen chloride placed between two platinum electrodes. For the sake of simplicity, we will assume that water oxidation is a slow process, and therefore the only phenomenon to be observed at the anode is the oxidation of chloride to dichorine. Protons are reduced to dihydrogen at the cathode. The faradic yield of both half-reactions is therefore 100%. The electrolysis cell has unidirectional geometry, and thanks to forced convection the composition of the solution remains homogeneous outside the two diffusion layers which are next to the electrodes. In the absence of a supporting electrolyte, mass transport is therefore ensured by migration and diffusion in both diffusion layers, and by migration and convection in the homogeneous zone, as illustrated in figure 4.8.

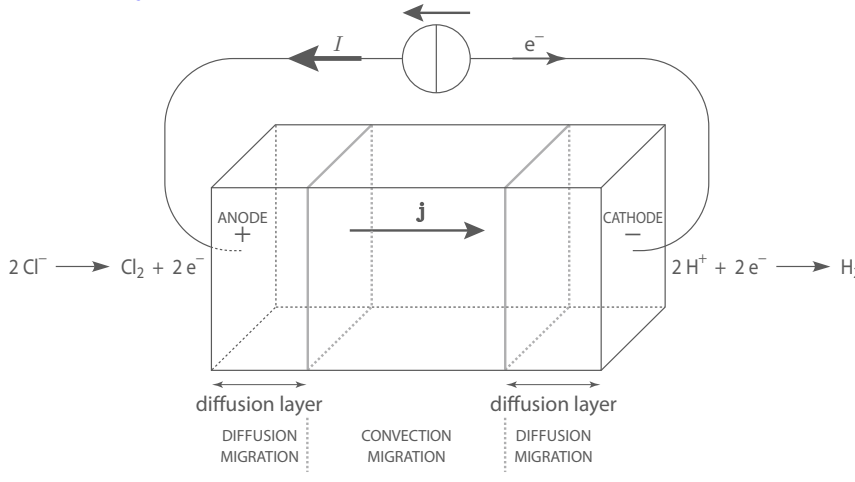

Figure 4.8 - Diagram of an electrolysis cell showing the various mass transport modes involved

[32] The first FICK law corresponds to the following equation for the diffusion molar flux density: $\mathbf{N}_i = - D_i$ **grad** C_i. *The second FICK law is then based on the volume mass balance:*

$$\frac{\partial C_i}{\partial t} = - \, div \, \mathbf{N}_i = D_i \, div \, (\mathbf{grad} \, C_i) = D_i \, \nabla^2 C_i \, .$$

Here it is also assumed that the molar conductivities are equal to their values at infinite dilution (see table 4.2 in section 4.2.2.4) and are independent of the concentrations: $\lambda_+ = \lambda_+^{\,0} = 35.0$ mS m^2 mol^{-1} and $\lambda_- = \lambda^0 = 7.6$ mS m^2 mol^{-1}. It is also assumed that the NERNST-EINSTEIN equation applies. Therefore, the following values emerge for the diffusion coefficients : $D_+ = 9.2\times10^{-9}$ m^2 s^{-1} and $D_- = 2.0\times10^{-9}$ m^2 s^{-1}.

- ***Direction of the various molar flux densities***

In the diffusion layers the overall molar flux densities for each ion are governed by the redox reactions (see FARADAY's law in section 4.4). In the homogeneous zone, since no diffusion occurs, the current is equal to the migration current which defines the direction of the ion molar fluxes (see section 2.2.4.2) as illustrated in figure 4.9.

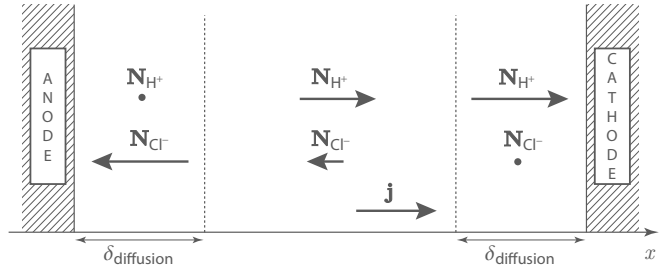

Figure 4.9 - Diagram of an electrolysis cell with the different molar flux densities of the ions in the three zones of the electrolyte (a dot represents a zero vector)

The equations outlined in the next parts of this example involve concepts that will be explained further on (see in particular section 4.3.1). However they rely on the equations for both molar flux densities and the FARADAY law, both of which have been already outlined.

- ***Steady-state concentration profiles***

In this 1-1 electrolyte, as there are only two types of ions, the medium's electroneutrality means that the cation (H^+) and anion (Cl^-) end up with equal concentrations at all points in the electrolyte (denoted by C). The diffusion layers show a concentration profile, however this must be identical for both ions. At steady state, the molar flux densities, which are identical at all points, are given by the FARADAY law. Let us focus on the anodic diffusion layer. The H^+ flux is zero because only Cl^- is electroactive at the anode:

$$\begin{cases} N_+ = 0 \\ N_- = -\dfrac{I}{\mathcal{F}S} \end{cases}$$

If one expresses the interfacial molar flux densities by introducing the NERNST-EINSTEIN equation, it gives the following:

$$\begin{cases} N_+ = -D_+\dfrac{\partial C}{\partial x} - D_+\dfrac{\mathcal{F}}{RT}C\dfrac{\partial \varphi}{\partial x} = 0 \\ N_- = -D_-\dfrac{\partial C}{\partial x} + D_-\dfrac{\mathcal{F}}{RT}C\dfrac{\partial \varphi}{\partial x} = -\dfrac{I}{\mathcal{F}S} \end{cases}$$

or:
$$\frac{\partial C}{\partial x} = -\frac{\mathcal{F}}{RT}C\frac{\partial \varphi}{\partial x}$$

hence:
$$\frac{\partial C}{\partial x} = \frac{I}{2D_-\mathcal{F}S}$$

At the anode, the concentration profiles only depend on the diffusion coefficient of the electroactive species, which in this case is the anion. It is as if we had pure diffusion with an apparent diffusion coefficient equal to 2 D_-.

- ***Relative contributions of the migration and diffusion molar flux densities at steady state***

  The fact that electroneutrality applies throughout the electrolyte imposes a strong constraint, which in turn creates a link between the diffusion molar flux densities of the two ions (algebraic normal components) at all points in the electrolyte:

$$\frac{N_{+_{\text{diffusion}}}}{N_{-_{\text{diffusion}}}} = \frac{-D_+ \dfrac{\partial C}{\partial x}}{-D_- \dfrac{\partial C}{\partial x}} = \frac{D_+}{D_-}$$

  As for the migration terms, a link is also made between the migration molar flux densities of the two ions at all points, since the electric field is the same for both ions:

$$\frac{N_{+_{\text{migration}}}}{N_{-_{\text{migration}}}} = \frac{-\lambda_+ C \dfrac{\partial \varphi}{\partial x}}{\lambda_- C \dfrac{\partial \varphi}{\partial x}} = -\frac{\lambda_+}{\lambda_-}$$

  Now if we return to the FARADAY law written for the H^+ ions in the anodic diffusion layer (flux equal to zero), you are able to deduce the way in which migration and diffusion distribute themselves for each ion in this zone at steady state:

$$\frac{N_{+_{\text{diffusion}}}}{N_{+_{\text{migration}}}} = -1 \quad \text{and} \quad \frac{N_{-_{\text{diffusion}}}}{N_{-_{\text{migration}}}} = \frac{N_{-_{\text{diffusion}}}}{N_{+_{\text{diffusion}}}} \frac{N_{+_{\text{diffusion}}}}{N_{+_{\text{migration}}}} \frac{N_{+_{\text{migration}}}}{N_{-_{\text{migration}}}} = -\frac{D_-}{D_+}\left(-\frac{\lambda_+}{\lambda_-}\right) = 1$$

  At steady state, the moduli of the migration and diffusion molar flux densities are therefore identical for any given species. The steady-state current is equally due to diffusion and migration. Let us stress the formal nature of such a distribution for the diffusion and migration fluxes, that is wholly based on the NERNST-EINSTEIN law. Furthermore, the current is fully transported by the electroactive species. Non-electroactive ions have no macroscopic movement at steady state. This is not the case in a transient state, since the steady-state profile has to be built up (the interfacial flux of the electroinactive ions is still zero however the transient flux density is not constant throughout the whole volume of the diffusion layer).

- ***Quantitative links between migration and the overall current densities at steady state***

  If you return to the equation for FARADAY's law for Cl^- ions in the anodic diffusion layer, you can write the following:

$$N_- = N_{-_{\text{diffusion}}} + N_{-_{\text{migration}}} = 2\,N_{-_{\text{migration}}} = -\frac{I}{\mathcal{F}\,S}$$

  and finally:

$$j_{\text{migration}} = j_{+_{\text{migration}}} + j_{-_{\text{migration}}} = \mathcal{F}\,(N_{+_{\text{migration}}} - N_{-_{\text{migration}}})$$
$$= \mathcal{F}\,N_{-_{\text{migration}}}\left(\frac{N_{+_{\text{migration}}}}{N_{-_{\text{migration}}}} - 1\right) = \frac{I}{2S}\left(\frac{\lambda_+}{\lambda_-} + 1\right)$$

  On the anodic side, the numerical values are therefore:

$$j_{\text{migration}} = 2.8\,j \quad \text{and} \quad j_{\text{diffusion}} = 1 - j_{\text{migration}} = -1.8\,j$$

  When applying the same type of reasoning to the cathodic side, you obtain the following:

$$\frac{N_{-_{\text{diffusion}}}}{N_{-_{\text{diffusion}}}} = -1 \quad \text{and} \quad \frac{N_{+_{\text{diffusion}}}}{N_{+_{\text{diffusion}}}} = 1$$

  hence:

$$j_{\text{migration}} = \frac{I}{2S}\left(\frac{\lambda_-}{\lambda_+} + 1\right)$$

on the cathodic side, the numerical values are:

$$j_{\text{migration}} = 0.6\, j \quad \text{and} \quad j_{\text{diffusion}} = 1 - j_{\text{migration}} = +\,0.4\, j$$

In this example, as in most cases, the migration current density has the same direction as that of the overall current density although they are not equal. These two vectors are identical when the two diffusion coefficients are equal.

4.2.2 - CONDUCTION PHENOMENA: MECHANISMS AND ORDERS OF MAGNITUDE

Scientific literature frequently presents microscopic mechanisms for electric conduction using examples which only involve migration. In fact, once the charge carriers have been well identified, one can assume that the microscopic mechanisms briefly presented below also apply to diffusion. They describe how the mass transport is carried out at the microscopic level, under the influence of an external force, regardless of the nature of the forces involved (in migration or in diffusion).

4.2.2.1 - EXAMPLES OF CONDUCTION MECHANISMS

Depending on the materials involved, there is a range of different conduction mechanisms that can be imagined at the microscopic level. In experimental data, the influence of temperature on the conducting properties is an important criterion for determining the conduction mechanism. Some types of mechanisms are described below.

⏩ *Electronic conduction in a metal*

A metal can be described as a fixed lattice of metal cations, with a gas of electrons circulating through it (band model – energy continuum). The model used to describe the movement of these conduction electrons is called the ' mean free path '. The electrons experience collisions but are not submitted to any force between two collisions. The collisions may be due to:

- impurities which create defaults in the crystalline lattice (primary phenomenon at very low temperature),
- phonons which describe the vibrations of the crystalline lattice (primary phenomenon at and over room temperature).

The electron mobility is therefore proportional to the mean time interval between two collisions, τ, which corresponds to the mean free path. This model accounts for the temperature influence in qualitative terms. When the temperature increases, the mobility decreases, as does τ. This model also takes into account how electronic mobilities depend on the nature of the metal in question by introducing different values for τ and for the amount of charge carriers per unit volume. The order of magnitude of τ is one nanosecond at very low temperature and one femtosecond at room temperature.

⏩ *Ionic conduction in an electrolytic solution*

In dilute solutions, one can assume that the ions move *via* a Brownian motion, that is to say by means of the ions and solvent molecules colliding together. In the absence of any

external force, the statistical mean value of ion displacement is zero. However, if there is an external force, for example when there is an external electric field, then a trend emerges in terms of the displacement direction. Collisions with solvent molecules are opposed in statistical terms to the ion movement in the direction of the external force. Very rapidly, a steady state is reached, in which the mean ion velocity is determined by the balance between the external force and the friction force exerted by the solvent. The time required for this to occur is around one picosecond in aqueous solution at room temperature (see the calculation below).

In a system without convection ($\boldsymbol{\omega}_{\text{medium}} = \mathbf{0}$),for a solvated ion with a $z_i$charge number, the NEWTON's law reveals the link between the acceleration and the sum of external forces. When there is an external applied electric field, $\mathbf{E}$, the forces involved are the electric force and the friction force. The latter**,** which is considered in the approximation of the viscous friction model, is proportional to the $\boldsymbol{\omega}_i$ velocity of the ion in the solvent, and the following equation is obtained:

$$z_i |\mathrm{e}| \mathbf{E} - \alpha \boldsymbol{\omega}_i = m \mathbf{a} = m \frac{\mathrm{d}\boldsymbol{\omega}_i}{\mathrm{d}t}$$

This first order differential equation can also be written as follows:

$$\frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t} + \frac{\alpha}{m} \boldsymbol{\omega}_i = \frac{z_i |\mathrm{e}|}{m} \mathbf{E}$$

It is easily solved when the external electric field is constant (with **A**: the integration constant):

$$\boldsymbol{\omega}_i = \frac{z_i |\mathrm{e}|}{\alpha} \mathbf{E} + \mathbf{A}\, \mathrm{e}^{-\frac{\alpha t}{m}}$$

After a transient period with a characteristic time constant of $\tau = m/\alpha$, the ions reach a steady state with a limiting velocity proportional to the electric field:

$$\boldsymbol{\omega}_{\text{lim}} = \frac{z_i |\mathrm{e}|}{\alpha} \mathbf{E}$$

In order to get an idea of the time needed to reach this steady state in aqueous solutions, you can evaluate α by using the electric mobility (around 10^{-7} m^2 s^{-1} V^{-1}, see table 4.1 in section 4.2.2.3) which is equal to the limiting velocity in a unit electric field.

$$\tau = \frac{m}{\alpha} \approx \frac{m}{|\mathrm{e}|} 10^{-7} = \frac{M}{\mathcal{N} |\mathrm{e}|} 10^{-7}$$

The molar mass of a solvated ion can be taken as 100 g mol^{-1} which brings an order of magnitude of 10^{-13} s for the characteristic time constant of the transient state.

The main effect observed when the temperature of the solution increases is a decrease in solvent viscosity, which coincides therefore with a decrease in the friction coefficient. Furthermore, one usually observes an increase in the electric mobility of the solvated ions [33].

In a concentrated solution the moving ions do not only collide with the solvent molecules but also with the other ions, especially those with opposite charges which also drag solvent molecules along with them. This slows down the movement by

[33] For instance, an aqueous solution containing potassium chloride with a concentration of 0.02 mol L^{-1} sees an increase in conductivity from 0.25 S m^{-1} at 20 °C to 0.33 S m^{-1} at 35 °C.

increasing the medium's friction. This phenomenon is called the electrophoretic effect, and plays a part in reducing mobility in concentrated solutions in comparison to diluted solutions. A second effect also comes into play in this reduction process: the relaxation effect. The ionic atmosphere around a moving ion is no longer symmetrical [34] because the formation/destruction of this atmosphere is not immeasurably fast. The electric dipole that is created as a result sets up a resistance to the external force and consequently slows down the ion's movement.

▸▸ *Ionic conduction in a crystalline solid*

In crystalline solids, the conduction mechanisms envisaged generally involve defects in the crystal lattice (vacancies or interstitial ions). The latter are created by local disorder, and their relative charge values always respect the bulk electroneutrality. For example, the relative charge of a vacancy is the opposite to that of the ion when the latter is in a normal position in the network.

The primary types of defects are:

- SCHOTTKY's disorders, which occur in many alkali halides: the alkali ion vacancies and the halide vacancies are equal in number;
- interstitial ions: when ions are in an interstitial position, such as in silver halides, electroneutrality is once again respected, because one cation vacancy is produced for every interstitial ion created (FRENKEL's disorder);
- as a way of improving the conduction properties, crystals are often doped with impurities with different valencies. This occurs for example in the case of zirconia doped with calcium oxide CaO or yttrium oxide Y_2O_3. These defects are called extrinsic defects. Electroneutrality is then ensured by creating either vacancies or interstitial ions.

The diagram in figure 4.10 shows the movement of an ion when conduction occurs *via* vacancies. The mechanism used here jumps from an occupied site to a vacant site.

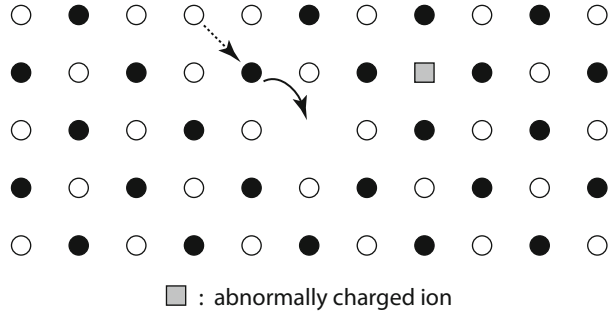

Figure 4.10 - Diagram showing a conduction mechanism in a crystalline solid

The higher the temperature, the higher the rate of intrinsic defects is. In addition, temperature increase makes it easier to cross the potential barrier from one site to another (activation energy).

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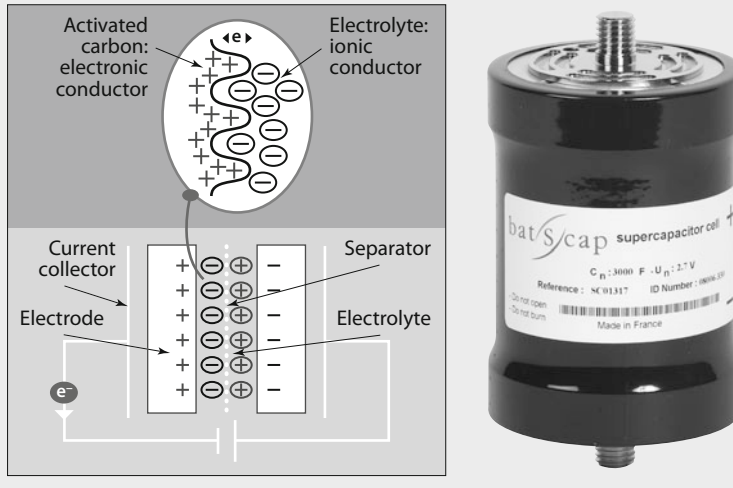
[34] Contrary to the hypothesis made in the DEBYE-HÜCKEL model (see appendix A.3.2).

ENERGY STORAGE: SUPERCAPACITORS

Document written with the kind collaboration of K. GIRARD, R&D engineer for Batscap, based in Quimper in France

In normal operating conditions, no redox reactions occur in supercapacitors. They function based on a well-known electrochemical phenomenon: the double layer phenomenon. In electrochemistry, this phenomenon reflects the accumulation of ions in the vicinity of a charged electrode (the charge of the electrode being opposite to that of ions). Following this principle, high amounts of charge can be accumulated based on the following relationship: $q = C_{dl} S (E - E_0)$, whereby C_{dl} is the double layer capacitance, S the area of the surface developed and E_0 the system's open-circuit potential.

The thickness of the HELMOTZ double layer, which is about a few nanometers, over an extensively developed area, means that a significantly greater quantity of charge can be accumulated compared to classical capacitors. It is possible to obtain a capacitance of several thousand Farads for one unit element.



Schematic view of a supercapacitor *(© Batscap)* ***and unit element (2.7 V, 3000 F)*** *(photo Batscap)*

Supercapacitors are composed of:
- two porous electrodes (to maximize the surface) based on active carbon,
- a separator based on polymer or cellulose,
- an organic electrolyte, which is a good ionic conductor.

In the absence of any electrochemical reaction, the kinetic rate is significantly boosted as a result. This extremely high-speed operation results in a high power density, both in charge and discharge, reaching power densities of over 10 000 W/kg. On the other hand, there is a relatively low amount of embedded energy, about a few Wh/kg in such systems. They also have a high level of cyclability, clocking up some several thousand cycles. Supercapacitors can be particularly useful for applications which need to attain high power levels during a short time period with frequent recharging. For example, a tramway which runs without a catenary requires a considerable power surge to set it off at the start, but can subsequently be recharged at each stop.

▸▸ *Ionic conduction in a polymer electrolyte*

In a polymer electrolyte at temperatures higher than a certain value called glass transition temperature, the polymer chains behave in a similar way to solvent molecules in a liquid, although no macroscopic displacement occurs. The conduction model, called the free volume model, is close to the model that can be developed in certain liquid conducting media. The ion moves as a result of deforming neighbouring polymer chains (or moving molecules in a liquid) which provide an adjacent cavity or free volume in which this ion can lodge itself.

4.2.2.2 - CONDUCTIVITY MEASUREMENTS

Whenever diffusion can be disregarded, the overall current density is equal to the migration current density, as presented in the following equation:

$$\mathbf{j} = \sum_i \lambda_i \, C_i \, \mathbf{E} = \sigma \mathbf{E}$$

One method for obtaining the overall conductivity parameter is to impose a potential difference across the conductor, with a well-known geometry, and then to measure the resulting current. The ratio between these two quantities enables us to determine the resistance, as well as to calculate the conductivity through the conductor's geometric parameters.

For instance, the following equation shows the voltage, U, between two sections separated by a ℓ distance in a homogeneous unidirectional conductor and with an equipotential section of area S:

$$U = R\,I \qquad \text{with} \qquad R = \frac{\rho\,\ell}{S} = \frac{\ell}{\sigma\,S}$$

Transparent electronic conductors are required in certain applications. A thin layer of an electronically conducting oxide deposited on a glass substrate is then used.

Given this rather particular geometric configuration, as shown in figure 4.11, the parameter that defines the conductor's properties combines both the material's conductivity (or resistivity) and its thickness:

$$R = \frac{\rho\,L}{S} = \frac{\rho}{e}\frac{L}{\ell}$$

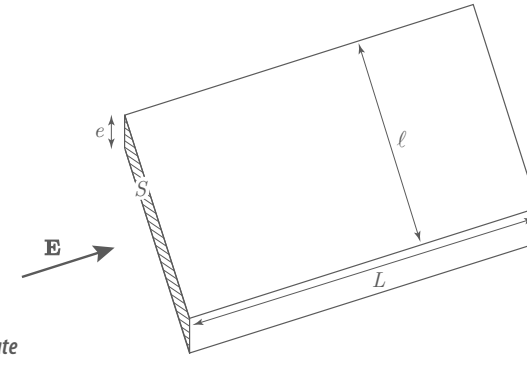


Figure 4.11 - Diagram of a conducting plate

The sheet resistance of a given thin conductor, $R_{\square}$, expressed in Ω per square, is the resistance of a square plate sample of the conductor ($\ell = L$).

For example, for a thin layer of SnO_2:F (tin oxide doped with fluorine with a conductivity of $\sigma = 2.5 \times 10^5$ S m^{-1}, see table 4.1) and a thickness $e = 5\,000$ Å, the square resistance is the following:

$$R_{\square} = \frac{1}{\sigma e} = \frac{1}{5 \times 10^{-7} \times 2.5 \times 10^5} = 8\ \Omega_{/\square}$$

It is relatively easy to apply this technique to a metal (direct potential and current). When dealing with electronic conductors with lower conductivity (e.g., semiconductors), then some improvements are needed, such as the ' four-points device ' or developing samples with a particular geometry.

The experimental conductivity values show dramatically different orders of magnitude: from 10^7 S m^{-1} for the best metallic conductors to 10^{-15} S m^{-1} for insulators [35].

For an ionic conductor (or similarly for a semiconductor), applying this method is, by definition, a much more complicated affair: measuring currents or potential differences requires metallic contacts to be put in place with the conductor in question. A minimum of two electrochemical interfaces must therefore be introduced, which generally leads to deviations from OHM's law. It is assumed that in usual experimental conditions (see below) one can keep the influence of these interfacial phenomena to a minimum in the relationship between U and I.

In addition, for precise conductivity measurements, one always takes the precaution of calibrating the cell used with a reference ionic solution. This is most often a decimolar KCl solution, at a controlled temperature. Knowing the value of this electrolyte's conductivity (see data tables for different temperatures), one can determine the proportionality factor, called the cell constant. One can then also measure the conductivity of a different electrolyte in the same conductivity range using the same conductivity cell. It should be noted that if the value of the cell constant obtained is very different from that given by the manufacturer [36] or from that deduced from the cell geometry, then it is not enough to simply correct the proportionality factor. In fact it should be seen as a sign that the measuring conditions are not adequately suitable (inappropriate choice for the selected frequency, damaged electrodes, modified side-effects, etc.).

The use of an alternative voltage generator with a low amplitude and an appropriate frequency (the orders of magnitude for an aqueous electrolytic solution at room temperature are the following: $\Delta V \approx$ a few mV and $f \approx$ a few kHz) minimises the current values flowing through the system and enormously increases the capacitive current compared to the faradic current. In these conditions, the system's impedance as determined through experiments comes out as equal to the resistance of the ionic conductor. The frequency must be neither too low, nor too high, the former to avoid the influence of electrode phenomena, and the latter to avoid the influence of the electrolyte's dielectric

[35] See table 4.1 in section 4.2.2.3.

[36] This value relates to the cell geometry and takes into account the possible side-effects. For instance for a parallelepiped cell, it can be slightly different from the ℓ/S ratio. This is what is sometimes called primary current distribution, which can be obtained by solving the LAPLACE equation in the particular system's geometry, assuming the electrolyte conductivity is constant. It is usually determined by an experimental measurement.

properties. In addition, using metallic electrodes with a very high roughness, opens up the choice range for the measurement frequency[37].

Since the quantity measured, namely the electric conductivity, depends significantly on temperature, then it is better to use a temperature-controlling device when making precise measurements.

When trying to differentiate the contributions of the various ions, it is not enough to simply have a conductivity measurement. One needs to carry out additional experiments to determine the transport numbers.

4.2.2.3 - ORDERS OF MAGNITUDE FOR CONDUCTION PARAMETERS

Table 4.1 (see the next two pages) gives the values for the mass transport quantities typically seen for various types of charge carriers in several typical examples of media.

4.2.2.4 - MODELS FOR SOLUTIONS AT INFINITE DILUTION

In a simple infinitely diluted solution, the parameters for charge transport can be linked to some of the solvent's properties. In fact, the movement of a solvated ion in the solution can be viewed as similar to the displacement of a rigid sphere in a viscous medium.

Based on the STOKES law (viscous friction hypothesis), for a sphere with r_i radius moving with a $\boldsymbol{\omega}_i^{\text{rel}}$ relative velocity, through a medium with η viscosity, the friction force is of the following type:

$$\mathbf{f}_{\text{fr}} = -\, 6\,\pi\, r_i\, \eta\, \boldsymbol{\omega}_i^{\text{rel}}$$

The balance at the microscopic level between the friction force and a unit external force (namely with a modulus equal to 1 N) applied to an ion i which is considered to be a sphere with an radius r_i, results in a movement with a steady-state velocity. The velocity modulus, once divided by the AVOGADRO constant, is equal to the electrochemical mobility:

$$\tilde{u}_i^0 = \frac{1}{6\,\pi\, \eta\, \mathcal{N}\, r_i}$$

Depending on the viscosity η of the solvent and on the radius r_i of the solvated ion, one can therefore write equations for the constants which characterise the following:

- migration: $\lambda_i^{\,0} = \dfrac{z_i^2\, \mathcal{F}^2}{6\,\pi\, \eta\, \mathcal{N}\, r_i}$
- diffusion (derived from the STOKES-EINSTEIN equation): $D_i^{\,0} = \dfrac{\mathrm{R}T}{6\,\pi\, \eta\, \mathcal{N}\, r_i}$

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[37] In this context, platinised platinum (the same as that used for hydrogen reference electrodes, see section 1.4.1.2) is often used. When the contact area with the electrolyte increases, the double layer capacity increases substantially, when compared to the system's dielectric characteristics. The reason for this is that mean roughness is larger than the thickness of the double layer. In terms of impedance measurements, this leads to a broader frequency range in which the system's impedance is equal to the electrolyte's resistance.

Table 4.1 – Concentration, electric and electrochemical mobilities, electric conductivity, molar conductivity and diffusion coefficient in some media at 25°C (unless otherwise specified)

		C *concentration* [mol L^{-1}]	u *electric mobility* [$m^2 s^{-1} V^{-1}$]	$\tilde{u}$ *electrochemical mobility* [mol s kg^{-1}]	$\sigma = \mathcal{F}\ C\ u$ *electric conductivity* [S m^{-1}]	λ *molar conductivity* [S m^2 mol^{-1}]	D *diffusion coefficient* [$m^2 s^{-1}$]
Metals							
Ag	electrons	97	6.6×10^{-3}	6.9×10^{-8}	6.2×10^{7}	6.4×10^{2}	1.7×10^{-4}
Cu	electrons	140	4.4×10^{-3}	4.5×10^{-8}	5.9×10^{7}	4.2×10^{2}	1.1×10^{-4}
Au	electrons	98	4.8×10^{-3}	5.0×10^{-8}	4.6×10^{7}	4.6×10^{2}	1.2×10^{-4}
Intrinsic semiconductors							
Si	electrons	2×10^{-11}	0.13	1.5×10^{-6}	3×10^{-7}	1.4×10^{4}	3.6×10^{-3}
	holes	2×10^{-11}	0.05	5.2×10^{-7}	1×10^{-7}	4.8×10^{3}	1.3×10^{-3}
C diamond (insulating)	electrons	$\approx 10^{-20}$	0.18	1.9×10^{-6}	$\approx 2\times10^{-16}$	1.7×10^{4}	4.6×10^{-3}
	holes	$\approx 10^{-20}$	0.12	1.2×10^{-6}	$\approx 10^{-16}$	1.1×10^{4}	3.1×10^{-3}
Extrinsic semiconductors							
As-doped Si	holes << electrons	8×10^{-5}	1.3×10^{-4}	1.3×10^{-9}	1.0	1.3×10^{1}	3.3×10^{-6}
F-doped SnO_2		0.7	3.7×10^{-3}	3.8×10^{-8}	2.5×10^{5}	3.6×10^{2}	9.5×10^{-5}

Aqueous solutions							
H^+		0.1	3.6×10^{-7}	3.7×10^{-12}	3.5	3.5×10^{-2}	9.2×10^{-9}
Na^+		0.1	5.2×10^{-8}	5.3×10^{-13}	0.5	5.0×10^{-3}	1.3×10^{-9}
OH^-		0.1	2.1×10^{-7}	2.2×10^{-12}	2.0	2.0×10^{-2}	5.5×10^{-9}
Cl^-		0.1	7.9×10^{-8}	8.2×10^{-13}	0.8	7.6×10^{-3}	2.0×10^{-9}
$K^+ Cl^-$ at 20°C		0.1	—	—	1.2	1.2×10^{-2}	—
$K^+ Cl^-$ at 35°C		0.1	—	—	1.6	1.6×10^{-2}	—
Dioxygen, dissolved O_2 (25°C and 1 atm)		3×10^{-4}	—	—	—	—	2.5×10^{-9}
Molten salts							
NaCl at 850°C	Na^+	26	8×10^{-8}	8.10^{-13}	2×10^{2}	8×10^{-3}	8×10^{-9}
	Cl^-	26	2×10^{-8}	2.10^{-13}	5×10^{1}	2×10^{-3}	2×10^{-9}
Ionic solids							
$(ZrO_2)_{0,9}(Y_2O_3)_{0,1}$ at 800 °C	oxygen vacancy	≈ 5	6×10^{-9}	6×10^{-14}	≈ 3	6×10^{-4}	5×10^{-10}
Polymer electrolytes							
$LiClO_4$ in POE at 60 °C	Li^+	≈ 1	10^{-10}	10^{-15}	$\approx 10^{-2}$	10^{-5}	3×10^{-12}
	ClO_4^-	≈ 1	4×10^{-10}	4×10^{-15}	$\approx 4\times10^{-2}$	4×10^{-5}	10^{-11}
Plasmas / gas							
Plasma He (25°C et 100 Pa)	electrons	10^{-9}	3×10^{2}	3×10^{-3}	30	3×10^{7}	7
Dioxygen, O_2 (25°C and 1 atm)		4×10^{-2}	—	—	—	—	2×10^{-5}
Dioxygen, O_2 (100°C and 1 atm)		3.2×10^{-2}	—	—	—	—	3×10^{-5}
Dioxygen, O_2 (25°C and 50 atm)		2	—	—	—	—	4×10^{-7}

The following values can be found in scientific literature.

Table 4.2 - Molar conductivity at infinite dilution for different ions in an aqueous solution at 25°C

	λ_+^0 [mS m^2 mol^{-1}]		λ_-^0 [mS m^2 mol^{-1}]
H^+	34.98	F^-	5.54
D^+	25	Cl^-	7.63
Li^+	3.86	Br^-	7.81
Na^+	5.01	I^-	7.70
K^+	7.35	OH^-	19.92
Ag^+	6.19	OD^-	11.9
NH_4^+	7.34	NO_3^-	7.14
Cu^{2+}	10.7	SO_4^{2-}	16.0
Ca^{2+}	11.9	$Fe(CN)_6^{3-}$	30.3
Zn^{2+}	10.6	$Fe(CN)_6^{4-}$	44.2
Fe^{2+}	10.8	CO_3^{2-}	13.9
Fe^{3+}	20.4	HCO_3^-	4.45

Scientific literature provides many tables that actually refer to the concept of an equivalent, now commonly abandoned [38], though they do not directly give the values of molar conductivities but rather the values of the terms: $\frac{1}{|z_i|}\lambda_i{}^0$.

What is confusing is that the conductivity data for ions with a charge number different from 1 are often presented in a way whereby a fraction is placed in front of the ion in question. For instance, scientific literature frequently presents the value for the Ca^{2+} ion as $\lambda_{\frac{1}{2}Ca^{2+}}$, with the following definition: $\lambda_{\frac{1}{2}Ca^{2+}} = \frac{1}{2}\lambda_{Ca^{2+}}$

If you look at the values in the previous table for ions sharing the same charge, then you can see that the molar conductivity tends to increase with the element's atomic number, for instance with the family of alkali cations (Li^+, Na^+ and K^+). This observation is the opposite to what one would expect given the size of the ions, if you follow what classical tables usually show as corresponding to a non-solvated ion in an ionic crystal. In fact, it is important to remember that when applying the equation for evaluating the mobility or the diffusion coefficient (see the STOKES-EINSTEIN equation in section 4.2.2.4) the actual size of the solvated ion in the medium must be used. For example, the Li^+ ion, which is small, interacts more strongly with a polar solvent such as water, and its coordination sphere is big. This trend is less clear in the family of halide ions which are bigger and therefore less solvated, except in the case of the F^- ion which is small.

One can see how the values for ions with different charges, such as the Fe ions, depend on the complexation and oxidation number of the Fe element. This is not surprising, however it is more difficult to understand from the raw values, because the charge can change depending on the complexation state. It is therefore better to make a

[38] This concept is mentioned in the transport number calculation described in section 2.2.4.3.

comparison between the values for electrochemical mobility or diffusion coefficients which do not involve the charge. Therefore one can note that at 25°C the Fe^{2+} diffusion coefficient given by the NERNST-EINSTEIN equation is 7.2×10^{-10} m^2 s^{-1} whereas that of Fe^{3+} is 6×10^{-10} m^2 s^{-1}. This shows that the bare Fe^{3+} ion, which is smaller, tends to have stronger interactions with water, especially because the charge is higher. Its solvation sphere is therefore slightly bigger than that of Fe^{2+}. There is a different scenario for media containing cyanide: the respective diffusion coefficients become 7.3×10^{-10} m^2 s^{-1} and 8.9×10^{-10} m^2 s^{-1}. The mobility order is changed, which can be explained by the fact that because the $Fe(CN)_6^{4-}$ ion has a higher charge, then it will be less mobile than $Fe(CN)_6^{3-}$ because of the stronger interactions with water molecules.

The unusually high value that can be observed in proton mobility involves very different concepts still controversial today. In fact, the solvated proton (hydronium H_3O^+) is roughly the same size as that of K^+, but the molar conductivities or the diffusion coefficients are very different (factor of 5). Assuming that only the STOKES process is used to displace the solvated H^+, the mobility value would be small given the large size of this ion. In fact, proton mobility is mostly due to an exchange of H^+ taking place between neighbouring water molecules which are well oriented. Here a 'tunnelling effect' process could occur, given the properties of the H^+ species. The influence of mass (through the comparison between H^+ and D^+) certainly works in favour of this interpretation. This particular mode has a hopping velocity that is governed by the time it takes for the molecules to be well oriented. This means aligning the free orbital of the O atom in the water molecule in front of an H atom in H_3O^+, as shown in the diagram in figure 4.12. Modelling is actually quite a complex process because each molecule involved in this mechanism is bound to neighbouring molecules by hydrogen bonds. It is generally recognised that the physical movement of the H_3O^+ (STOKES flow model) entity occurs only in a small proportion (20% of the overall mobility).

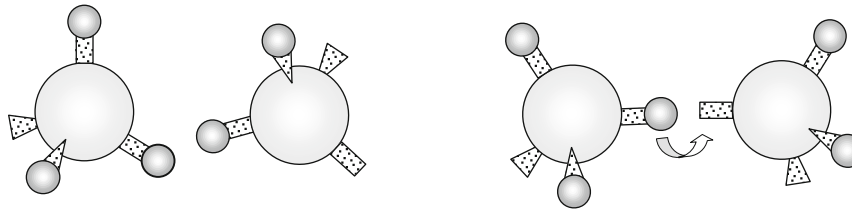

Figure 4.12 - Diagram of the tunelling conduction mechanism of protons in water

4.2.2.5 - CASE OF CONCENTRATED SOLUTIONS

Experimental studies that were carried out, in particular by KOHLRAUSH, on aqueous solutions containing only one strong electrolyte (a single type of cation and anion) produced an equation that showed how the molar conductivity is a function of the electrolyte's concentration. This is shown in the following:

$$\Lambda = \Lambda^0 - \text{Cst}\ \sqrt{C}$$

Λ^0 gives the value for the molar conductivity extrapolated to $C = 0$, and is called the ' molar conductivity at infinite dilution ' of the electrolyte (in S m^2 mol^{-1}). This quantity represents the molar conductivity for an ideal system with no interactions. The above experimental formula can be applied to systems whose concentrations are lower than about 0.1 mol L^{-1}.

Subsequently, this empirical law has been linked to the ionic conduction model in liquid electrolytes involving electrophoretic and relaxation effects, which are found to be very strong in concentrated solutions (see section 4.2.2.1). For a 1-1 strong electrolyte solution, the molar conductivity of an ion i is shown in the following equation:

$$\lambda_i = \lambda_i{}^0 - (A + B\,\lambda_i{}^0)\sqrt{C_i}$$

with $A = 60.3$ and $B = 0.229$ at 25 °C in water, if C_i is in mol L^{-1} and λ_i^0 in S cm^2 mol^{-1} ; λ_i^0 is called molar conductivity at infinite dilution of the ion i (in S m^2 mol^{-1}). A, B and λ_i^0 are temperature-dependent.

Given the values of A, B, the molar conductivity of an ion can be considered as independent of the concentration an equal, with an accuracy rate of about 5%, to its value at infinite dilution once the concentration is lower than a few 10^{-3} mol L^{-1} at 25 °C. In such conditions, the electric conductivity of the electrolytic solution is simply proportional to the electrolyte concentration.

4.2.3 - SITUATIONS IN WHICH THE OHMIC DROP DOES NOT FOLLOW THE MACROSCOPIC OHM LAW

In numerous experimental situations, one can assume that the conductivity is identical at all points throughout the electrolyte[39]. In this instance, the ohmic drop is then proportional to the current. Yet this is not always true: in the absence of a supporting electrolyte, such an approximation no longer applies if the diffusion layers contribute significantly to the electrolyte's overall resistance [40]. OHM's law ($\mathbf{j} = \sigma\,\mathbf{E}$) still applies [41] at a local level. However, since the electrolyte conductivity varies depending on the spatial position, then the link between the ohmic drop across the electrolyte and the current, (which results from integrating local OHM's law) is no longer proportional with a constant resistance factor.

In such cases, we can say that when the current increases in steady-state experiments, the overall resistance increases. This phenomenon is due to lower concentrations in the vicinity of one electrode resulting in a local decrease in the electrolyte conductivity. On the other hand, the electrolyte conductivity in the other diffusion layer may increase at the same time. However the zone with low levels of conductivity has a greater impact on

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[39] This is true in systems with a supporting electrolyte or in systems where the volumes of the diffusion layers are insignificant compared to the overall electrolyte volume.

[40] An example of this type is addressed in detail in appendix A.4.1: the contribution of transport by diffusion is significant in the overall electrolyte volume.

[41] An additional complication may arise if the media studied contain charge carriers with transport properties very different from each other. In fact we have seen in section 4.2.1.5 that, in such conditions, the migration current and the total current are not identical ($\mathbf{j} \neq \mathbf{j}_{\text{migration}} = \sigma\,\mathbf{E}$). The example outlined in appendix A.4.1 takes this aspect into account.

the overall resistance of the electrolyte. This goes hand in hand with a deviation from strict electroneutrality, which in turn has an immediate impact on the electrolyte's potential profiles. They are no longer linear, as one would predict when applying the LAPLACE law. When the current approaches the steady-state limiting current, the electrolyte's overall resistance greatly increases. In such operating conditions the electroneutrality can no longer be used, even for calculating the concentration profiles.

4.3 - CURRENT FLOW THROUGH AN ELECTROCHEMICAL INTERFACE

When a current flows through a heterogeneous system it gives rise to phenomena in the different volumes (mass transport and possible chemical reactions) as well as interfacial phenomena. This section focuses on the overall characteristics (U, I, t) of an electrochemical system in relation with the characteristics of the studied interfaces. The influence of these latter on how that system is described can be found in two different ways. On the one hand they define the conditions at the volume boundaries for concentration and potential profiles, and on the other hand they determine the interfacial contributions which, added to the ohmic drop, give the overall cell voltage [42].

For certain electrochemical systems it is possible to find experimental conditions which minimise the interactions between the anode and the cathode. Both electrodes remain related to each other since they are crossed by the same current, yet the difference is that the mass transport phenomena occurring at both interfaces do not interact with each other. This type of scenario, which is typically sought after in analytical experiments, is explored in this paragraph, focused exclusively on describing one single electrochemical interface [43]. Moreover, it is worth noting that the same approach can be applied to any interface, such as for instance an ionic junction.

4.3.1 - POTENTIAL AND CONCENTRATION PROFILES AT AN INTERFACE

4.3.1.1 - POTENTIAL PROFILE

In electrochemistry, on usual time scales ($\gg 10^{-15}$ s) it can be assumed that electron exchange is immeasurably fast (no energy barrier) at the junction between two metals. In these conditions, the current flow through a metallic junction does not modify the latter in any way. In particular, the electronic junction voltage is the same as in equilibrium, when the current is zero, as represented in figure 4.13.

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[42] Refer to section 2.2.3 and to figures 2.15 and 2.16 in section 2.2.4.2 for the qualitative description of potential profiles in an electrochemical cell, including the different contributions to the voltage across an electrochemical system with a current flowing. In addition, remember that the description of the concentration or potential profiles is on the spatial scale of the diffusion layers and not on the double-layers' scale (see section 3.3.1). In particular, while the potential profile is continuous on the scale of the double-layer dimensions, it shows discontinuities on the scale of the diffusion layers at the interfaces.

[43] Section 4.4 provides examples where both the electrodes strongly interact as a result of mass transport phenomena.

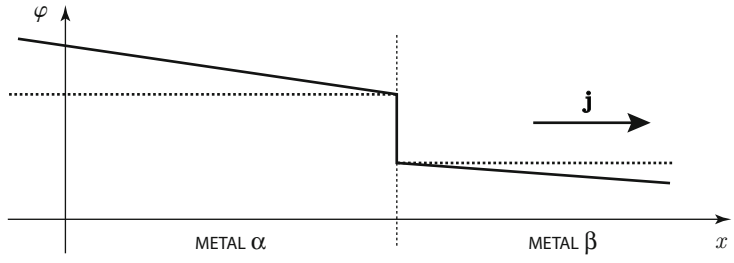

Figure 4.13 - Potential profiles at a junction between two metals with different conductivities (different slopes with $\sigma_\alpha < \sigma_\beta$) in equilibrium (dotted line) and when a current is flowing (solid line)

On the other hand, the current flow disrupts the interface in the case of electrochemical interfaces and ionic junctions. The voltage across the interface (or the junction voltage for an ionic junction) is generally different from that observed at open circuit. It depends *a priori* on the parameters of the system and deviates from a linear law, such as OHM's law. Most often it can be assumed that the double layer thickness is much lower than that of the diffusion layers [44]. Typically, one ends up with the following:

$$\left.\begin{array}{l}\delta_{\text{double layer}} \approx 10\ \text{Å} \\ \delta_{\text{diffusion layer}} \approx 10\ \mu\text{m}\end{array}\right\} \quad \Rightarrow \quad \delta_{\text{double layer}} \ll \delta_{\text{diffusion layer}}$$

In the following we will stay with such systems where both layers have very different scales. In this configuration, on the scale of the diffusion layer, the potential gradient (i.e., the electric field) is negligible compared to those in the double layer, as illustrated in figure 4.14.

The electric field is extremely strong in the double layer, yet it is much weaker throughout the rest of the electrolyte. However, since one may be dealing with large distances in the electrolyte, this relatively low electric field in the electrolyte may result in a non-negligible voltage across the electrolyte, corresponding to the ohmic drop.

On the other hand, the driving force behind the electrochemical reaction occurring in the interfacial zone is related to the double layer voltage (denoted by $\Delta\varphi_0$ in figure 4.14). The relationship between the double layer voltage and the current is precisely the subject of studies and models in electrochemical kinetics [45].

4.3.1.2 - CONCENTRATION PROFILES

Remember that the mass balance at an interface displays each interfacial molar flux density (and therefore also the current densities and currents of each type of charge carrier) in terms of the sum of two terms, their names being faradic and capacitive (see section 4.1.3.3).

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[44] There are exceptions to the typical situation described here: for example in electrolytes with very low conductivity, and therefore with a very thick double layer (see section 3.3.1) or for experiments lasting for a very short duration (such as in voltammetry with a high scan rate) or in systems in which the electrodes are very close to each other. In these two last instances the diffusion layer is thinner than 10 µm.

[45] Section 4.3.2 gives a brief overview of the models found in electrochemical kinetics.

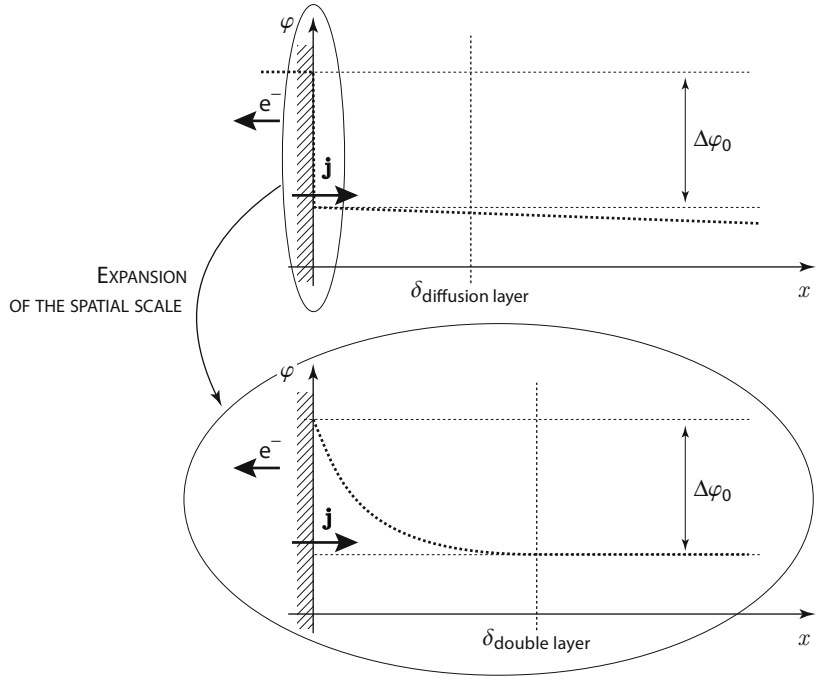

Figure 4.14 - Potential profile at an electrochemical interface with current flow
$\Delta\varphi_0$ is the voltage across the double layer.

For an electrochemical interface, the molar flux density is divided as follows:

$$(N_i)_{\text{interface}} = (N_i^{\text{capac}})_{\text{interface}} + (N_i^{\text{farad}})_{\text{interface}} = -\frac{\partial \Gamma_i}{\partial t} + w_{S_i}$$

Using FARADAY's law it is easy to introduce the current in these equations. For example, if only one half-reaction is involved at the interface, one can write:

$$(N_i^{\text{farad}})_{\text{interface}} = \frac{1}{\mathscr{F}} \frac{\nu_i}{\nu_e} j^{\text{farad}} = \frac{1}{\mathscr{F} S} \frac{\nu_i}{\nu_e} I^{\text{farad}}$$

When there is a supporting electrolyte, one can show that the migration currents are negligible for the electroactive species when compared to their diffusion currents[46]. In addition, the normal component of the convection flux density at the interface is inevitably zero: the electrode constitutes an impervious wall for the overall movement of the electrolyte medium. Therefore when there is a supporting electrolyte, one should only take into account the normal component of the interfacial diffusion flux density for an electroactive species.

In these conditions, when one has a single redox half-reaction at the interface, the slope for the concentration profile of each electroactive species is proportional to the faradic current.

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[46] This property is widely accepted in electrochemistry, and is demonstrated in the case of an example in appendix A.4.1.

Take for example the oxidation of Fe^{2+} ions to Fe^{3+} ions in a unidirectional system with a planar interface between a platinum electrode and an aqueous solution which contains both ferrous and ferric ions and a supporting electrolyte. If the capacitive current can be ignored, then the boundary conditions for the two electroactive species can be presented in the following way:

$$\left(N_{Fe^{2+}}\right)_{x=0} = \left(N_{Fe^{2+}\,diffusion}\right)_{x=0} = -\frac{I}{\mathcal{F}\,S} = -D_{Fe^{2+}}\left(\frac{\partial[Fe^{2+}]}{\partial x}\right)_{x=0}$$

$$\left(N_{Fe^{3+}}\right)_{x=0} = \left(N_{Fe^{3+}\,diffusion}\right)_{x=0} = \frac{I}{\mathcal{F}\,S} = -D_{Fe^{3+}}\left(\frac{\partial[Fe^{3+}]}{\partial x}\right)_{x=0}$$

At the interface, the slopes for the Fe^{2+} and Fe^{3+} concentration profiles have opposite signs. For an oxidation half-reaction, the slope for Fe^{2+} is positive, while that for Fe^{3+} is negative, with the direction of the x-axis pointing from the electrode towards the electrolyte $(I > 0)$. Figure 4.15 illustrates the shape of the Fe^{2+} and Fe^{3+} concentration profiles, at a given instant, when the thickness of the diffusion layer [47] is low compared to the dimensions of the overall system. For instance, this applies to situations involving semi-infinite mass transport in a transient state (see section 4.3.1.3).

Since $D_{Fe^{2+}} > D_{Fe^{3+}}$ (see table 4.2 in section 4.2.2.4 [48]), the absolute value of the Fe^{3+} concentration profile slope at the interface is higher than that of Fe^{2+}, as shown in the diagram in figure 4.15.

Remember not to get mixed up between the concentration profiles which are variations in space, and the concentration variations over time. Fe^{3+} is produced by the half-reaction at this interface, therefore the amount of Fe^{3+} ions increases over time (increasing function) whereas its concentration profile in space decreases. If you examine the concentration profile as shown in figure 4.15, you can see how the concept of production (or consumption) over time can be visualized through the surface (i.e., the integral) lying between the profile at instant t and the initial profile. This surface represents the amount of species produced (or consumed) per unit surface area between these two instants. In particular, the fact that just as many Fe^{3+} ions are produced as Fe^{2+} ions are consumed is depicted visually in figure 4.15 since both surfaces, denoted by + and –, are equal in absolute value [49].

---

[47] As outlined in section 2.2.1.1, here the diffusion layer thickness depends mainly on the time factor, and the diffusion coefficient of Fe^{2+}. Section 4.3.1.3 provides more quantitative data on the different values of diffusion layer thickness in a semi-infinite transient state.

[48] The diffusion coefficient values can be calculated from the molar conductivities at infinite dilution (see table 4.2 in section 4.2.2.4) using the NERNST-EINSTEIN equation (see section 4.2.1.4) :

$$D_i^0 = \lambda_i^0 \frac{1}{z_i^2} \frac{RT}{\mathcal{F}^2}$$

To get a clearer view of the effect of diffusion coefficient differences between different electroactive species, one should note that the ratio selected for plotting the concentration profiles in figure 4.15 is 2, whereas in actual fact the values shown in table 4.2 give a ratio equal to 1.2 in the case of the Fe^{3+}/Fe^{2+} couple.

[49] This property can be stretched to apply to the differences in concentration profiles at different instants. However remember that this type of reasoning is not applicable to concentration profiles

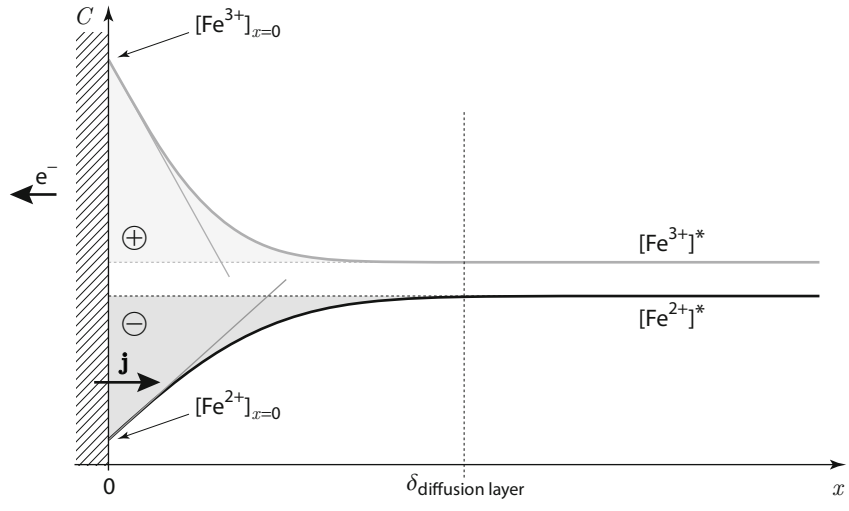

Figure 4.15 - Concentration profiles of Fe^{3+} ions (grey) and Fe^{2+} ions (black) during oxidation
$[Fe^{2+}]_{x=0}$ and $[Fe^{3+}]_{x=0}$: interfacial concentrations,
$[Fe^{2+}]^*$ and $[Fe^{3+}]^*$: bulk concentrations, far from the interface.

The charge balance of the electroactive species in the diffusion layer shows a change in charge distribution. This would also be the case even if the diffusion coefficients were identical. In the example illustrated in figure 4.15, just as in any oxidation half-reaction, the charge balance for the electroactive species reveals a positive charge excess in the diffusion layer in relation to the bulk of the solution. In this example, it results in a decreasing profile for the sum of $2\,[Fe^{2+}] + 3\,[Fe^{3+}]$ in the diffusion layer. The electroneutrality of the solution within the diffusion layer still applies. This means that the other non-electroactive ions (belonging to the supporting electrolyte or the counter-ions if no supporting electrolyte) compensate for these charge modifications in the diffusion layer caused by the redox reaction. For these non-electroactive species, the concentration profiles also present variations in the diffusion layer [50].

Let us return to the example of an oxidation reaction occurring at the interface between a platinum electrode and an aqueous solution containing ferrous and ferric nitrates with a KNO_3 supporting electrolyte. To simplify, we assume that all the ionic diffusion coefficients are close to each other. We have already dealt with the concentration profiles of the electroactive species. However, the concentration profiles of non-electroactive species, which are rarely touched upon because they are often not a subject of great interest, are not flat. We should however keep in mind that although the diffusion fluxes share the same order of magnitude as electroactive species, their relative variations appear to be negligible because these non-electroactive species are much more concentrated. The two approaches outlined below enable one to determine in qualitative terms the shapes of the concentration profiles of the non-electroactive species K^+ and NO_3^-.

in steady or quasi-steady state conditions. In this instance, the significance of the surface lying between the steady-state profile and the initial profile is more complex to interpret. A simple example is explored in appendix A.4.2.

[50] In addition to the next example, one can also refer to the example outlined in appendix A.4.1.

- ***Qualitative reasoning based on there being electroneutrality throughout the electrolyte***

  The oxidation reaction replaces Fe^{2+} ions with Fe^{3+} ions in the electrolyte. As far as electroactive species are concerned, it therefore produces an excess of positive charge in the diffusion layer. This charge excess must be compensated by non-electroactive ions. Here, both types of non-electroactive ions of the supporting electrolyte help compensate for this positive charge excess. There is an excess of NO_3^- anions and a deficit of K^+ cations in the diffusion layer, when compared to the original concentrations (see figure 4.16).

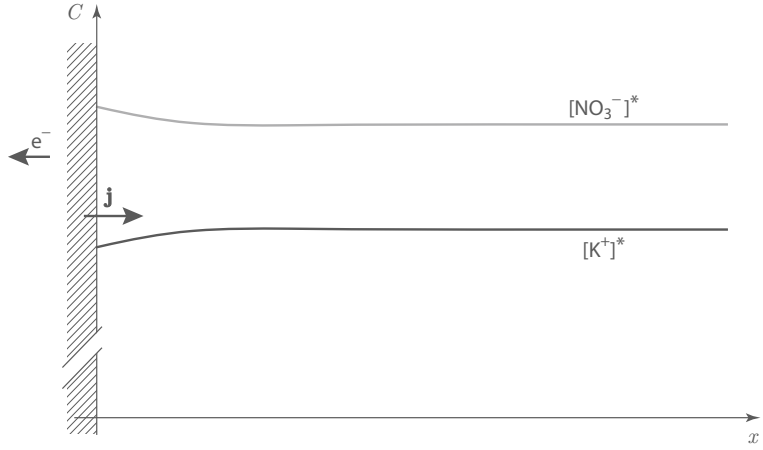

Figure 4.16 - Concentration profiles of non-electroactive ions during an oxidation half-reaction

In this figure, the concentration scale is proportionately eight times smaller than that in figure 4.15. Therefore the origin (zero concentration) cannot be seen here. The difference between the bulk concentrations of the two non-electroactive ions, $[K^+]^*$ and $[NO_3^-]^*$, is explained by the fact that the nitrate ion is also the counter-ion of the two electroactive cations.

- ***Qualitative reasoning based on the molar interfacial fluxes***

  This reasoning can only be strictly applied to interfacial molar fluxes. It can be extended to apply to the whole diffusion layer in a system with unidirectional geometry at steady state, since the molar flux densities in this case are homogeneous. In the other cases, this type of reasoning produces curves that can be considered generally correct in qualitative terms.

  The interfacial conditions for the non-electroactive species are:

$$(N_i)_{x=0} = (N_{i_{\text{diffusion}}})_{x=0} + (N_{i_{\text{migration}}})_{x=0} = 0$$

  In other words, since the interfacial molar fluxes are zero, then the migration and diffusion components at the interface have opposite values different from zero.

  The overall current and the migration current are identical [51]. Anions migrate towards the anode and cations towards the cathode. Here anions migrate towards the interface and cations in the opposite direction. Remember that because there is a supporting electrolyte here, there is a negligible migration of electroactive species. The directions of the molar flux densities in the diffusion layer are represented in figure 4.17, in which only the directions are significant, and the sizes chosen are arbitrary.

  At this interface you therefore have: $(N_{K^+_{\text{migration}}})_{x=0} > 0$ and $(N_{K^+_{\text{diffusion}}})_{x=0} < 0$

$$(N_{NO_3^-_{\text{migration}}})_{x=0} < 0 \quad \text{and} \quad (N_{NO_3^-_{\text{diffusion}}})_{x=0} > 0$$

[51] Assuming here that the diffusion coefficients are equal, this property emerges when writing the various molar fluxes, as explained in section 4.2.1.5.

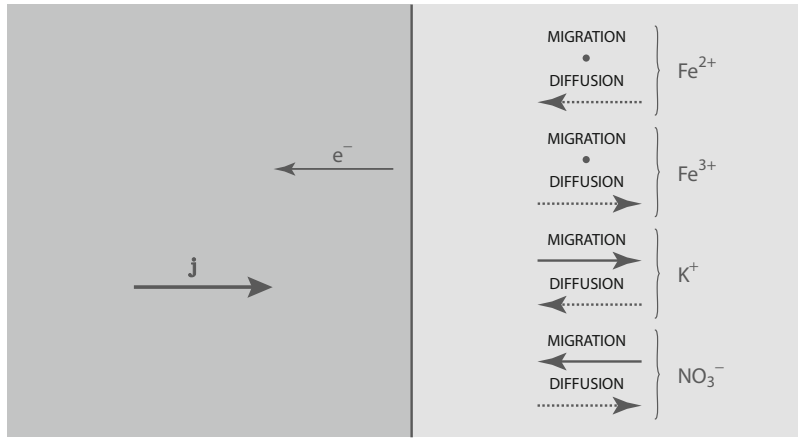

Figure 4.17 - Directions of the molar flux densities in the diffusion layer for oxidation of Fe^{2+} to Fe^{3+}

The diffusion flux of the K^+ ions is directed towards the electrode, and the concentration profile of these ions therefore is increasing. The result can be confirmed either by mathematical equation presenting the molar flux density as being proportional to the opposite of the concentration gradient or by remembering that species move by diffusion from the more concentrated zones towards less concentrated zones. The reasoning applied to the NO_3^- is symmetrical: these ions present a decreasing concentration profile in the diffusion layer.

Obviously, you end up with the same shape as the one found applying the previous reasoning (see figure 4.16) which is based on electroneutrality prevailing throughout the solution.

The two following sections outline two common experimental situations in which both electrodes can be shown to be independent as far as mass transport is concerned:

- a system with no convection and for a limited observation time: the system's transient state is then characterised by semi-infinite mass transport. We will represent qualitatively the shapes of the expected concentration profiles for chronoamperometry (figure 4.18) and chronopotentiometry experiments (see figure 4.19);
- a system with controlled stirring (forced convection): the system quickly reaches a quasi-steady state.

4.3.1.3 - EXAMPLE OF A TRANSIENT STATE: SEMI-INFINITE DIFFUSION

In a convection-free system, and for a limited observation time (when compared to the characteristic time of the system, which itself depends on the diffusion coefficients and the inter-electrode distance) the electrolyte can be separated into three zones: two diffusion layers close to the two reactive interfaces and an intermediate homogeneous zone within the electrolyte. The diffusion layers thicknesses increase with time, but they are both considered as small when compared to the inter-electrode distance. Here one refers to a transient state and each interface is defined as being in a semi-infinite mass transport condition. Both electrodes are independent, in spite of the fact that they are crossed by the same current.

To simplify the description, we choose a system with unidirectional geometriy [52], which contains a supporting electrolyte. Therefore we can ignore the migration of electroactive species in comparison to their diffusion within the diffusion layers. On the other hand, again for reasons of simplicity, we are confining ourselves to fast redox systems which have identical diffusion coefficients for all the electroactive species. In this case, the following elements are brought into play:

- the volume mass balance, which is simply expressed as the second FICK law:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}$$

  with the following initial condition: $t = 0$, $\forall x$, $C_i = C_i^*$.

- FARADAY's law applied at the electrochemical interface and the equation coming from the redox reaction kinetics (for the fast system, it takes the form of the NERNST law with interfacial concentrations [53], written here for the following simple redox couple $\mathrm{Ox} + n\,\mathrm{e}^- \rightleftharpoons \mathrm{Red}$):

$$\forall t \qquad N_{i_{x=0}} = - D_i \left(\frac{\partial C_i}{\partial x} \right)_{x=0} = \frac{\nu_i}{\nu_e} \frac{I}{\mathcal{F} S} \qquad \text{and} \qquad E = E^\circ + \frac{RT}{n \mathcal{F}} \ln \frac{[\mathrm{Ox}]_{x=0}}{[\mathrm{Red}]_{x=0}}$$

- the semi-infinite boundary conditions: the concentrations tend to the initial concentrations, which are the bulk concentrations, when the distances from the interface tend towards infinite (on the scale of the system). To give an equivalent formulation, one can also write that the molar flux density tends towards zero:

$$\forall t \qquad C_i \xrightarrow[x \to \infty]{} C_i^* \qquad \text{or} \qquad N_i = - D_i \frac{\partial C_i}{\partial x} \xrightarrow[x \to \infty]{} 0$$

▸▸ *Chronoamperometry experiment*

Figure 4.18 shows, during a chronoamperometry experiment, typical concentration profiles, at different instants, of the species consumed at the left electrode with no interaction with the right electrode. A constant potential is imposed to an electrode over time and the result in a fast redox system is that the interfacial concentration of the consumed species (here at the left electrode) is fixed [54]. In such a case, the slope of the concentration profile at the interface, namely the current, changes over time [55].

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[52] When dealing with systems with unidirectional geometry, numerous authors would apply the term 'semi-infinite linear diffusion' to the example in question. However, in this book we prefer to use the term 'unidirectional semi-infinite diffusion' because the word linear is ambiguous. It is also often used in opposition to the 'non-linear diffusion', that is to say, it is applied in the mathematical sense. The second FICK law, as it is usually written (the same as in this document), represents a linear differential equation, and is based on the assumption that the diffusion coefficient is a constant. When this approximation does not apply, the mass balance is: $\partial C/\partial t = \partial/\partial x (D \partial C/\partial x)$ and then the differential equation is usually non-linear.

[53] The definition of a fast couple is given in section 4.3.2.6, and the impact on the laws of kinetics is outlined in section 4.3.3.2.

[54] The relationships between the interface concentrations and potential are given in appendix A.4.2 and demonstrated in a case involving equal diffusion coefficients for the two electroactive species.

[55] For the simple systems described here, the current variations over time enables one to calculate the diffusion coefficient of the species in question. This is the COTTRELL law: $I(t) = n\mathcal{F}SC^* \sqrt{D/\pi t}$.

In this chronoamperometry experiment the thickness of the diffuse layer increases with time. One can gain a good order of magnitude for this thickness by looking at the intersection between the interfacial slope of the concentration profile and the initial flat profile: $\sqrt{\pi Dt}$ [56]. Even if this value is sometimes confused with the diffusion layer thickness, it is best still to distinguish between them [57]: for instance, at a distance equal to $\sqrt{\pi Dt}$, the concentration is still 18% off from the initial concentration. The thickness of the diffusion layer is equal to $2.0\sqrt{\pi Dt}$ for an accuracy of 1% and $2.6\sqrt{\pi Dt}$ for an accuracy of 0.1%.

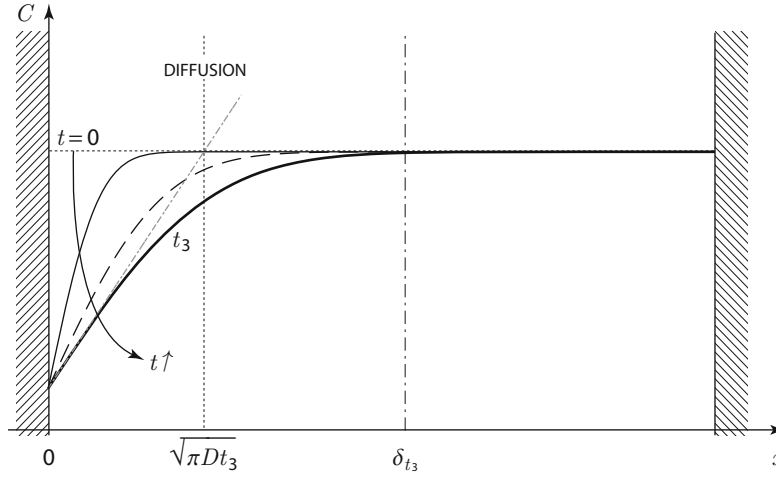

Figure 4.18 - Time evolution of the concentration profile of a species consumed in a chronoamperometry experiment

▸▸ *Chronopotentiometry experiment*

Figure 4.19 shows the results of a chronopotentiometry experiment, that is to say with a constant current density fixed over time. This involves fixing the slope at the interface (left in this case) of the electroactive species' concentration profile. The interfacial concentration then changes over time [58].

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[56] The set of equations defining the system can be analytically integrated using the LAPLACE transform. However, the task of actually solving the equation stretches beyond the goals of this book. Here, we will only retain the orders of magnitude that emerge as a result.

[57] Let us recall that, as defined in section 2.2.1.1, the thickness of the diffusion layer matches the thickness of the volume experiencing significant diffusion phenomena. One can characterise this in quantitative terms, for example, by using a negligible difference of 0.1% (or 1% or 10%… depending on the accuracy required) for the concentration of at least one species compared to the value in the homogeneous zone where diffusion plays a minimal role.

[58] In this type of experiment it is easy to determine the time needed to obtain a near-zero interfacial concentration. In fact, if one continues the experiment, the imposed current can no longer be ensured by the main reaction. At this point another redox system is called into play, which leads to a sharp variation in the potential measured. This characteristic time can be used to determine the mass transport parameters. For a simple system, the equation involved is known as SAND's law:

$$\sqrt{\tau} = \frac{n\,\mathcal{F}\,S\,C^*}{2\,I}\sqrt{D\pi}\,.$$

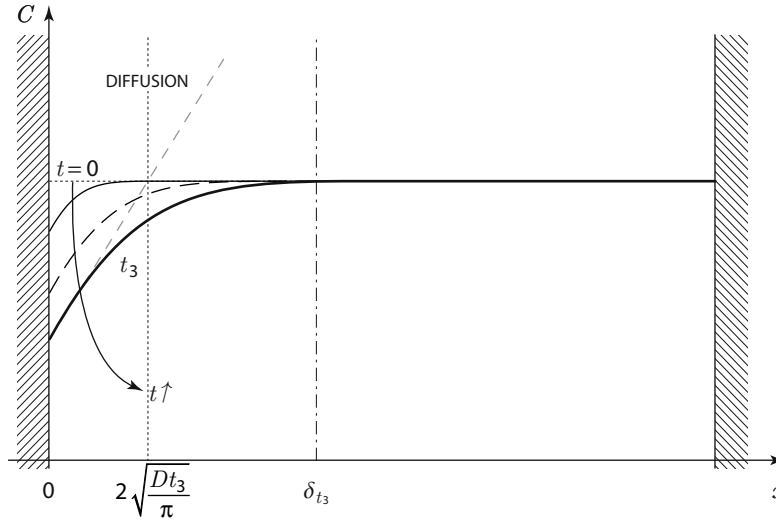

Figure 4.19 - Time evolution of the concentration profile of a species consumed during a chronopotentiometry experiment

In this chronopotentiometry experiment the thickness of the diffusion layer also changes over time. One can gain a good order of magnitude for this thickness by looking at the intersection between the interfacial slope of the concentration profile and the initial flat profile [54]:

$$2\sqrt{\frac{Dt}{\pi}}$$

Although this value is different from the previous one, it still has the same order of magnitude. Here, at a distance equal to this value, the concentration differs by 14% from the initial concentration. The diffusion layer thickness is a multiple of the thickness previously defined, with a factor 2.2 for an accuracy of 1% and 2.8 for an accuracy of 0.1%.

4.3.1.4 - EXAMPLE OF A STEADY STATE: THE NERNST MODEL

There is another usual set of boundary conditions which emerge when, for example, forced convection is imposed within a system. This applies to a small electrolyser with an RDE in analytical chemistry, or in the case of industrial electrolysers when a system is installed which imposes forced circulation of the electrolyte or of the electrode. It can be shown in simple cases that the diffusion layer has a time-independent thickness [59]. This thickness is a function of the stirring conditions and of the transport properties of the mobile species, and is typically about 10 µm. At this point, the NERNST layer model described in section 2.2.1.1 is then used.

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[59] This rather complicated reasoning calls for hydrodynamic calculations to be used to quantify the convection molar fluxes. Such a calculation was developed by LEVICH in the case of the RDE (some authors call it the LEVICH theory). It legitimates the use of the simplified model of the NERNST layer and, above all, provides a mathematical equation to express the thickness of that layer as a function of the system's parameters. This expression, called the LEVICH law, $\delta_i = 1.611\ D_i^{1/3} \nu^{1/6} \Omega^{-1/2}$, is used in appendix A.4.2.

According to this model, the concentration is equal to the initial concentration beyond a distance to the electrode equal to δ_{NERNST}. At steady state this model leads to a mathematical discontinuity in the concentration profiles at this δ_{NERNST} distance from the electrode. The actual steady-state profile does not show any angular point. Therefore the model gives incorrect results in the area surrounding δ_{NERNST}. However, it makes it easy to describe the exact characteristics of the concentration profile at the interface, and therefore it gives a correct value for the current density.

According to the NERNST model, the concentration profile of the electroactive species within the diffusion layer is described by the following system of equations:

$$\frac{\partial C_i}{\partial t} = 0 = D_i \frac{\partial^2 C_i}{\partial x^2}$$

and the following boundary conditions:

$$N_{i_{x=0}} = - D_i \left(\frac{\partial C_i}{\partial x} \right)_{x=0} = \frac{\nu_i}{\nu_e} \frac{I}{\mathcal{F} S}$$

$$C_{i_{x \geq \delta_{\text{NERNST}}}} = C_i^* \qquad \text{(fixed concentration at } \delta_{\text{NERNST}})$$

Figure 4.20 shows, during a chronopotentiometry experiment, typical actual concentration profiles, at different instants, of the species which is consumed at the left electrode, with no interaction at the right electrode [60].

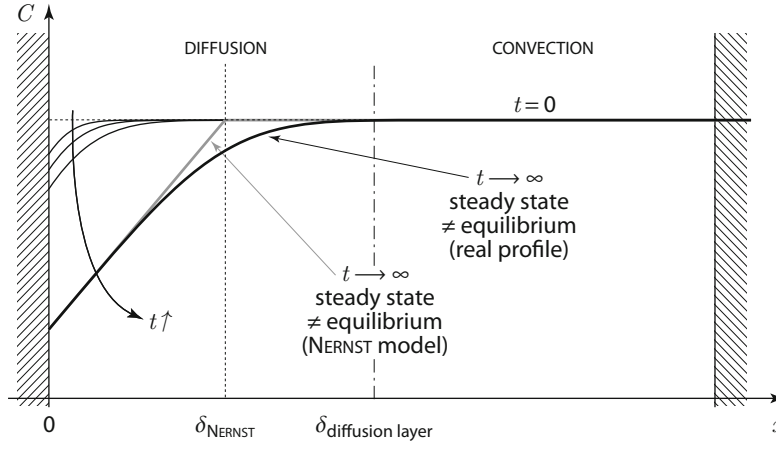

Figure 4.20 - Time evolution of the concentration profile of a species consumed in a system with forced convection

[60] As previously mentioned in note [82] of section 1.6.3, the term chronopotentiometry is used here in its etymological sense. In other words, it is not confined to cases where diffusion is the only mass transport mode for the electroactive species. Although forced convection is imposed on the system, which rapidly reaches a steady state as a result, here we are partly focusing on the transient period leading up towards that state. Therefore, we are interested in the development of the concentration profile over time when a current is imposed. In addition, the current imposed must be lower, in absolute value than a limiting value, which correlates with a steady-state interfacial concentration equal to zero. This concept of a limiting current, which has already been introduced in section 2.3.3.1 in qualitative terms when describing the current-potential curves, is outlined in quantitative terms in section 4.3.3.1.

A steady state with a non-zero current[61] is reached very quickly in these forced convection conditions. The interfacial slope is identical to that in the NERNST model as shown in figure 4.20. The NERNST layer thickness is lower than that of the diffusion layer since, at that distance from the electrode, the actual profile[62] still has a significant slope with a relative concentration difference of 11% with respect to the initial concentration. The diffusion layer thickness is equal to 1.5 δ_{NERNST} for a target accuracy of 1% and to 1.8 δ_{NERNST} for a target accuracy of 0.1%.

These few examples illustrate how one can, in simple cases, represent the concentration profiles in qualitative terms as a function of the system's specific boundary conditions. They also highlight the fact that obtaining a steady state with a non-zero current requires specific experimental conditions.

4.3.1.5 - DIRECTIONS OF THE VARIOUS CURRENT DENSITIES

One can come across a whole range of possible movement directions for electroactive species, by migration and diffusion, depending on their charge number.

The migration current direction is generally the same as that for the overall current, which in turn is directly related to the redox reaction's direction of advancement. The diffusion current direction can often be determined by difference, as illustrated in the examples below.

- In each of the following three cases, illustrated in diagrams in figures 4.21, 4.22 and 4.23, the redox half-reaction is the reduction of Cu(II):

  $$Cu(II) + 2\,e^- \longrightarrow Cu$$

  The sizes of the molar flux density vectors are arbitrarily chosen. Only their signs are significant.

  - Cu(II) has the chemical form of a cation: for example, in a $Cu(NO_3)_2$ aqueous solution with no supporting electrolyte

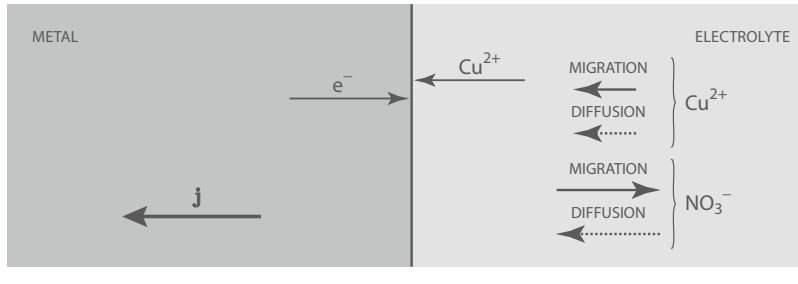

Figure 4.21 - Directions of the molar flux densities

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[61] By using the results from the preceding example, it is possible to estimate the time needed to reach the steady state: it is the time value such that $\sqrt{Dt}$ reaches the value of the NERNST layer, 10 µm. For a diffusion coefficient of about 10^{-5} cm^2 s^{-1}, it comes out as 0.1 s. Therefore, in usual experimental conditions, the characteristic time needed to reach the steady state is small compared to the total length of the experiment.

[62] In more precise terms, it is the concentration profile resulting from the LEVICH calculation.

- Cu(II) is in an anionic complexed form: for example, in a $K_2Cu(CN)_4$ aqueous solution with no supporting electrolyte

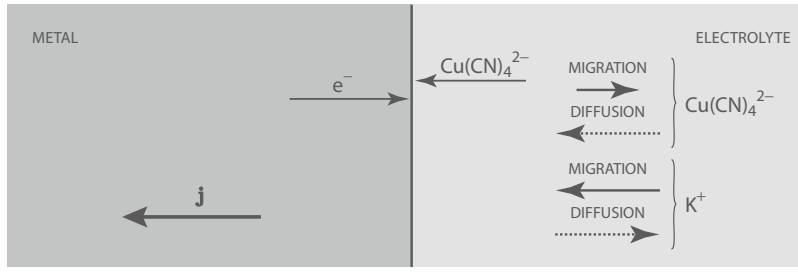

Figure 4.22 - Directions of the molar flux densities

- Cu(II) is in a neutral complexed form: for example, in a $CuCl_2$ + KCl aqueous solution

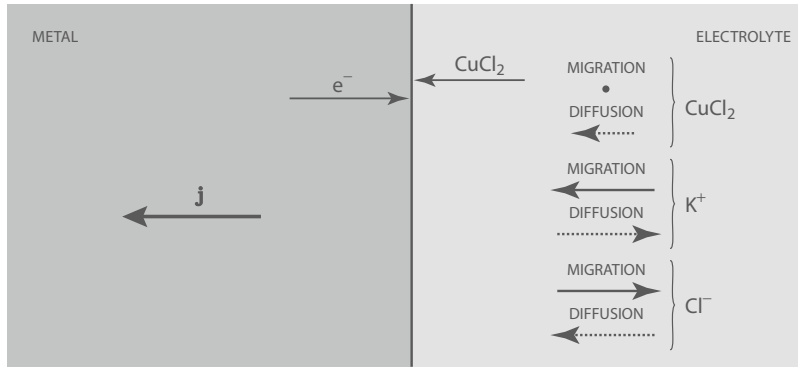

Figure 4.23 - Directions of the molar flux densities

As in the case of all non-electroactive species, the ions of the supporting electrolyte have components for migration and diffusion movement that are opposite in directions, and compensate each other perfectly in the area next to the electrode [63].

4.3.2 - KINETIC MODEL FOR A HETEROGENEOUS REACTION

4.3.2.1 - GENERAL

Many phenomena may occur when a current flows through an electrochemical interface:

- charge transfer reactions in the double layer,
- mass transport by diffusion, migration and convection in the electrolyte,
- homogeneous chemical or redox reactions in the electrolyte,
- adsorption-desorption reactions in the double layer,
- reactions between adsorbed species in the double layer,
- insertion reactions in the electrode: concentration profiles of inserted species then develop in the electrode volume,

[63] Section 4.3.1.2 gives an example of the concentration profile for the ions of the supporting electrolyte.

- interfacial diffusion along the interface (surface diffusion),
- crystallisation, etc.

Interfacial electrochemistry focuses on the charge transfer reaction, but it is not usually possible to dissociate the latter from the other phenomena.

In the case of charge transfer, which occurs in the double layer, the driving force is related to the internal potential difference across the double layer. More precisely, it is linked to the difference between the potentials of the metal and the electrolyte at the HELMHOLTZ plane[64].

4.3.2.2 - RATE OF A HETEROGENEOUS REACTION

Electrochemical kinetics represents a particular category of chemical kinetics, featuring a set of specific characteristics that will be outlined here.

We will focus on electrochemical reactions, which occur at interfaces, and which are therefore surface reactions and not volume reactions. The surface reaction rate is therefore defined as follows:

$$v = \frac{1}{\nu_i}\,\frac{1}{S}\left(\frac{\partial n_i}{\partial t}\right)_{\text{interface}}$$

with ν_i representing the algebraic stoichiometric number of species i in the reaction in question. A surface reaction rate is expressed in mol m^{-2} s^{-1}.

As in the case of chemical reactions in volume, surface reactions can be broken down into a set of elementary steps. When applying the VAN'T HOFF equation the overall order for each elementary step in the rate law is equal to the absolute value of the sum of the stoichiometric numbers of the reactants. In addition, the partial order of each reactant is equal to the absolute value of its stoichiometric number in the reaction in question. This gives the following equation:

$$v = k \prod_{i=\text{reactant}} (C_{i\,\text{interface}})^{|\nu_i|}$$

If one of the reactants is in much larger amount than the other reactants, then one can assume that its concentration is constant. The corresponding concentration is included in the rate constant, thus reducing the order of the rate law, written with a pseudo-constant.

As the concentration of free electrons in a metal is much greater than that of electroactive compounds in an electrolytic solution, then one can assume that this concentration is constant, and it no longer features in the equation for the apparent rate law of the elementary redox half-reactions at a metal|electrolyte interface. This would be different if we wanted to write kinetic laws for a redox half-reaction at an interface between a semiconductor and an electrolyte. However, here the description will be confined to metallic electrodes.

For example, the redox half-reaction of the Fe^{3+}/Fe^{2+} couple, which can be considered as an elementary step, corresponds to the following reactions:

---

[64] See a simplified description of the double layer in section 3.3.1.

$$Fe^{2+} \xrightarrow{v_{oxidation}} Fe^{3+} + e^-$$

$$Fe^{3+} + e^- \xrightarrow{v_{reduction}} Fe^{2+}$$

The rate law at a metal | electrolyte interface is:

$$v_{oxidation} = k_{oxidation} [Fe^{2+}]_{interface}$$

$$v_{reduction} = k_{reduction} [Fe^{3+}]_{interface}$$

For this mechanism, called an E mechanism [65], the rate constants are expressed in m s^{-1}.

Other redox-type elementary mechanisms exist in electrochemistry:

- electrosorption, where one of the redox species is in an adsorbed state,
- insertion, where one of the redox species is an insertion compound,
- deposition, where one of the redox species is a solid.

The following description is confined to systems that follow an E mechanism at a metallic electrode. As is usual in most documents dealing with this aspect of electrochemistry, we have taken a redox reaction involving only two species, Ox and Red, with $|\nu_{Ox}| = |\nu_{Red}| = 1$, but possibly $|\nu_e| = n \neq 1$. However, according to kinetic theory and mechanism, an elementary step can only involve few species and in particular the exchange of several electrons is unlikely in such a step. When a redox couple involves two or more exchanged electrons, then the overall number n is often involved in the final equation of the current-potential curve. However, all the kinetic equations must be written for each elementary step involved. This generally complex task will not be tackled in this document.

4.3.2.3 - SIMPLIFIED KINETIC MODEL OF THE E MECHANISM (SINGLE STEP)

In the case of a redox reaction, the driving force for the reaction, and consequently for the rate constants, in particular depends on the potential difference at the interface. More precisely, this driving force depends on the difference between the potential at the surface of the metal and the potential in the electrolyte at the very point where the electroactive species is located when the electron transfer occurs. The kinetic models which reflect precisely these features are complex, and therefore we are kee ping ourselves confined to equations based on common and simplified descriptions for electrochemical kinetics for the E mechanism. In this context, any changes in the redox reaction rate constant can be described using the following two kinetic parameters:

- the standard rate constant of the redox reaction, denoted by $k°$, which is homogeneous to the rate constant and therefore expressed in m s^{-1} (or also cm s^{-1});
- the symmetry factor, denoted by α, which is a dimensionless number between 0 and 1, defined here for the reaction in the direction of oxidation [66].

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[65] Here E stands for ' electrochemical '. In this nomenclature, a volume reaction step in the electrolyte is denoted by C. One of the most frequent complex mechanisms is the EC mechanism.

[66] Note that, in some documents, notations such as $\alpha_{oxidation}$ and $\alpha_{reduction}$ are used, with $\alpha_{oxidation} + \alpha_{reduction} = 1$, since the ratio between the two kinetic constants must be equal to the

The kinetic rate constants are then expressed as:

$$k_{\text{oxidation}} = k^\circ \, \mathrm{e}^{+\alpha \frac{n\mathscr{F}}{\mathrm{R}T}(E-E^\circ)}$$

$$k_{\text{reduction}} = k^\circ \, \mathrm{e}^{-(1-\alpha)\frac{n\mathscr{F}}{\mathrm{R}T}(E-E^\circ)}$$

Consequently, k° represents the oxidation and reduction rate constant value at the standard potential E°.

In most cases it is difficult to give a precise physical meaning to α. However, for very simple species, such as proton electrosorption for instance, this parameter characterises the difference in curvature between the system's potential energy curve in its oxidised state (proton) and in its reduced state (adsorbed hydrogen), depending on the distance to the metal surface. Based on this model, the MORSE potential wells are represented by parabolic curves around the minimum, as shown in figure 4.24.

If one wanted to take a more comprehensive approach, then one could resort to the activated complex model for reactions in a homogeneous phase. Here we could say that the α parameter gives the link between the thermodynamic characteristic, $\Delta_\mathrm{r}G^\circ$, and the kinetic characteristic, namely the GIBBS energy of activation, $\Delta G^{\neq}$.

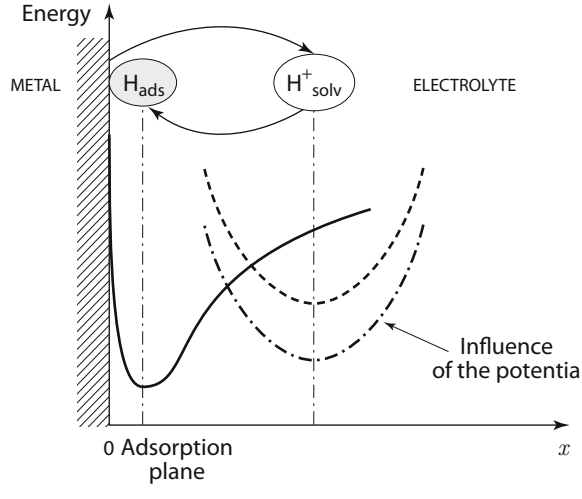

Figure 4.24 - Shape of the potential wells for the reactants and the products of the proton electrosorption reaction: $H^+_{solv} + e^- \longrightarrow H_{ads}$

This simplified description implies in particular that the medium is ideal (with activity coefficients equal to 1) or at least it implies that the activity coefficients of the species in question can be seen as constant, while the concentrations vary due to the current flow. This is true in particular in systems with a supporting electrolyte, because the ionic strength is fixed by the supporting electrolyte and remains unchanged throughout the experiment. Here we assume that the term involving activity coefficients is constant, and furthermore that it is included in the reaction's standard rate constant.

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thermodynamic equilibrium constant. Some authors may prefer to choose the $\alpha_{\text{reduction}}$ parameter, although here $\alpha_{\text{oxidation}}$ has been chosen.

To simplify the notations, a parameter is sometimes used, denoted by ξ, called the ' dimensionless potential ' which for a given couple is defined by the following equation:

$$\xi = n \frac{\mathscr{F}}{\mathrm{R}T} (E - E^\circ) = n f (E - E^\circ)$$

and, at 25°C : $f = \frac{\mathscr{F}}{\mathrm{R}T} = 38.9\ \mathrm{V}^{-1}$ and $\frac{1}{f} = 25.7\ \mathrm{mV}$

we then have:

$$k_{\text{oxidation}} = k^\circ\, \mathrm{e}^{+\alpha \xi}$$

$$k_{\text{reduction}} = k^\circ\, \mathrm{e}^{-(1-\alpha) \xi}$$

In electrochemistry, the notion of rate is used to quantify a system's ability to pass more or less current when equilibrium is disrupted. This property is usually determined by many parameters. For example, electrochemical reactions are generally associated with mass transport, namely to provide the interface with a reactant or to remove a product.

Numerous terms are put to use in the field of electrochemical kinetics to characterise typical situations which are limiting cases with particular shapes for the corresponding current-potential curves. In scientific literature, these terms are not always applied with the greatest rigour. In the forthcoming sections we will give a precise definition for the common terms: nernstian redox systems in section 4.3.2.4; reversible/irreversible redox reactions in section 4.3.2.5; slow/fast redox systems in section 4.3.2.6.

4.3.2.4 - RATE-LIMITING OR DETERMINING STEP

As already noted above, when there is a current flow then mass transport phenomena are automatically brought into play in addition to the electron transfer itself. The link between current and voltage generally involves all of the system's kinetic parameters. It is often interesting to consider the two following limiting cases, which are illustrated here on the E mechanism (remember we assume that $|\nu_{\mathrm{Ox}}| = |\nu_{\mathrm{Red}}| = 1$):

- the current/voltage link only involves quantities related to mass transport phenomena. In this case one says that the mass transport phenomena are rate-limiting or rate-determining, according to kinetic theory, or that the system is controlled by mass transport. In these conditions, the interfacial concentrations obey the following equation:

$$E = E^\circ + \frac{\mathrm{R}T}{n\mathscr{F}} \ln \frac{[\mathrm{Ox}]_{\text{interface}}}{[\mathrm{Red}]_{\text{interface}}}$$

  This equation corresponds to the NERNST law written with the interfacial concentrations in the argument of the logarithm. Beware that it is not the NERNST law in its strictest sense because, in the case here of a system carrying a current, the interfacial concentrations are necessarily different from the concentrations in the bulk of the solution (even if they may be very close in numerical terms). These parallel ways for writing the equation help to explain the origin of the term nernstian, which is often used to qualify such systems[67]. Some authors also use the terms ' local equilibrium at the interface ' which is incorrect since this interface crossed by a current is not in equilibrium;

[67] These two concepts (control by mass transport and nernstian system) as terms are not strictly synonymous. Quasi-fast redox couples (see section 4.3.2.6) close to equilibrium conditions are nernstian, but they are not strictly controlled by mass transport.

- the current/voltage link only involves quantities which are related to electron transfer. One then says that the electron transfer step is rate-limiting or rate-determining, based on kinetic theory, or that the system is controlled by redox kinetics. In these conditions, the concentrations are practically constant throughout the electrolyte, and the interfacial concentrations can be taken as equal to the initial concentrations or to the bulk concentrations, [Ox]* and [Red]*:

$$[\mathrm{Ox}]_{\mathrm{interface}} \approx [\mathrm{Ox}]^* \quad \text{and} \quad [\mathrm{Red}]_{\mathrm{interface}} \approx [\mathrm{Red}]^*$$

Generally, these limiting cases only apply in a restricted potential range.

4.3.2.5 - REVERSIBILITY CHARACTER OF AN ELEMENTARY REACTION STEP

In kinetic theory, reversibility as a concept is defined in relation to reaction rates. In a reaction mechanism, when an elementary step can be said to occur in both directions, the rate of this step is always equal to the difference between the forward rate, $v_{\rightarrow}$, and the backward rate, $v_{\leftarrow}$:

$$v = v_{\rightarrow} - v_{\leftarrow}$$

This step is called reversible in terms of kinetic theory, which is different from the thermodynamic meaning, if and only if the overall reaction rate is very small compared to both the forward and backward rates:

$$v \ll v_{\rightarrow} \quad \text{and} \quad v \ll v_{\leftarrow}$$

An important consequence of this is that the forward and backward rates are practically equal:

$$v_{\rightarrow} \approx v_{\leftarrow}$$

Remember that the rates are not strictly equal. Therefore it would be wrong to write their difference, in other words the overall rate, as equal to zero. To give a numerical example, if the forward rate were equal to 1 000 001 and the backward rate equal to 1 000 000 (in mol m^{-2} s^{-1}), the overall rate, equal to 1, is different from zero. The same type of confusion is made by authors who use the term local equilibrium to refer to a reversible heterogeneous reaction [68].

This step is called irreversible, for example in the forward direction, if and only if the backward rate is negligible compared to the forward rate:

$$v_{\rightarrow} \gg v_{\leftarrow}$$

Consequently, the overall rate is almost equal to the forward rate:

$$v \approx v_{\rightarrow}$$

In such a case, the overall reaction is usually written using only one arrow.

Still following these two definitions, keep in mind that one can have a reaction step which is neither reversible nor irreversible.

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[68] Similarly, the term reversible is not synonymous with nernstian. Even for an E mechanism, it is possible to find cases where nernstian systems are reversible only in a very narrow potential range close to equilibrium.

This typical case is sometimes referred to as quasi-reversible in scientific literature [69].

In electrochemistry, given that reaction rates depend on the potential, then these concepts need to be examined for each value of this parameter. A given system may present a reversible charge transfer step in one particular potential range and an irreversible one in another range. Therefore, strictly speaking, one should not use the term reversibility about a redox couple, but rather qualify the reversibility of the corresponding redox reaction at a given potential.

4.3.2.6 - RAPIDITY OF A REDOX COUPLE

The concept of reversibility as defined above is sometimes used incorrectly and mixed up with the concept of the rapidity of a couple, which is defined in this section. Even if a reversible redox reaction involves a fast redox couple in many circumstances, these two notions are nonetheless different in nature.

To define in precise terms the concept of rapidity of a redox couple for an E mechanism, one says that a redox couple is fast (respectively slow) if the standard rate constant of the redox reaction is very high (respectively very low) compared to the mass transport rate constant (denoted by m and expressed in m s^{-1}):

$$\text{fast redox couple} : \frac{k^\circ}{m} \gg 1 \qquad \text{slow redox couple} : \frac{k^\circ}{m} \ll 1$$

In the simple examples considered here, the mass transport rate constant is the ratio of the diffusion coefficient of the species in question to the diffusion layer thickness of the latter [70]:

$$m = \frac{D}{\delta}$$

Rigorously speaking, one should take into account all the mass transport rate constants of the various electroactive species.

The concept of fast or slow couples is therefore independent of the potential applied, since it is intrinsic to the system. However it does depend on other experimental parameters through the mass transport rate constant. The latter parameter is in fact a function of the quantities specific to the mass transport of the species in question (diffusion coefficient or electrochemical mobility), but it also depends on other characteristics in the system which vary according to each type of experiment, as illustrated in the examples below.

---

[69] This terminology is rather clumsy since general cases are no more quasi-reversible than quasi-irreversible.

[70] In process engineering this parameter is called the mass transfer constant. It is denoted by some authors by k_m (a notation which has the advantage of underlining the parallel shown with the reaction rate constants denoted by k). To be precise, this quantity is not based on the diffusion layer thickness as defined in this document, but rather the value calculated from the interfacial slope of the concentration profile (see section 4.3.1.4). For example, in the case of an experiment involving forced convection, one should use the thickness of the NERNST layer in order to define the mass transport rate constant.

When dealing with the same redox couple, it can behave either like a slow system or a fast system, depending on the experimental conditions chosen:

- in a steady-state experiment using a rotating disc electrode, the mass transport rate constant, m, depends on the rotation speed of the electrode and on the solvent viscosity;
- in a voltammetry experiment, m depends on the sweep rate used;
- in a chronoamperometry or chronopotentiometry experiment, m depends on the time elapsed;
- in a thin-layer cell, m depends on the inter-electrode distance, etc.

To fix some orders of magnitude, let us imagine a redox couple with an E mechanism in an aqueous solution, with usual values for the diffusion coefficients, namely about 10^{-5} cm^2 s^{-1}:

- for an experiment using an RDE (with a rotation speed of around 1000 rpm [71]), the redox system will be considered as:

  fast if $k^\circ \gg 10^{-2}$ cm s^{-1}

  slow if $k^\circ \ll 10^{-4}$ cm s^{-1}

- for a voltammetry experiment, a redox couple with a standard reaction rate constant of $k^\circ = 10^{-3}$ cm s^{-1} will be fast or slow, depending on the sweep rate:

  fast if $v_{\text{sweep}} \ll 0.1$ mV s^{-1}

  slow if $v_{\text{sweep}} \gg 1$ V s^{-1}

- for a chronoamperometry experiment without convection a redox couple with a standard reaction rate constant of $k^\circ = 10^{-3}$ cm s^{-1} will be considered, depending on the length of the experiment, as:

  fast if $t \gg 1000$ s

  slow if $t \ll 0.1$ s

Remember that when defining in full the complex phenomenon that is associated with current flow, it is not enough to only use the concept of the rapidity of a redox couple. In particular, if the characteristics related to current flow actually depend on the k°/m ratio, they also vary as a function of the electrode potential and of the concentrations in the solution.

4.3.3 - POLARISATION OF AN ELECTROCHEMICAL INTERFACE AT STEADY STATE

The polarisation of an electrode is a function of the current flowing through it, and the product πI is usually positive [72]. Here we will give some quantitative equations but keep to simple cases. These examples highlight the key phenomena involved, and their impact on the shape of the steady-state current-potential curves.

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[71] rpm: revolution per minute.

[72] This property is illustrated in section 2.3.1 which outlines how to plot a current-potential curve in qualitative terms.

Let us consider an electrode interface in a unidirectinal system where a redox reaction is occurring, that is wholly undisturbed by the phenomena occurring at the other electrode. Steady-state conditions prevail here, and moreover, migration phenomena are negligible. This case applies, for instance, to a system with a supporting electrolyte. When the latter is present, one can ignore both the ohmic drop phenomena, and also the migration of the electroactive species.

4.3.3.1 - CONCENTRATION PROFILES AND EQUATION FOR THE LIMITING CURRENTS

The steady-state current-potential curves reflect the influence of the mass transport kinetics of the electroactive species by showing current plateaus, whatever the redox kinetics is. The concentration profiles of the electroactive species account for this particular situation, as illustrated in figure 4.25 for the Fe^{3+}/Fe^{2+} couple.

Here one can recognise several properties that are typical of the concentration profiles of electroactive species at steady state [73]: the concentration profiles are linear for a Fe^{3+}/Fe^{2+} couple with a supporting electrolyte and unidirectional geometry. To simplify, we assume that the diffusion coefficients are equal. The diffusion layer thickness is fixed since the steady state has been reached, and it is identical for both electroactive ions. In the homogeneous solution (such as a stirred solution for instance) the concentration of Fe^{2+} ions is set higher than the concentration of Fe^{3+}. The Fe^{3+}/Fe^{2+} couple chosen in this example is fast, however this feature has no impact on the shape of the concentration profiles plotted here, nor so on the equations written in this section (only the shape of the current-potential curve will be affected).

In both anodic and cathodic domains of the current-potential curve, the concentration profiles for the operating points with a current equal to the limiting current all show that the interfacial concentration of the species consumed is negligible compared to the concentration in the bulk of the solution, i.e., the reductant Fe^{2+} in oxidation and the oxidant Fe^{3+} in reduction. The mathematical equations for the limiting currents indicated below are derived themselves from this peculiarity in the concentration profile. To obtain general equations we consider possible different diffusion coefficients for the oxidant and the reductant and any stoichiometric numbers, thus ignoring the simplification introduced in figure 4.25.

In such a system with unidirectional geometry, where diffusion is the only transport mode for the electroactive species, the molar flux density at steady state is homogeneous and proportional to the slope of the linear concentration profile:

$$N_{i\,0\le x\le\delta_i} = N_{i\,x=0} = -\,D_i\,\frac{C_i^{*} - C_{i\,x=0}}{\delta_i}$$

Remember that FARADAY's law produces the relationship to the current. Here, for a redox reaction with a 100% faradic yield, the slope of the concentration profile is also proportional to the current:

$$N_{i\,x=0} = \frac{\nu_i}{\nu_e}\,\frac{I}{\mathcal{F}\,S} = -\,D_i\,\frac{C_i^{*} - C_{i\,x=0}}{\delta_i}$$

[73] These characteristics correspond to the NERNST model described in section 4.3.1.4.

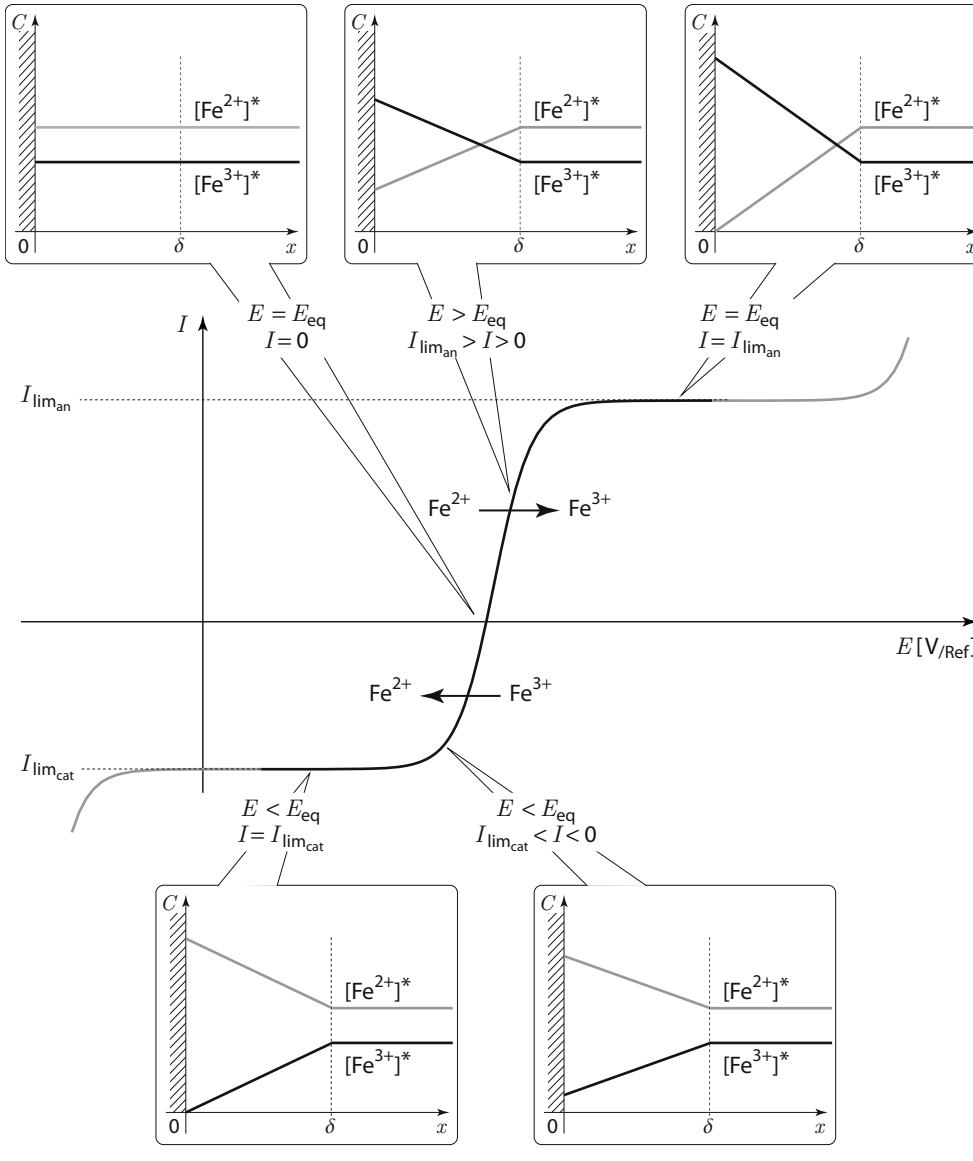


Figure 4.25 - Shape of the concentration profiles for various points on the steady-state current-potential curve for a Fe^{3+}/Fe^{2+} system

In the particular case of where the interfacial concentration of the consumed species is zero, or more precisely is negligible compared to the bulk concentration, the following equation emerges for the limiting current:

$$I_{\text{lim}} = -\frac{\nu_e}{\nu_i} D_i \mathcal{F} S \frac{C_i^*}{\delta_i}$$

Using the kinetic mass transport constant, m_i, which is the ratio of the diffusion coefficient to the diffusion layer thickness:

$$m_i = \frac{D_i}{\delta_i}$$

one obtains the following expression of the limiting current:

$$I_{\text{lim}} = -\frac{\nu_{\text{e}}}{\nu_i}\mathcal{F}\, S\, m_i\, C_i^*$$

with: m_i the mass transport rate constant of the consumed species i [m s^{-1}]
C_i^* the concentration of the consumed species i in the bulk electrolyte [mol m^{-3}]
$\mathcal{F}$ FARADAY's constant [C mol^{-1}]
ν_i the algebraic stoichiometric number of the consumed species i
ν_{e} the algebraic stoichiometric number of the electron
I_{lim} the algebraic limiting current [A]
S the area of the interface surface [m^2]

Remember that for this equation, the reactant is the reductant in an oxidation reaction, while the reactant is the oxidant in a reduction reaction. Therefore in the previous example, i.e., the Fe^{3+}/Fe^{2+} couple, one has the following:

$$I_{\text{lim cat}} = -\frac{\nu_{\text{e}}}{\nu_{\text{Ox}}}\mathcal{F}\, S\, m_{\text{Ox}}\, [\text{Ox}]^* = -\mathcal{F}\, S\, m_{Fe^{3+}}\, [Fe^{3+}]^*$$

$$I_{\text{lim an}} = -\frac{\nu_{\text{e}}}{\nu_{\text{Red}}}\mathcal{F}\, S\, m_{\text{Red}}\, [\text{Red}]^* = \mathcal{F}\, S\, m_{Fe^{2+}}\, [Fe^{2+}]^*$$

Given the sign conventions used, once again one finds that the anodic limiting current is positive, while the cathodic one is negative.

The general link between the current and the concentration profiles also describes the interfacial concentrations at any working point. Therefore, based on the equations outlined above (FARADAY's law and limiting current) one has:

$$\frac{I}{I_{\text{lim}}} = \frac{C_i^* - C_{i_{x=0}}}{C_i^*}$$

hence the following equation for the interfacial concentration:

$$C_{i_{x=0}} = C_i^*\left(1 - \frac{I}{I_{\text{lim}}}\right)$$

This algebraic equation must involve the anodic limiting current for the reductant and the cathodic limiting current for the oxidant.

Therefore, in the case of the Fe^{3+}/Fe^{2+} couple, one has:

$$[Fe^{2+}]_{x=0} = [Fe^{2+}]^*\left(1 - \frac{I}{I_{\text{lim an}}}\right)$$

$$[Fe^{3+}]_{x=0} = [Fe^{3+}]^*\left(1 - \frac{I}{I_{\text{lim cat}}}\right)$$

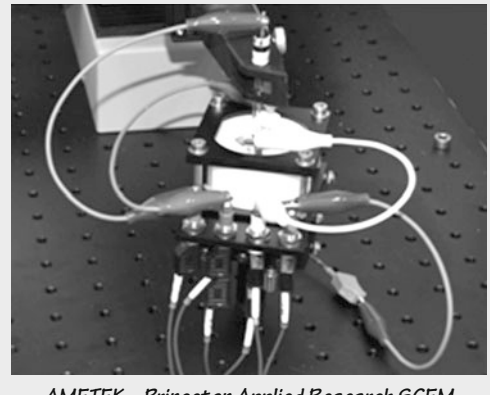
One then finds for example that the interfacial concentration in Fe^{2+} is less than the bulk value, in the case of an anodic current ($I > 0$). On the other hand, the Fe^{3+} concentration is larger in the zone next to the interface than in the bulk of the electrolyte ($I/I_{\text{lim}_{\text{cat}}} < 0$).

SCANNING ELECTROCHEMICAL MICROSCOPE

Document written with the kind collaboration of Dr Rob SIDES, Applications Specialist,
AMETEK - Princeton Applied Research, Oak Ridge, in USA

In a traditional electrochemical measurement, a potentiostat measures an average current over the entire electrode/electrolyte interface. Rarely is a sample homogenous. Samples often consist of local sites of passivate/active nature or sites of anodic/cathodic character. This need to investigate localized electrochemistry led to the development of the Scanning ElectroChemical Microscope (SECM). Since the imaging mechanism is based on electrochemistry, the applications of a SECM are as varied as the applications offered by electrochemistry itself. Some key applications include biological sensors, reaction kinetics, porous membrane study, fuel cell catalysts, and corrosion mechanisms.

The SECM integrates a positioning system, a bipotentiostat, and an ultramicroelectrode tip. The positioning system moves the tip close to the surface of the sample. The bipotentiostat polarizes both the sample and the tip independently and measures both resulting currents. The tip is an ultramicroelectrode with a specific tapered polish and active radius lower than 100 microns. The positioning system scans the measurement tip and charts position with measured electrochemical parameters, creating a data map of the local current.



AMETEK – Princeton Applied Research SCEM

One particular SECM experiment is the approach curve in feedback mode. In this experiment, a redox active salt, the mediator, is introduced into the electrolyte. A single potentiostat polarizes the tip to cause an electrochemical reaction; however, the sample itself is not polarized. The resulting current is recorded as the tip is moved closer towards the sample. When the tip is positioned appropriately close to the sample, a local response is seen. If the specific location on the sample is conductive, the resulting nernstian response observed at the surface sample causes the current to increase when compared to the ' bulk current ' (i.e., when the tip is far from the substrate). This is called ' positive feedback '. If the specific location on the sample is insulating, then mass transport to the electrode of the tip is hindered, and the current decreases when compared to the bulk current. This is called ' negative feedback '. A range of intermediate types of behavior may also occur with different samples. The quantitative analysis of such approach curves allows for a very accurate analysis of local surface kinetics to be carried out.

For imaging experiments, the same kind of approach curve is also used in order to position the tip in the sample's local imaging zone, without actually making contact with it. In surface imaging experiments the tip-to-sample distance is typically 2 to 4 times the probe diameter. Given that the tip measures 10s microns, it is important to establish a non-visual means by which to identify this zone.

In generator-collector mode, the SECM uses the bipotentiostat's second channel to polarize the sample and to actively control the redox reactions within the system. For example, if the redox species exists in the bulk solution in the oxidation state, Ox, then the sample can be polarized so as to electrochemically convert species Ox into species Red. If the tip is polarized to a more positive value, sufficient to cause an electrochemical reaction with Red, no bulk current is initially generated at the tip, since the initial Red concentration is negligible. However, when the tip enters into an area where products resulting from the electrochemical reaction at the sample (Red) can be found, then a current is generated at the probe. This provides an imaging mechanism, which enables the probe to determine in spatial terms where exactly on the surface of the sample the electrochemical reactions are occurring most efficiently. A high current at the tip is due to a greater concentration of Red at the probe, which is in turn due to a more active Ox → Red transition in that position.

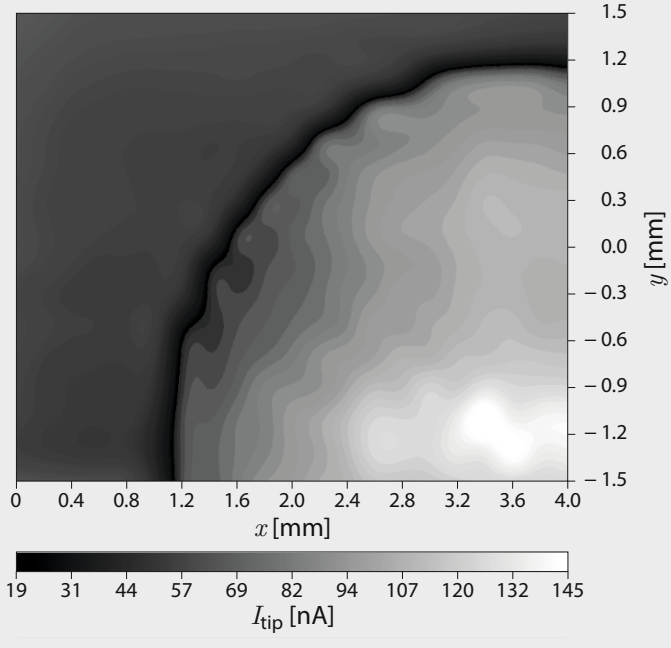


Image generated using Generator-Collector Mode by Princeton Applied Research SECM
Sample is epoxy/gold in the presence of ferricyanide. Note the high current (activity) over the gold.

Sensor evaluations or fuel cell catalyst evaluations commonly use the oxygen reduction reaction and do not require the use of any external salt. The tip can use electrochemistry to detect products as they diffuse through porous membranes. Corrosion products may be able to undergo further electrochemical reactions, or could additionally benefit from using an ion-selective electrode as the tip. Many different applications can benefit from the ability to both control and monitor electrochemical reactions, with the added dimension of being able to provide spatial resolution thanks to the SECM.

In the three following sections, we focus on redox couples following the E mechanism (with $|\nu_{Ox}| = |\nu_{Red}| = 1$).

4.3.3.2 - FAST REDOX SYSTEMS

Remember that such a redox couple is called fast if its standard redox rate constant is very large compared to the mass transport constants of the electroactive species. Fast redox couples can be shown to be nernstian and reversible systems, in a potential range surrounding the standard potential. As for large interface polarisations in this potential range, the rate limitation due to mass transport phenomena gives rise to a limiting current at steady state. With these fast systems, when the polarisation values are very high, such systems remain nernstian, yet their reaction is no longer reversible at these potentials. In spite of this, given that the current has reached its limiting value, this change does not modify the current-potential curves in any way.

By bringing into play the nernstian character of these systems, combined with the equations for both the interfacial concentrations as a function of the current and the limiting currents given in section 4.3.3.1, one then obtains the following equations:

$$\begin{aligned} E &= E^\circ + \frac{RT}{n\mathcal{F}} \ln \frac{[Ox]_{x=0}}{[Red]_{x=0}} \\ &= E^\circ + \frac{RT}{n\mathcal{F}} \ln \frac{[Ox]^*}{[Red]^*} + \frac{RT}{n\mathcal{F}} \ln \frac{I_{lim\,an}}{-I_{lim\,cat}} + \frac{RT}{n\mathcal{F}} \ln \frac{I - I_{lim\,cat}}{I_{lim\,an} - I} \\ &= E^\circ + \frac{RT}{n\mathcal{F}} \ln \frac{m_{Red}}{m_{Ox}} + \frac{RT}{n\mathcal{F}} \ln \frac{I - I_{lim\,cat}}{I_{lim\,an} - I} \end{aligned}$$

One can also build an equation for the steady-state current-potential curve of a fast system involving only the following three quantities: anodic and cathodic limiting currents, $I_{lim\,an}$ and $I_{lim\,cat}$, and half-wave potential, $E_{1/2}$. The half-wave potential is simply the electrode potential (*vs* a reference electrode) when the current is equal to the half-sum of the anodic and cathodic algebraic limiting currents. It also represents the inflexion point of the current-potential curve [74]:

$$E = E_{1/2} + \frac{RT}{n\mathcal{F}} \ln \frac{I - I_{lim\,cat}}{I_{lim\,an} - I} \qquad \text{with} \qquad E_{1/2} = E^\circ + \frac{RT}{n\mathcal{F}} \ln \frac{m_{Red}}{m_{Ox}}$$

If the diffusion coefficients of the two reactive species are very close, then their mass transport rate constants are also very close and the half-wave potential is equal to the standard potential of the redox couple: $E_{1/2} \approx E^\circ$

This general equation can also be applied to studying a mixture of oxidised and reduced species. Here one would rather introduce the overpotential, η which is equal to:

$$\eta = E - \left(E^\circ + \frac{RT}{n\mathcal{F}} \ln \frac{[Ox]^*}{[Red]^*} \right) = \frac{RT}{n\mathcal{F}} \ln \frac{I_{lim\,an}}{-I_{lim\,cat}} + \frac{RT}{n\mathcal{F}} \ln \frac{I - I_{lim\,cat}}{I_{lim\,an} - I}$$

---

[74] The analytic equations for the current-potential curve give one the opportunity to confirm that the second derivative of the current with respect to the potential at the half-wave potential is zero.

In the following one can see again the shapes for the current-potential curves previously described in qualitative terms as being a function of the limiting currents:

- if both limiting currents are different from zero, then this leads to the shape in figure 4.26. In such a case, the point for $I = 0$ corresponds to an equilibrium state.

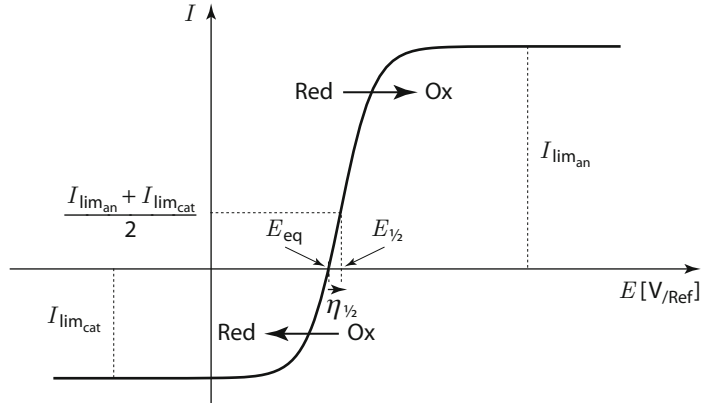


Figure 4.26 - Steady-state current-potential curve in a solution containing Ox and Red

- if one of the limiting currents is zero, for example if the initial solution contains no oxidant species: $I_{lim_{cat}} = 0$, then this leads to the shape in figure 4.27. In this case, $I = 0$ does not correspond to an equilibrium state: the potential at this point is a mixed potential.

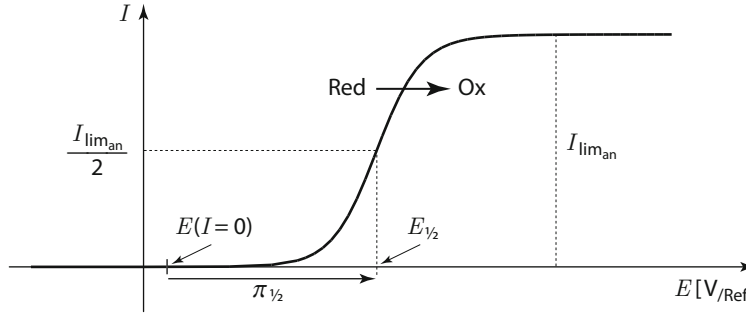


Figure 4.27 - Steady-state current-potential curve in a solution containing only Red

In the particular case of rate control by mass transport, the overpotentials or polarisations are sometimes called concentration overpotentials or concentration polarisations.

4.3.3.3 - SLOW REDOX SYSTEMS

Remember that a redox couple involving the E mechanism is called slow if its standard redox reaction rate constant is very small compared to the mass transport rate constants of the electroactive species.

Slow redox couples can be shown to be systems where the relationship between current and potential is controlled by the electron transfer phenomena in a potential range around the standard potential. The concentration profiles near the interface are not marked and the interfacial concentrations can be considered as equal to the concentrations in the bulk of the electrolyte.

In these conditions, by expressing the rates as outlined in section 4.3.2.3, and by including the fact that the concentrations are almost constant, one can obtain the following equation for the current:

$$I \approx n \mathcal{F} S k^\circ (e^{+\alpha \xi} [\text{Red}]^* - e^{-(1-\alpha)\xi} [\text{Ox}]^*)$$

If the oxidant and reductant are both present, then the equilibrium potential is defined, and one can therefore introduce the overpotential, η to the preceding equation:

$$I = n \mathcal{F} S k^\circ (e^{+\alpha n f \eta} e^{+\alpha \xi_{eq}} [\text{Red}]^* - e^{-(1-\alpha) n f \eta} e^{-(1-\alpha)\xi_{eq}} [\text{Ox}]^*)$$

Using the notations introduced in section 4.3.2.3, the NERNST law then becomes:

$$\xi_{eq} = \ln \frac{[\text{Ox}]^*}{[\text{Red}]^*}$$

The following equation, known as the BUTLER-VOLMER equation, is obtained:

$$\boldsymbol{I = S j_0 (e^{+\alpha n f \eta} - e^{-(1-\alpha) n f \eta})}$$

where j_0, the exchange current density, is linked to the standard reaction rate constant via the following equation:

$$\boldsymbol{j_0 = \mathcal{F} S k^\circ ([\text{Red}]^*)^{(1-\alpha)} ([\text{Ox}]^*)^{\alpha}}$$

Remember that the number, n, of electrons exchanged in these equations must be treated with caution. In fact, these equations have been demonstrated in the case of an elementary step. They should therefore only be applied to reactions involving a single electron exchange ($n = 1$). When a multi-step mechanism is involved, it may happen that one of the steps governs the kinetics. In such a case, if this step is of the E-type, then one ends up with an equation resembling the following:

$$I = S j_0 (e^{+\alpha f \eta} - e^{-(1-\alpha) f \eta})$$

with:

$$j_0 = n \mathcal{F} k^\circ \left([\text{Red}]^*\right)^{(1-\alpha)} \left([\text{Ox}]^*\right)^{\alpha}$$

The total number of electrons exchanged in the overall reaction, (a value which is also used in FARADAY's law) appears in the equation for j_0 but it is not in the exponential terms in the BUTLER-VOLMER equation.

The exchange current or current density is proportional to the standard rate constant of the redox reaction. Consequently, the slower the couple, the lower the exchange current is. It should be noted that the exchange current also depends on the concentration levels in the solution. This parameter is therefore not intrinsic to the redox couple in question, unlike the standard reaction rate constant. Numerical examples of j_0 and k° values for a few experimental situations are collected together in table 4.3.

Table 4.3 - Examples of kinetic parameters

The various data sources used to compile this table often provide incomplete information regarding the experimental conditions. This means therefore that it is difficult to make comparisons. The strictly precise measurement for kinetic constants is hard to attain.

Redox couple	Conditions, at 25 °C	j_0 [A m^{-2}]	$k°$ [m s^{-1}]
H^+/H_2	on Pt, 1.2 mol L^{-1} HCl	5	
H^+/H_2	on Hg, 1 mol L^{-1} HCl	$10^{-7.5}$	
H^+/H_2	on Pb, 0.25 mol L^{-1} H_2SO_4	$10^{-7.3}$	
H^+/H_2	on Pb		6×10^{-17}
H_2O/H_2	on Pt, 0.1 mol L^{-1} NaOH	0.6	
H_2O/H_2	on Pb, 6 mol L^{-1} NaOH	4×10^{-2}	
O_2/H_2O	onPt, 1 mol L^{-1} H_2SO_4	$10^{-4.6}$	
Cl_2/Cl^-	on Pt, 1 mol L^{-1} HCl	10	
$Cd^{2+}/Cd(Hg)$	on Hg, extrapolated 1 mol L^{-1} Cd^{2+}	8×10^4	
$Cd^{2+}/Cd(Hg)$	on Hg		10^{-2}
Fe^{3+}/Fe^{2+}	on Pt		4×10^{-5}
Fe^{3+}/Fe^{2+}	on Pt, equimolar 10^{-2} mol L^{-1}	10^2	10^{-4}
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	on Pt, 1 mol L^{-1} KCl		10^{-3}

The shape of the current-potential curve that emerges, resulting from the addition of two exponential terms, is represented in figures 4.28 and 4.29, whereby $\alpha = 0.7$ and with two different values for j_0. When $\alpha = 0.5$ (a particular case which is not shown here[75]) then the curve is symmetrical around the point ($E = E_{eq}$; $I = 0$).

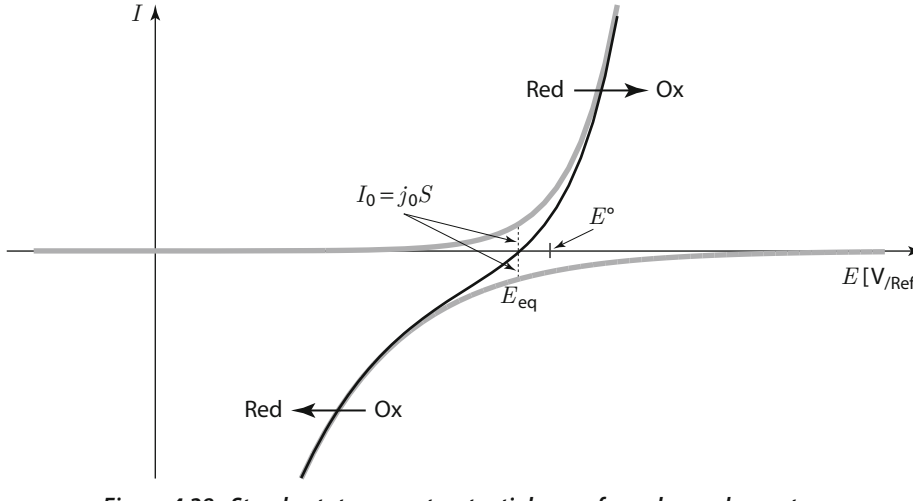


Figure 4.28 - Steady-state current-potential curve for a slow redox system whereby $\alpha = 0.7$ and with an arbitrary value for j_0

[75] When the kinetic parameters are not precisely known, then it is typically assumed that $\alpha = 0.5$.

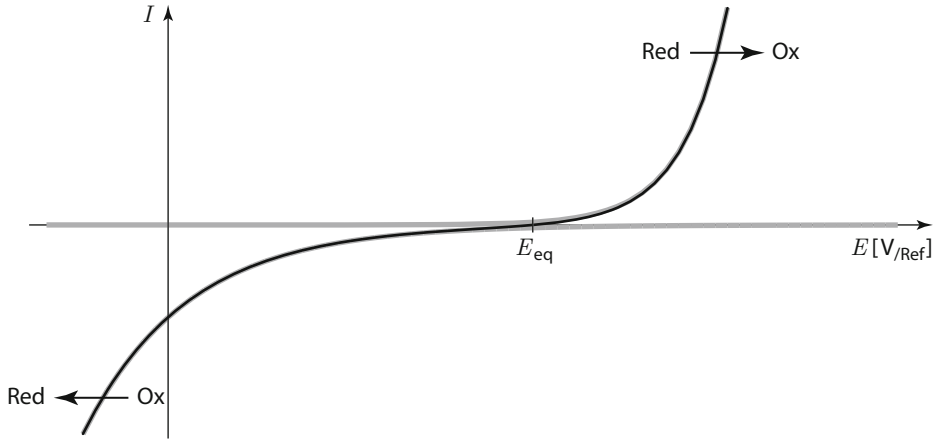


Figure 4.29 - Steady-state current-potential curve for a very slow redox system whereby $\alpha = 0.7$ and with $j_0' \ll j_0$ (in figure 4.28)

The charge transfer control conditions are limited to moderate polarisations, however if the system is slow enough, the corresponding polarisation zone can extend to over several hundred millivolts. By using the experimental data one can then easily determine the kinetic parameters, as outlined below. To do this, a TAFEL plot is often used: $\log |I| = f(\eta)$ as illustrated in figure 4.30.

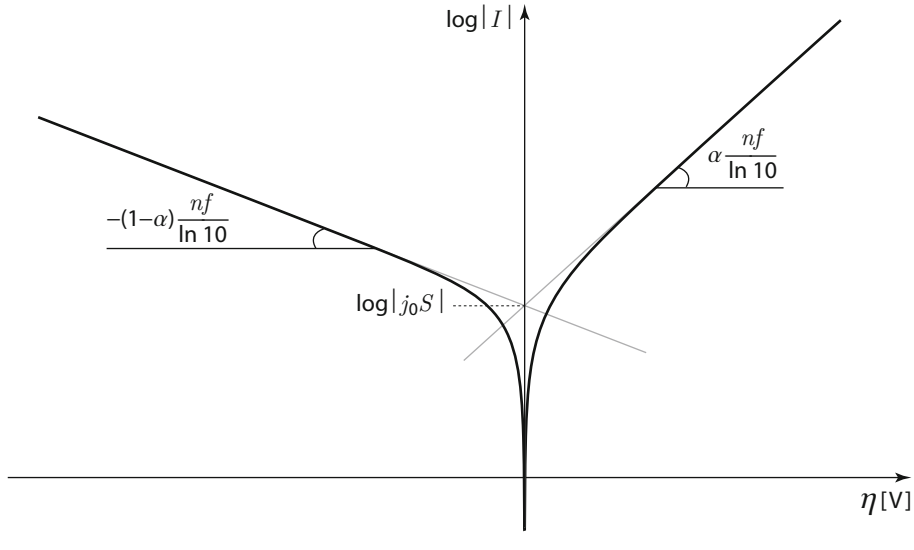


Figure 4.30 - TAFEL plot for a steady-state current-potential curve

For these types of slow systems, the redox reaction is reversible for polarisations lower than a few millivolts, however it becomes irreversible when the polarisation increases (the absolute value of the polarisation is only over 80 mV when the error on I calculated as irreversible is less than 5%, with $n = 1$ and $\alpha = 0.5$). Linear asymptotes then appear, because one of the exponentials outweighs the other, which is tantamount to irreversibility.

These asymptotes enable one to determine the kinetic parameters by using the experimental data easily extracted from the TAFEL plot (see figure 4.30):

- intercept $\log |j_0 S|$
- slope of the anodic branch $\alpha \frac{n f}{\ln 10}$
- slope of the cathodic branch $-(1-\alpha)\frac{n f}{\ln 10}$

For aqueous solution systems, with concentrations in the electroactive species of about 10^{-2} mol L^{-1}, this simple data processing is possible if the standard redox reaction rate constant is lower than 10^{-4} cm s^{-1}. This limit corresponds to an exchange current density lower than 10^{-4} A cm^{-2} = 100 µA cm^{-2} = 1 A m^{-2}.

For even greater polarisations, the slow systems can no longer be regarded as controlled by charge transfer. This is a mixed zone, where charge transfer is irreversible, and where both mass transport and charge transfer are simultaneously brought into play. The concentration profiles have steep slopes, in connection to currents which share the same order of magnitude as the limiting currents. The current-potential curve shape is almost identical for all slow systems, though showing a more or less pronounced shift with respect to the standard potential of the redox couple. Therefore the influence of the standard reaction rate constant is only shown in the potential range where these dramatic current shifts can be seen, as illustrated in figure 4.31 for two different slow redox couples. To simplify the diagram, the same standard and equilibrium potentials and the same limiting currents in oxidation and reduction have been chosen. For example, this figure depicts the current-potential curves obtained with the same solution containing Fe^{3+} and Fe^{2+} ions reacting at two electrodes with different metallic natures, which would therefore lead to different reaction kinetics.

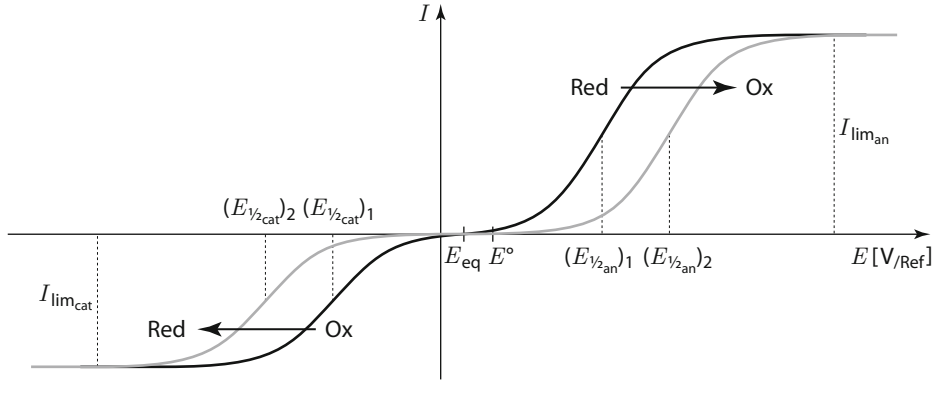


Figure 4.31 - Overall steady-state current-potential curves for two slow redox systems with the same mass transport parameters, the same concentrations, and therefore the same limiting currents. The standard reaction rate constants are different: $k°_1$ (black) > $k°_2$ (grey).

Let us stress the fact that, as indicated in figure 4.31, the comparison between the current-potential curves for two different slow systems results in horizontal translational shifts in opposite directions for both the anodic and cathodic branches. There are no

changes in the slope and curvature of the current-potential curves plotted for two different slow couples, quite unlike the changes observed when moving from a fast to a slow couple.

The half-wave potentials of these slow systems are expressed by the following equations:

- in oxidation : $$E_{1/2\ \text{an}} = E^\circ - \frac{1}{\alpha}\frac{RT}{n\mathcal{F}}\ln\frac{k^\circ}{m_{\text{Red}}}$$
- in reduction : $$E_{1/2\ \text{cat}} = E^\circ + \frac{1}{1-\alpha}\frac{RT}{n\mathcal{F}}\ln\frac{k^\circ}{m_{\text{Ox}}}$$

Note that the definition of the half-wave potential is not the same here as for fast couples, despite the fact that they share identical notations and terms. For a slow couple, two half-wave potentials are defined, one for the anodic branch and the other for the cathodic branch, with each of them at the operating point having a current equal to half the value of the corresponding limiting current.

4.3.3.4 - GENERAL CASE

When defining the overall current-potential curve in general cases, which are sometimes called mixed control or quasi-reversible systems, first one needs to write the equation for the current, based on general rate laws involving the interfacial concentrations:

$$I = n\mathcal{F}\,S\,k^\circ\,(e^{+\alpha\,\xi}[\text{Red}]_{x=0} - e^{-(1-\alpha)\,\xi}[\text{Ox}]_{x=0})$$

The latter can then be expressed in terms of current and bulk concentrations as follows:

$$C_{i\,x=0} = C_i^*\left(1 - \frac{I}{I_{\text{lim}}}\right)$$

Therefore, the following relationship can be demonstrated and applied to all general cases (E mechanism with any k° value in unidirectional systems):

$$\frac{1}{I} = \frac{1}{I_{\text{d}}} + \frac{1}{I_{\text{ct}}}$$

whereby I_{d} and I_{ct} respectively stand for the current values of a virtual situation, in which mass transport and respectively charge transfer limits or controls the current flow (see section 4.3.2.4) [76].

When both the oxidant and the reductant are in the bulk, then at low overvoltages it is possible to linearise the exponential terms. The behaviour that emerges is similar to that of a resistance, which is called polarisation resistance at equilibrium, R_{peq}. This is basically the sum of two resistances, called charge transfer resistance, R_{ct}, and concentration resistance, R_{d}, which are separately ascribed to each of the two phenomena involved:

$$R_{\text{peq}} = \underbrace{\frac{RT}{n\mathcal{F}}\frac{1}{S\,j_0}}_{R_{\text{ct}}} + \underbrace{\frac{RT}{n\mathcal{F}}\left(\frac{1}{I_{\text{lim an}}} - \frac{1}{I_{\text{lim cat}}}\right)}_{R_{\text{d}}}$$

---

[76] This general equation for a current illustrates the concept of control or limitation by one of the two phenomena. For instance, if it is mass transport that is limiting, this means that $I_{\text{ct}} >> I_d$ and therefore that $I \approx I_d$.

When the overvoltage is sufficiently low, then it can be divided into the sum of two terms which are frequently called the activation overpotential, η_{ct}, on the one hand, related to charge transfer kinetics and on the other hand the concentration overpotential, η_d, related to mass transport kinetics:

$$\eta \approx \eta_{ct} + \eta_d$$

However, whatever the overvoltage value, the two different phenomena of mass transport and charge transfer are usually coupled together, and cannot be considered as the mere sum of two independent terms, with one being related to mass transport and the other to charge transfer. *A priori*, one cannot split the overvoltage into two such terms. As shown in figure 4.32, the stronger the overpotential, the larger the error brought by considering such a sum. The actual overpotential is represented by a black line in figure 4.32. This gives an absolute value, which is larger than that of the grey curve representing the sum of the activation and concentration overpotentials, both regarded as independent. However, when the overpotentials are very high, then the current gets very close to the limiting current. Therefore even if there is a big error in the overpotential at high values of I/I_{lim}, it has little impact on the current-potential curve.

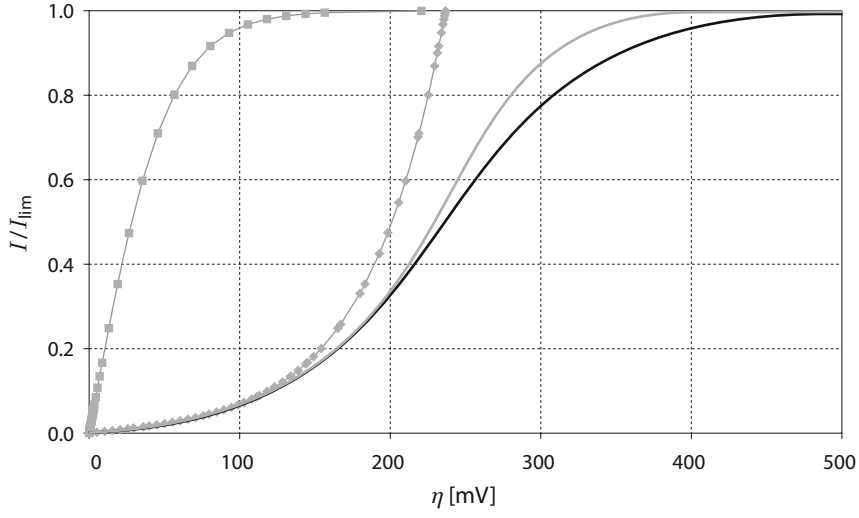


Figure 4.32 - Comparison of the current-potential curve for a redox couple whereby $k°/m$ is equal to 0.01 with curves resulting from the various virtual components
Total overpotential (black), overpotential in a situation of control by charge transfer (activation overpotential, η_{ct}, grey diamonds), overpotential in a situation of control by mass transport (concentration overpotential, η_d, grey squares) and sum of the last two terms (grey).

One can assume therefore that in the conditions indicated in figure 4.32, it is numerically acceptable to split the overpotential into an activation term and a concentration term, even if this has no real physical meaning. For overpotentials lower than 200 mV, the error is below 2% of the limiting current, whereas the maximum error is 10% for an overpotential of around 300 mV.

However, one must not conclude from this result that it is always possible to break the overpotential down into two independent phenomena added together, even if only as a

rough approximation. For example, if you took the same system but in different operating conditions, in particular when using transient electrochemical methods, this type of assimilation would lead to totally wrong results.

4.4 - COMPLETE ELECTROCHEMICAL SYSTEMS WITH A CURRENT FLOWING

When dealing with analytical applications in electrochemistry, the focal point is generally the working electrode's interface: the descriptions outlined in the previous section are adequate. However, in many electrochemical applications, it is not possible to consider the kinetic and mass transport phenomena to an electrode as being separate from the other electrode's phenomena. Various examples will be given here to illustrate this point, the first describing two simple cases where both electrodes are in the same electrolyte, therefore constituting a one-compartment cell. We will then study various cases involving electrolysis cells with two compartments. In addition, we will outline the basic principle and the suitable conditions relating to mass balances known as the HITTORF mass balance.

4.4.1 - ONE-COMPARTMENT CELL

The simplest electrochemical cell is a cell where both electrodes are in contat with the same electrolyte. This is called a one-compartment cell, with no ionic junction. In industrial-size cells, one cannot generally overlook the presence of convection phenomena, either natural or forced. In this section we will focus on the case of a closed cell, where convection can be disregarded. This for example is the case with either a solid-type electrolyte, a gel or polymer electrolyte, or a small volume of liquid electrolyte, typically with less than 1 mm between both interfaces. Then we will describe a one-compartment cell with forced convection, which relates to industrial cells with electrolyte circulation (open systems).

4.4.1.1 - CASES WHERE ALL STEADY STATES CORRESPOND TO ZERO-CURRENT

In a closed electrochemical system in which the anode and the cathode are in contact with a common electrolyte, the current flow most often involves two different redox couples, one at the anode and the other at the cathode. The electrolyte changes composition over time as shown in the example in figure 4.33. This diagram depicts a chronoamperometry experiment, whereby the left electrode potential is controlled and involves a rapid and nernstian redox system with a supporting electrolyte, with no convection, and in unidirectional geometry. Therefore, the interfacial concentration is fixed for the electroactive species at the left electrode, whereas their molar flux density at the right electrode is zero since here they are not electroactive.

Firstly, let us note the fact that shortly after the start of the experiment, the concentration profile follows the same pattern as that of chronoamperometry in semi-infinite geometric conditions (see figure 4.18 in section 4.3.1.3). The specific condition of there being zero flux in the zone located far away from the left interface leads to a constant

concentration in that same area. However, if the experiment is carried on further in time, then there is a change in concentration at the right interface, and the concentration of the whole electrolyte becomes non-homogeneous. In this kind of time range, it is no longer possible to view the phenomena at the two electrodes as independent [77].

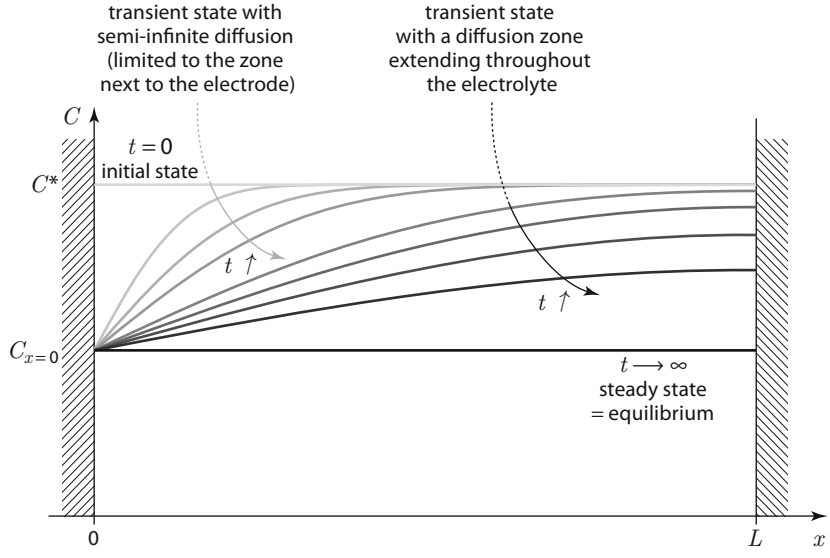


Figure 4.33 - Evolution of the concentration profile in chronoamperometry

The current decreases to the point of reaching zero. Here in such a system it is impossible to attain a steady state with a current that is anything other than zero. In a potentiostatic experiment, the only steady state that can be observed is therefore the equilibrium state with zero-current. This equilibrium state eventually settles once the transient current flow has homogenized the electrolyte composition. This composition correlates with the potential imposed at the working electrode, according to the NERNST law.

▶ A similar situation occurs when a thin film of a conducting material is being deposited on the electrode. The example shown in the diagram in figure 4.34 illustrates a thin film of mercury (an electronic conductor) that is deposited on a platinum electrode, whereby only the mercury is in contact with a liquid electrolyte containing Au^{3+} ions. By reduction at the interface between mercury and the electrolyte, these ions produce gold metal in the form of an amalgam:

$$Au^{3+} + 3\,e^- \longrightarrow Au(Hg)$$

The film is gradually transformed into an amalgam. For the Au(Hg) species, the platinum | mercury interface, which is an electronic junction, is non-reactive while the mercury | electrolyte interface is reactive.

---

[77] In a motionless electrolyte (namely without convection), such as a gel for example, one can estimate the time at which an interaction occurs between the electrodes in terms of mass transport. This is done by calculating the moment when the diffusion layer in a semi-infinite diffusion experiment (thickness of about $\sqrt{Dt}$ see section 4.3.1.3) becomes approximately as thick as the inter-electrode distance. Therefore, in a system containing an electroactive species with a diffusion coefficient of about 10^{-5} cm^2 s^{-1} and an inter-electrode distance of 3 mm, it would take an experiment lasting around 3 h for the diffusion layer to reach a thickness matching the inter-electrode distance.

As in the case described above in figure 4.33, here the steady state can only correspond to an equilibrium state with a non-zero, homogeneous gold concentration in the amalgam.

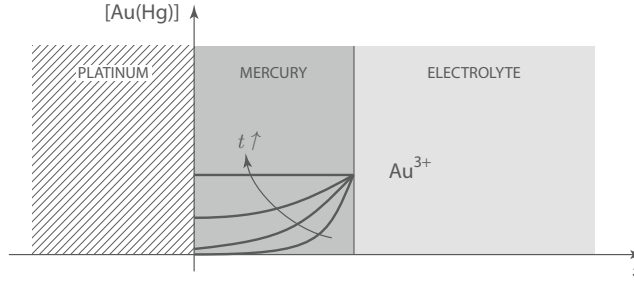


Figure 4.34 - Diagram of a device with a thin mercury film on the surface of a platinum electrode

- Another situation found in industry, which is akin to these cases, is that of lead-acid batteries. In most commercial batteries, the separator, which has a primarily mechanical role of avoiding direct contact between both electrodes, also serves to suppress almost completely the convection in the electrolyte, though without significantly reducing the mass transport parameters by diffusion and migration. When a lead-acid battery is being discharged, the redox couples involved at the electrodes are different, although they involve the same ions. You therefore have:
  - at the negative electrode (the anode during a discharge):

$$Pb + HSO_4^- \longrightarrow PbSO_4 + 2\,e^- + H^+$$

  - at the positive electrode (the cathode during a discharge):

$$PbO_2 + HSO_4^- + 3\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$$

  As before, the whole electrolyte is the seat for diffusion and migration phenomena after a transient period. Unlike the previous cases, both interfaces are reactive for the electrolyte ions. However, the fact that the two electrode half-reactions are different means that different stoichiometries appear in the equations, with therefore different slopes on each side as a result of applying FARADAY's law. Here again, one cannot obtain a non-zero steady-state current.

  To illustrate this, figure 4.35 shows the typical changes in concentration profile that emerges over time when a lead-acid battery is being discharged at a constant current.

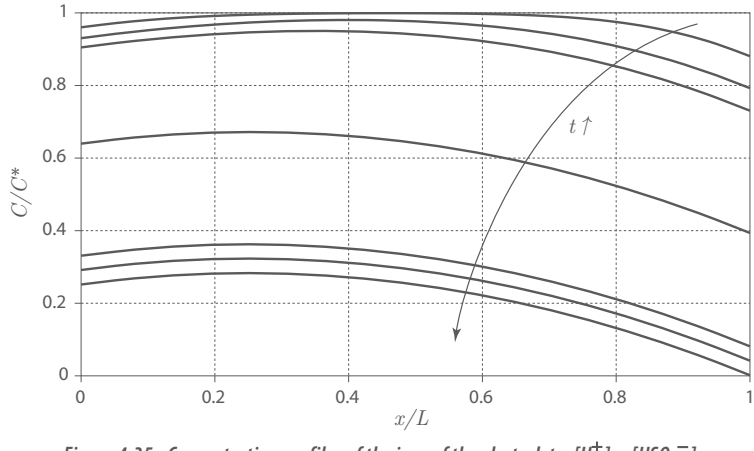


Figure 4.35 - Concentration profiles of the ions of the electrolyte, $[H^+] = [HSO_4^-]$, at various instants while a lead-acid battery is being discharged at a constant current
The results are obtained by numerically solving the migration and diffusion equations for $t_+ = 0.75$

4.4.1.2 - OBTAINING NON-ZERO-CURRENT STEADY STATES

For such a type of closed electrochemical cell with no convection, it is possible to obtain a non-zero-current steady state (in the strictest sense of the term as regards the electrolyte) if all the electroactive species present in the electrolyte have the same stoichiometries in both electrode redox reactions. The average composition of the electrolyte does not change over time, as illustrated in the example in figure 4.36 which shows concentration profiles for a chronopotentiometry with a fast and nernstian redox system in the presence of a supporting electrolyte with no convection [78].

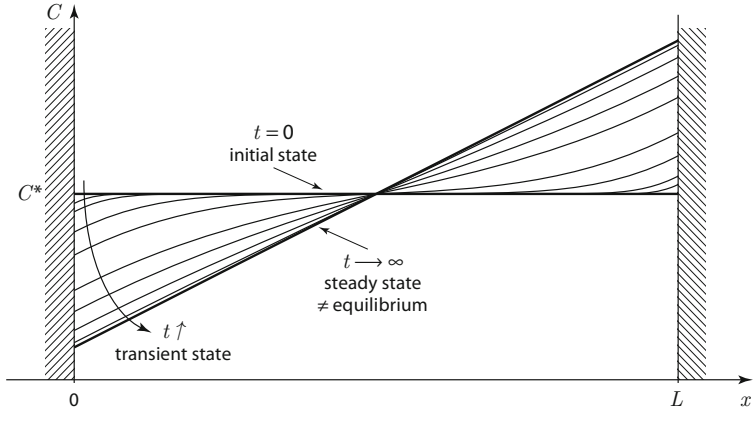


Figure 4.36 - Concentration profile in chronopotentiometry

Here again, in this system without convection, the composition throughout the electrolyte is non-homogeneous, with the diffusion phenomena occupying the entire volume after a transient period.

This case is a simplified version of how a lithium battery works [79]. For example, when a lithium battery has two insertion materials a and b, the electrode phenomena can be written in the following simplified manner:

- at the negative electrode (the anode during a discharge):

$$\langle \mathrm{Li} \rangle_a \longrightarrow \langle \ \rangle_a + e^- + Li^+_{electrolyte}$$

- at the positive electrode (the cathode during a discharge):

$$\langle \ \rangle_b + Li^+_{electrolyte} + e^- \longrightarrow \langle \mathrm{Li} \rangle_b$$

Although the two redox couples are not identical, as regards the electrolyte both redox reactions involve a supply or consumption of Li with the same stoichiometry. This applies to a Li-ion battery with two insertion materials or to a Li-polymer battery with Li as the negative electrode and an insertion material at the positive electrode. When a lithium battery is in operation, one must take into account simultaneously the migration and diffusion of the ions in the electrolyte, however, this makes no change in qualitative terms to what has just been illustrated.

[78] Appendix A.4.1 adresses in detail the characteristics for such a system at steady state, as well as the establishment of that steady state.

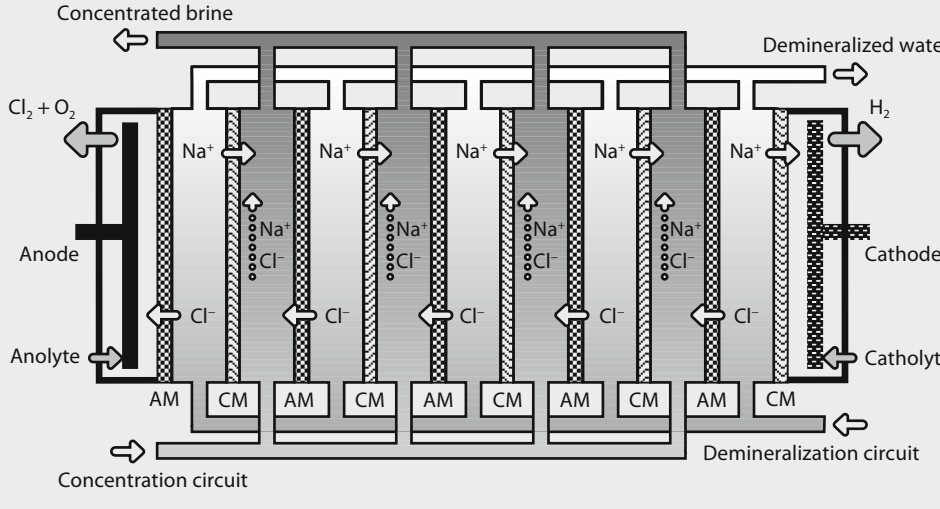
[79] These batteries are described in the illustrated board entitled 'Energy storage: the Li-Metal-Polymer (LMP) batteries'. They are often called 'rocking chair batteries' by the specialists when, during operation, the Li^+ ions are de-inserted at one of the interface and simultaneously inserted at the other interface. Lithium is thus tilted from one side to the other during charge or discharge.

ELECTRODIALYSIS

Document written with the kind collaboration of A. SAVALL,
from the Paul Sabatier University in Toulouse, and F. LUTIN, from the company Eurodia

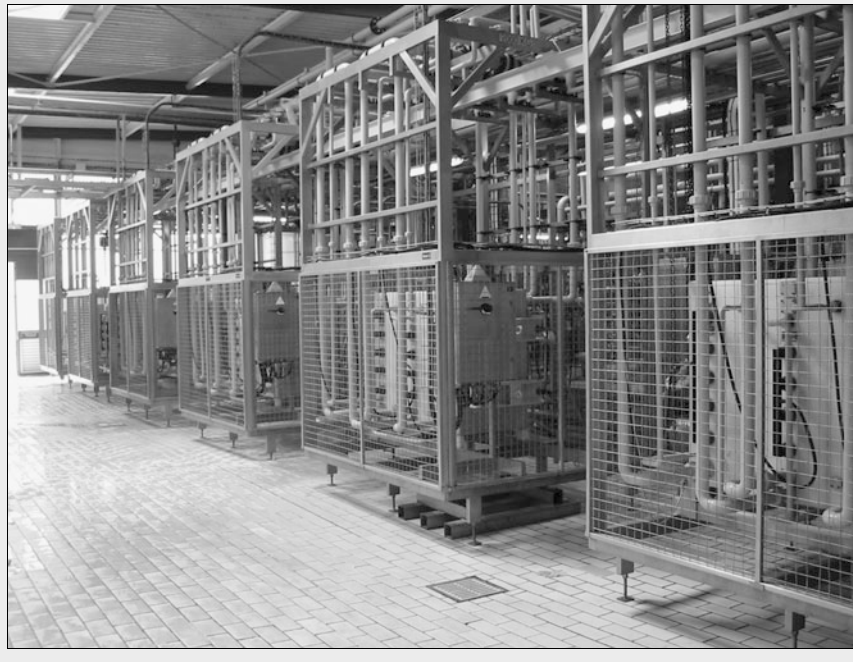
Membrane electrolysis cells have many applications in the food industry (dairy, wine, fruit juice, etc.), water softening, purification or recovering effluents from electroplating and other chemical processes. Possibly the best known processes are desalinating brackish water with a moderate salt content (other processes such as reverse osmosis are used upstream) and demineralising whey in the dairy industry.

In electrodialysis, two types of monopolar membranes are used (with only one type of ion allowed to penetrate). Anionic membranes (AM) only allow the anions through, and cationic membranes (CM) only allow the cations through. This characteristic derives from a specific way of functioning in the constituting polymer. A cationic membrane therefore serves as the conducting material, with sulfonic or sulfonate groups for instance grafted on to the constituting polymer. Such groups block the movement of anions (which have the same sign), and let the cations through the polymer. Anionic membranes have alkylammonium groups which block the cations. The following figure illustrates the operating principle. The solution flowing between the two membranes (anionic and cationic) becomes either depleted or enriched in salt, depending on the direction of the current. The electrode reactions occur at the far ends of the cell, in the anolyte and catholyte compartments which can be chemically distinct from the solutions flowing between the membranes so as to reduce polarisations.



Working diagram of an electrodialysis cell

To attain better results, several modules (pairs of membranes) are connected in parallel as far as the flow of liquids is concerned and in series electrically with the current running in an identical fashion across each compartment. The entire installation has several operating modes: either by single flow through a cell with the possibility of having several cells arranged in series depending on fluid flow or in a loop (recirculation) via a tank.



Industrial electrodialysis installation *(photo provided by the company Eurodia, Wissous, France)*

The filter-press type configurations are made up of a set of modules which are arranged in alternating anionic and cationic membranes. The thin intermembrane compartments contain spacers to improve the hydrodynamic conditions. High-pressure pumps push the fluids inside the hydraulic circuits so as to overcome any drops in pressure that may occur along the flow line.

Industrial cells consist of one or two hundred modules with membrane surfaces that can reach up to one m^2. These facilities are able to soften brackish water with flow rates spanning from a few hundred up to one thousand m^3 per day, and all with an energy cost of about 1 kWh per m^3. The precise nature of the electrode reactions taking place in the compartments at both ends of the cell plays no direct role in the electrodialysis process. The intermembrane space has a thickness lower than 1 mm, in order to decrease the ohmic drop. However if the solution requires a stronger demineralising effect, then the ohmic drop can be very large because this solution will become poorly conducting.

When the system is in operation, deposits may build up on the membrane surface, namely due to local pH variations which can cause hydroxides to be formed with the metallic cations of the solutions being processed. Such a phenomenon clogs and weakens the membranes which are then difficult to maintain. It is advisable to periodically reverse the polarity so as to eliminate these deposits. Regularly dismantling is still a necessary step to clean the various elements.

If there is a wide distance between the two electrodes in a liquid electrolyte, then it is not possible to overlook the natural convection. In fact, it is this natural convection that homogenises the concentration in the electrolyte's middle zone. For example, if we keep to the same interfacial reactions as those described above and assume that only a short time is needed for the two diffusion layers to reach equal thickness δ, then the changes over time in the concentration profiles illustrated in figure 4.37 show how, yet again, a non-zero-current steady state is achieved.

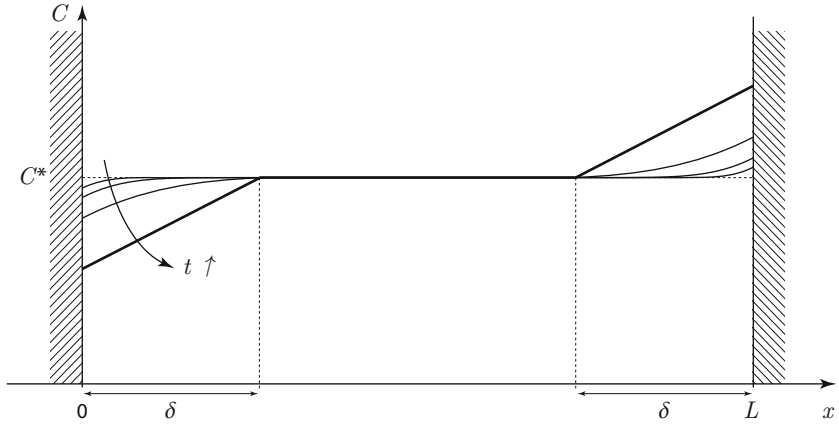


Figure 4.37 - Establishing the steady-state concentration profile in chronopotentiometry involving convection

As in the previous example, the average composition of the electrolyte does not change. The major differences between the two systems lie in the thickness of the diffusion layer, which is found to be lower in the second example: in aqueous media, the thickness of the diffusion layer due to natural convection is estimated at around a few 100 µm. Therefore, the values for the steady-state currents are higher, and less time is needed for the steady state to become settled.

In addition, for open industrial cells involving a circulating electrolyte (the electrolyte is in continuous renewal) forced convection must be taken into account. Under such conditions, a quasi-steady state can be achieved even when the anodic and cathodic reactions do not involve the same redox couple.

In all cases where convection occurs, it is not easy to establish the volume mass balance for each species in simple quantitative terms, unlike in other situations (see section 4.4.2.3 on the HITTORF mass balance).

4.4.2 - CELL WITH TWO SEPARATE COMPARTMENTS

In many industrial processes where soluble species are involved, it is sometimes necessary to keep the homogenisation of the electrolyte to a minimum so as to prevent a species that is produced at one electrode from reacting at the other electrode[80]. Here

[80] This phenomenon, which is sometimes called the chemical shuttle, is equally unwelcome in the case of batteries, because it would preclude the possibility of any efficient energy storage.

we will give a few examples to explore electrochemical systems that comprise a device which separates the catholyte from the anolyte[81], though all the while maintaining the electrical contact between them. In particular, we will focus on the role of this separator in terms of mass transport, as well as studying how the nature of the material can be used as a way of influencing the mass balances.

4.4.2.1 - DIFFERENT TYPES OF SEPARATION

Some laboratory devices have compartments separated by a long tube with a small section (capillary). Figure 4.38 shows a simplified view of this type of device. The diffusion coefficients and the mobilities of the various species remain unchanged throughout the electrolyte volume.

To simplify, let us assume that the systems have a unidirectional geometry, although strictly speaking this does not apply to zones where the section areas change. What is peculiar about this type of cell is the form of equations that can be written for the molar fluxes in the cell's various zones. In fact the following equations show how the molar flow rates for each species are preserved:

$$\left(N_{\text{anolyte}}\right)_{x=L} S_{\text{electrodes}} = \left(N_{\text{capillary}}\right)_{x=L} S_{\text{capillary}}$$

$$\left(N_{\text{catholyte}}\right)_{x=L+\ell_{\text{capillary}}} S_{\text{electrodes}} = \left(N_{\text{capillary}}\right)_{x=L+\ell_{\text{capillary}}} S_{\text{capillary}}$$

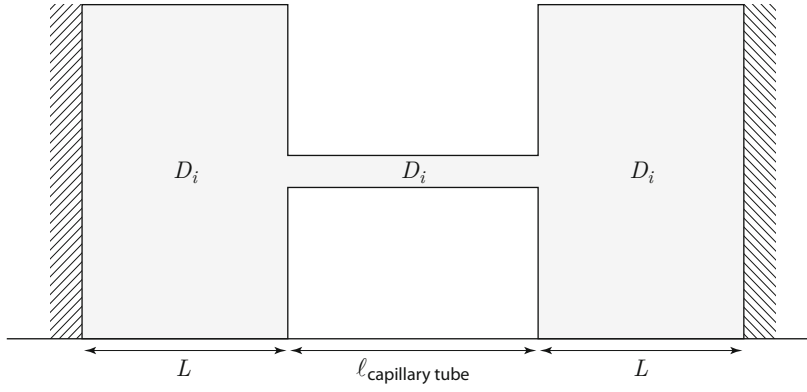


Figure 4.38 – Simplified diagram of a cell with a separating tube

If there is a large enough difference between the section areas, then one can therefore assume that the molar flux densities in the anolyte and the catholyte are low compared to the corresponding quantities within the capillary tube. The impact of this property is addressed in the following sections. On the other hand, using a capillary tube with a narrow section makes the natural convection negligible in this part of the cell.

Therefore, in this instance, the solution chosen is generally based on the use of solid electroactive materials that are insoluble in the electrolyte. This issue will not be dealt with in this work.

[81] The term anolyte refers to the electrolyte on the anodic side. The term catholyte means the electrolyte on the cathodic side.

It is more common to use various types of porous materials (porous frits, polymer membranes) to separate the two compartments in an electrolysis cell[82]. Figure 4.39 gives a simplified view of such a type of cell.

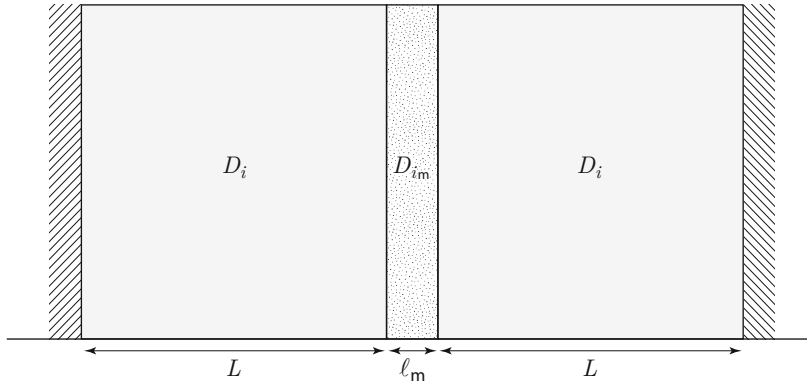


Figure 4.39 – Simplified diagram of a two-compartment cell with a membrane

The aim here is not to go into thorough detail about mass transport in porous materials. We will merely describe these phenomena in macroscopic terms using the effective mass transport parameters (diffusion coefficients and mobilities) denoted by the index m and adapted to the material's macroscopic geometry.

In the absence of any specific properties (which is wholly opposite to the case of selective membranes) these effective parameters can sometimes be related to microscopic parameters, such as the porosity and tortuosity in the materials used. Assuming that the membrane is not ion-selective with respect to the different ions, one can consider the transport numbers to be constant in all the electrolytic media. In the examples outlined below (see sections 4.4.2.2 and 4.4.2.3), it is assumed that the effective diffusion coefficients and mobilities are significantly lower than in the free electrolyte. This is due for example to a low porosity in the material used. Note that if these particular experimental conditions are chosen, then it implies that there is a significant ohmic drop in the electrolysis cell, which requires high electrolysis voltages (typically over 10 V). These conditions are not suitable for industrial applications.

In this simplified system, with unidirectional geometry and negligible convection in the porous material, the continuity of the molar flux densities for each species at the two ionic junctions has consequences that are quite similar to those arising when a capillary tube is used. Here again the convection in the central part of the system is overlooked. However, the two systems are not equivalent to each other because in the case where there is separation by a membrane, the equations indicating the time evolution for the concentration at any point (equations deduced from the volume mass balances) are different in the three cell zones. This is not the case when there is separation by a capillary tube.

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[82] To find an example of an industrial process using membrane electrolysis cells, one can refer to the illustrated board entitled ' Electrodialysis '.

4.4.2.2 - STEADY STATES WITH A NON-ZERO CURRENT

Let us imagine an electrolyte with two monovalent ions, $A^+ X^-$, such that the couple at the anode is identical to that at the cathode, and only A^+ is an electroactive species. A^+ is produced at the anode and consumed at the cathode. Remember that in this case it is possible to attain steady states different from equilibrium states[83]. For example in a chronopotentiometry, after a while the concentration profile ceases to change. Remember also that electroneutrality requires the anion and cation concentrations to be equal at all points throughout the electrolyte. In systems with unidirectional geometry, linear concentration profiles emerge in the zones where there is no convection, and the slopes depend solely on the current and the diffusion coefficient of the electroactive species A^+.

Therefore, when the cell has a membrane, given that the reasoning outlined above applies to each diffusion layer in the electrolyte, then the steady-state concentration profile takes the form of straight segments[84]. If the diffusion coefficient appears to be smaller in the membrane than in the compartments, then significant differences can be seen in the slopes for the various cell zones, as shown in figure 4.40.

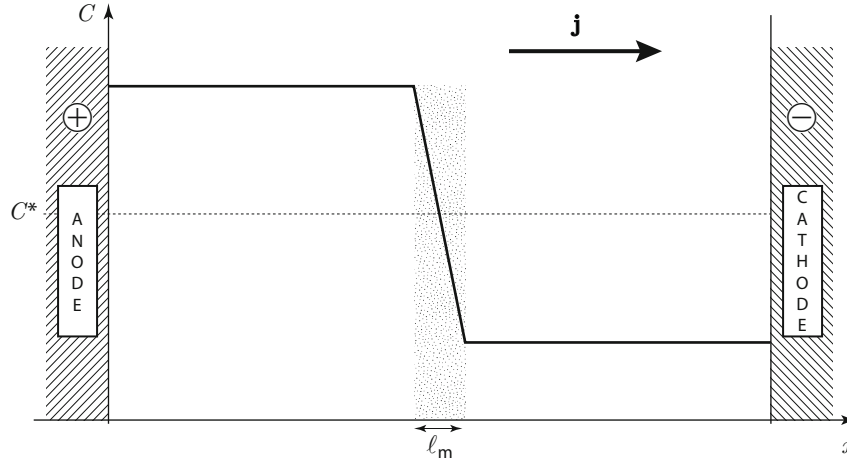

Figure 4.40 - Concentration profile during an electrolysis experiment at steady state for a membrane cell with a diffusion coefficients ratio, D_i/D_{i_m}, equal to 100

At steady state, the electrolyte composition difference between the two compartments on each side of the membrane reaches a steady value. This value depends mainly on the imposed current, the diffusion coefficient of the electroactive ion in the membrane and

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[83] This example is addressed in detail in appendix A.4.1 for a one-compartment cell.

[84] So as to take into account the natural or forced convection, the electrolyte is divided into 7 zones: the electrolyte inside the membrane (no convection), then each compartment is divided into a central homogeneous zone with two diffusion layers (one is next to the electrode and the other is next to the membrane). Five of these zones are clearly seen in the figure 4.41 in the transient period. The slopes for the steady-state concentration profiles are negligible in the four diffusion layers of the electrolyte outside the membrane. This is due to the difference between the diffusion coefficients chosen. In figure 4.40, these zones cannot be distinguished from the two zones which are homogenised by convection.

the membrane thickness. A limiting current value can also be defined for which the steady-state concentration at the cathode is zero. When dealing with numerical values such that one can disregard the concentration profiles slope in the compartments at each end, the limiting current value is given by the following:

$$I_{\text{lim}} = \frac{2D_{+\text{m}}\,\mathcal{F}\,S_{\text{electrodes}}\,C^*}{\ell_{\text{m}}}$$

Similar reasoning can be applied to a cell with a capillary tube. If the area of the capillary section is much smaller than that of the two compartments on either side, then the concentration profile slope in the electrolyte's intermediate zone is much more pronounced than in the two anolyte and catholyte zones. The limiting current at steady state is then given by the following:

$$I_{\text{lim}} = \frac{2D_{+}\,\mathcal{F}\,S_{\text{capillary}}\,C^*}{\ell_{\text{capillary}}}$$

4.4.2.3 - CHARACTERISTICS OF THE TRANSIENT PERIOD: THE HITTORF MASS BALANCE

Studying transient states is interesting because the mass balances, often called the HITTORF mass balance, enable one to accurately determine the mass transport parameters. The experimental conditions used are such that the characteristic time needed for the steady state to be established greatly exceeds the actual length of the experiment. Therefore, the system is in transient states throughout the experiment. Moreover, for this purpose, the current imposed is far larger than the limiting current defined above.

The characteristic time needed for the steady state to be established is given by the following equation [85]:

- $\tau = \left(\frac{\ell_{\text{capillary}}}{2}\right)^2 \frac{1}{D_{\pm}}$ for the capillary cell with a high value for $\ell_{\text{capillary}}$ (see figure 4.38).

  Typically in this case, for a capillary length of around 5 cm with a mean AX diffusion coefficient [86] of around 10^{-5} cm^2 s^{-1}, the characteristic time needed for the steady state to be established is around 10^6 s, that is to say one week.

- $\tau = \left(\frac{\ell_{\text{m}}}{2}\right)^2 \frac{1}{D_{\pm\text{m}}}$ for the membrane cell with a small value for $D_{\pm\text{m}}$ (see figure 4.39)

  Typically in this case, with a membrane thickness of around 2 mm and a mean AX diffusion coefficient of around 10^{-7} cm^2 s^{-1}, the characteristic time needed for the steady state to be established is around 10^5 s, that is to say 30 hours.

Figure 4.41 shows the change in the concentration profiles in a membrane cell for the middle zone of the electrolyte (around the membrane) at the beginning of the transient state [84].

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[85] Since the concentration profiles build up symmetrically on both sides of the capillary or the membrane, then $\ell/2$ is to be considered as the characteristic distance for establishing the steady state.

[86] $D_{\pm} = t_{-}D_{+} + t_{+}D_{-}$, see section 4.2.1.2.

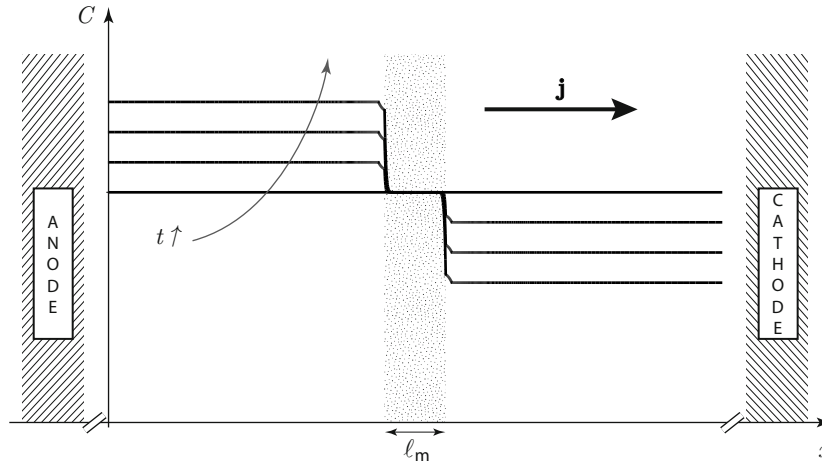


Figure 4.41 - Changes over time of the ions concentration profiles at the beginning of the transient period of a chronopotentiometry with unidirectional geometry (membrane cell)

During the beginning of the transient period, the concentration in the membrane remains unchanged, except in its two diffusion layers, which remain very thin. This means that the major part of the membrane is not a seat for diffusion phenomena. Based on this outcome, it is possible to show that in the transient period, as long as the concentration in the membrane remains constant, the anolyte concentration varies linearly with time, and the corresponding slope is characteristic of the ion transport numbers (see demonstration below: HITTORF's mass balance). The same applies for the catholyte concentration. Therefore, if it is possible to find experimental means to monitor the change in the ion concentrations in the anolyte (and/or the catholyte) over time, or after a given duration, then one can determine the mass transport parameters of both ions.

In general, establishing a HITTORF mass balance comes down to writing the mass balance for an electrolyte volume that is bound on one side by the electrochemical interface and on the other side by a zone in which only migration phenomena play a role in the current flow, as shown in the diagram in figure 4.42 using the example detailed below the figure. In fact, at this surface one simply has the following:

$$j_i = j_{i\,\text{migration}} = t_i\, j$$

In these conditions, the mass balance is given by:

$$\mathrm{d}n_i = \mathrm{d}n_i^{\text{farad}} - t_i \frac{I\,\mathrm{d}t}{z_i\,\mathscr{F}}$$

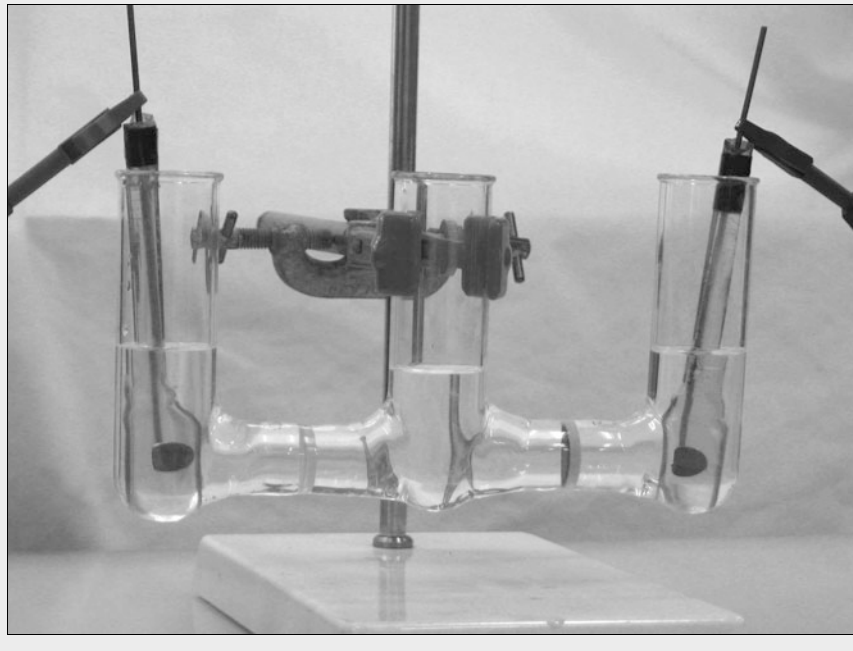
or, between the initial time and instant t:

$$\Delta n_i = \frac{\nu_i}{\nu_e\,\mathscr{F}}\,Q - \frac{t_i}{z_i\,\mathscr{F}}\,Q$$

HITTORF'S MASS BALANCE EXPERIMENT

Document written with the kind collaboration of A. DENOYELLE, Laboratoire d'Electrochimie et Physico-chimie des Matériaux et des Interfaces, at Phelma, Grenoble INP, France

By drawing up the results of a HITTORF mass balance from a laboratory electrolysis experiment (see section 4.4.2.3) one can measure the transport numbers in a single-solute electrolyte using the measurement of change in the composition of the electrolyte resulting from the current flow. In order to achieve this a cell can be used with three different compartments separated by porous sintered glass so as to prevent the solutions from becoming rapidly mixed up by convection between the compartments.



Example of a three-compartment glass cell used for student's practical work at Phelma (Grenoble INP)

To carry the experiment, an electric power supply is needed to impose a constant current so as to simplify determining the amount of charge that has circulated during the experiment. Since porous materials have high resistance to current flow, a high voltage power supply must be used (about a hundred volts).

For example, in the cell pictured above, with a copper sulphate solution with a concentration of 5×10^{-2} mol L^{-1} it takes about two hours of electrolysis with the current set at 20 mA to observe significant concentration changes (about 20%). With an accurate measurement of these variations from complexation or precipitation titration reactions, the transport number of Cu^{2+} ions can be determined: $t_+ = 0.4$ to the nearest few %, close to the values stated in scientific reports. As expected from the HITTORF mass balance, the concentration in the central compartment does not fluctuate a great deal.

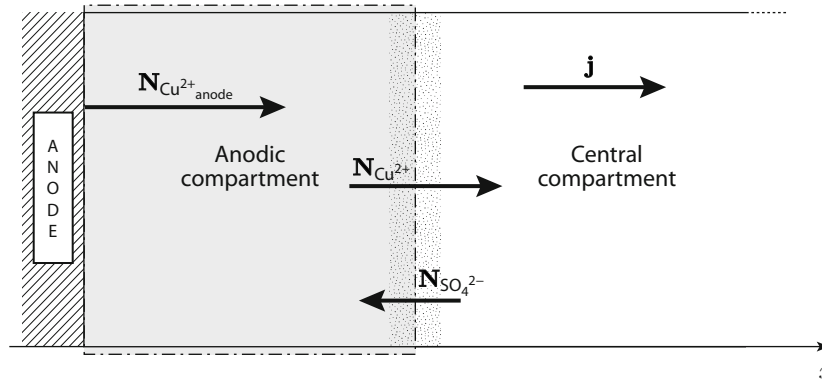


Figure 4.42 - Principle of the particular mass balance called the HITTORF mass balance, illustrated on the Cu oxidation in a $CuSO_4$ aqueous solution (see example below)

The electrolyte volume concerned by the mass balance is put in grey and delimited by a dashed and dotted line.

For example, electrolysis can be carried out in a cell with three compartments, separated by two porous frits, filled with an aqueous solution containing copper sulphate $CuSO_4$, and with two copper electrodes in the outer compartments [87]. The amount of substance inside the two porous frits is negligible compared to the large amounts in the volumes contained in each cell compartment. The electrolysis current is adjusted to a moderate constant value so that only the main electrolysis reactions occur, in other words with a faradic yield of 100% at the anode and cathode.

- at the anode, oxidation of the copper electrode occurs:

$$Cu \longrightarrow Cu^{2+} + 2\,e^-$$

- a copper deposit is produced at the cathode:

$$Cu^{2+} + 2\,e^- \longrightarrow Cu$$

Once the electrolysis has been underway for a few hours, the titration of the three compartments enables one to accurately check that the concentration change in the central compartment is very low (theoretically zero), and also check that the changes in the amount of Cu^{2+} ions are opposite quantities in the two outer compartments. As expected, after such an experiment, the concentration of copper sulphate increases in the anodic compartment while it decreases in the cathodic compartment.

The HITTORF mass balance determines the transport numbers of these two ions from the following experimental data: concentration variations, compartment volumes and the total quantity of charge transferred during electrolysis. In fact, in the anodic compartment you have the following equations:

$$\Delta n_{Cu^{2+}} = \frac{Q}{2\mathcal{F}} - \frac{t_+}{2\mathcal{F}}Q = t_- \frac{Q}{2\mathcal{F}}$$

$$\Delta n_{SO_4^{2-}} = 0 + \frac{t_-}{-2\mathcal{F}}Q = t_- \frac{Q}{2\mathcal{F}}$$

The same variation is obtained for the amount of each type of ion, since the system remains electrically neutral throughout the whole experiment.

The HITTORF mass balance in the cathodic compartment shows an opposite variation in the amount of substance, in comparison to that in the anodic compartment, since these equations are written in algebraic terms: at the cathode the current, and therefore the charge Q, are both negative.

[87] For an illustration of this type of experiment, refer to the illustrated board entitled ' HITTORF's mass balance experiment '.

4.4.2.4 - INDUSTRIAL APPLICATIONS

In most industrial applications in electrochemistry, different redox couples are involved at the anode and at the cathode. A steady state with a non-zero current can therefore never be attained if there is no convection at play.

Given the high electric power levels that are involved, care is generally taken to keep the ohmic drop phenomena to a minimum, and equally by consequence the JOULE effect too. This stretches even to cases where a membrane is used to separate the anolyte from the catholyte. For this to be possible, the membrane must therefore have low resistive properties. The mass transport parameters in these porous media do not differ greatly from those in the surrounding media. In such applications, the experimental conditions are a far cry from the strict validity conditions required for any HITTORF mass balance, as outlined above. In industrial applications that require a separator between the two parts of the cell, the membrane's role in terms of mass transport mainly relates to convection phenomena. The membrane generally prevents or at least slows down the convective mixing process of the anolyte and the catholyte. On the other hand, it is incorrect to assume that there is no diffusion flux through the membrane. HITTORF-type arguments only enable one to make qualitative predictions in terms of materials increase or decrease in the amount of substances in the electrolyte. Nevertheless, they remain interesting from a practical point of view.

To conclude, one should note that the mass balances can also be modified by using permselective or specific membranes in some industrial processes. A good example of such applications includes the use of anionic and cationic membranes to desalinate sea water [88] or other methods of separation or purification.

[88] See the illustrated board entitled ' Electrodialysis '.

QUESTIONS ON CHAPTER 4

1 - Complete the following diagram for the interfacial reaction

$$Co + 4\,Cl^- \longrightarrow CoCl_4^{2-} + 2\,e^-$$

by indicating, in qualitative terms, in both phases:

- the various molar flux density vectors ($\mathbf{N}_i$)
- the various current density vectors ($\mathbf{j}_i$)
- the overall current density vector ($\mathbf{j}$)
- the vector normal to the surface ($\mathbf{n}$) following the usual sign convention for the current

2 - When a species is adsorbed at the interface, the interfacial flux and the production rate at steady state are both zero true false

3 - In a given electrochemical experiment, where only the current and the potential can vary, a redox couple or reaction can be:

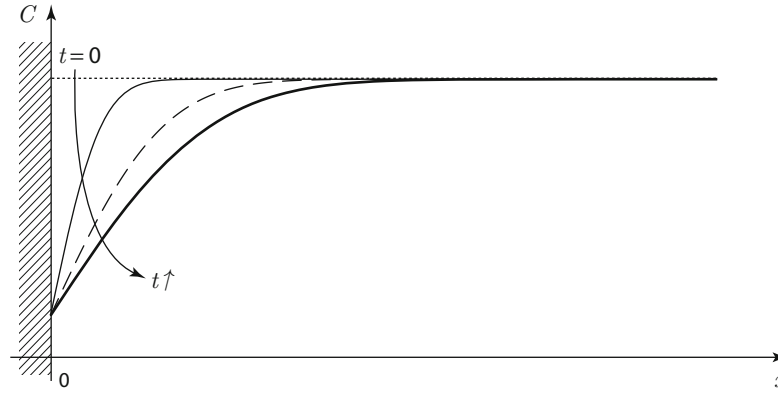
- fast or slow, depending on the operating conditions true false
- reversible or irreversible, depending on the operating conditions true false

4 - For an aqueous solution at room temperature containing anions and cations with a concentration of 0.1 mol L^{-1}, what is the order of magnitude and the unit of the electric conductivity? .....

5 - What is the order of magnitude and the unit of the diffusion coefficient of an ion in an aqueous solution at room temperature? .....

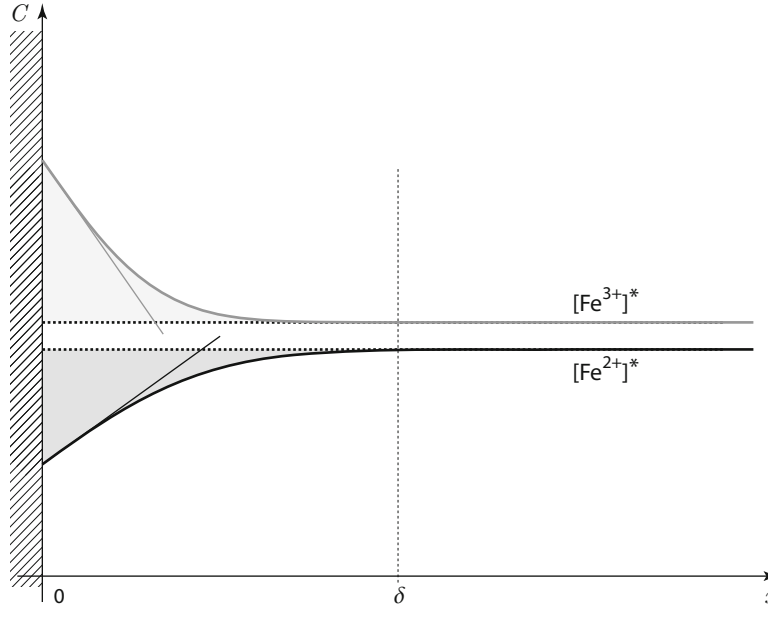
6 - The diagram below shows the changes over time in the concentration profile for an electroactive species of a fast redox couple in an experiment:

- at steady state true false
- of voltammetry true false
- of chronoamperometry true false
- of chronopotentiometry true false



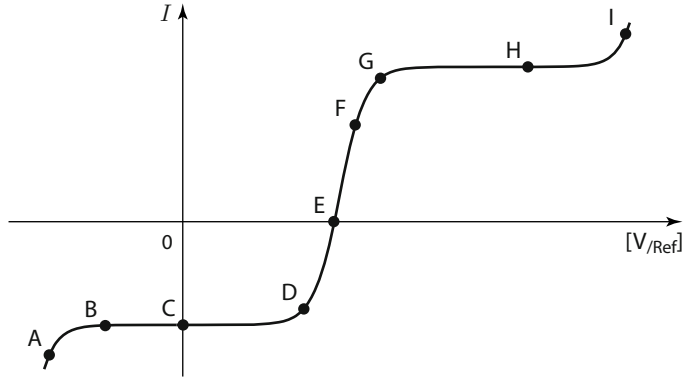
7 - The following diagram shows the concentration profiles for a solution containing Fe^{3+} (grey) and Fe^{2+} (black) ions. The dotted lines represent the initial instant, and the solid lines represent instant t. These profiles result from current circulation through an interface between a platinum electrode and a solution with negligible convection and migration of the electroactive species, Fe^{3+} and Fe^{2+}.

- the case shown corresponds to an oxidation reaction true false
- what is the quantity δ called? .....
- the diffusion coefficient of Fe^{2+} is larger than that of Fe^{3+} true false
- the two shaded areas are equal true false
- complete the diagram with a qualitative drawing of the concentration profiles that one would observe for a larger current, yet with the same value for δ.



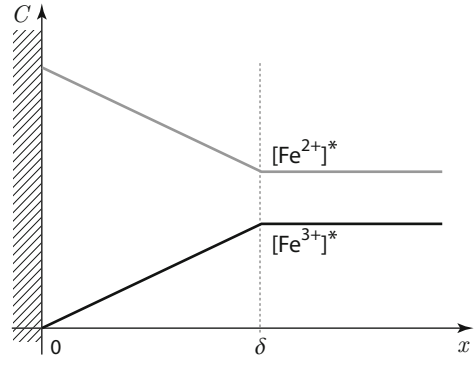
8 - Close to a metal|electrolyte electrochemical interface, one defines the double layer and the diffusion layer. The diffusion layer is usually much thinner than the double layer. true false

9 - Look at the following steady-state current-potential curve:



Among the working points indicated above, which ones correspond to the concentration profile shown in the diagram below?

A B C D E F G H I



10 - In usual cases, the value of the steady-state limiting anodic current is proportional to the concentration:

- in the oxidant at the electrode interface true false
- in the oxidant in the bulk solution true false
- in the reductant at the electrode interface true false
- in the reductant in the bulk solution true false