APPENDICES

A.1.1 - LIQUID IONIC JUNCTION VOLTAGE WITHOUT CURRENT

When there are ionic junctions involved in an electrochemical chain, in many instances the open-circuit junction voltages (or potential differences, see section 1.5) may be overlooked, although this is not a general rule. In particular, it is rare that this type of approximation can be applied in equilibrium conditions to single-exchange ionic junctions (for example when a solid electrolyte is involved, see section 3.3.4.1), nor indeed in the case of multiple junctions with two electrolytes of a dissimilar nature (for instance two electrolyte solutions in two different solvents, see section 3.3.5). When the liquid junction in question is between two electrolytes in the same solvent, then the ionic junction voltage in thermodynamic equilibrium is zero, because the two solutions are perfectly mixed together in equilibrium (see section 3.3.5). Nevertheless, the result is ultimately immaterial, because the experiments carried out to implement such junctions often make use of devices that are specifically designed to considerably slow down the mixing process of the solutions. This happens with salt bridges, involving a porous material at each contact between one end of the bridge and one of the two different solutions. When approaching the question from an experimental point of view, it is thus very important to focus on the junction voltage's quasi-steady-state value (not at thermodynamic equilibrium) between the two solutions, whose compositions are still not the same. Therefore at open circuit, the species fluxes between the two solutions are very small, although not zero. Significant concentration profiles and potential profiles are only found inside the porous plugs (see below).

Here, let us firstly focus on the conditions required in order to minimise such junction voltages. This section revolves around a series of numerical calculations that are based on what is commonly known as the HENDERSON equation: an equation which makes it possible to evaluate the junction voltage between two solutions with different compositions in the same solvent. Basic elements will then be given about the hypotheses and the reasonings leading to this equation. It is strongly advisable to first read chapter 4 and appendices A.3.4 and A.4.1 in order to gain a better understanding of the second part of this appendix.

THE HENDERSON EQUATION AND ITS IMPACT IN PRACTICAL TERMS

The HENDERSON equation is useful if one is seeking to estimate the junction voltage between two solutions α and β in the same solvent in quasi-steady-state conditions:

$$\varphi_\beta - \varphi_\alpha = \frac{RT}{\mathcal{F}} \frac{\sum_i \frac{\lambda_i}{z_i}\left(C_{i_\beta} - C_{i_\alpha}\right)}{\sum_i \lambda_i \left(C_{i_\beta} - C_{i_\alpha}\right)} \ln \frac{\sum_i \lambda_i C_{i_\alpha}}{\sum_i \lambda_i C_{i_\beta}}$$

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

$$\varphi_\beta - \varphi_\alpha = 0.059 \frac{\sum_i \frac{\lambda_i}{z_i}\left(C_{i_\beta} - C_{i_\alpha}\right)}{\sum_i \lambda_i \left(C_{i_\beta} - C_{i_\alpha}\right)} \log \frac{\sum_i \lambda_i C_{i_\alpha}}{\sum_i \lambda_i C_{i_\beta}} \quad \text{V at 25°C}$$

Here we will focus on two cases which are important from an experimental point of view:

- the first one is a reference electrode with a liquid junction (such as an electrode based on the AgCl/Ag couple or a calomel electrode SCE, see section 1.5.1.2). Here we will study the influence on the junction voltage of the internal solution's composition;
- the second one is a salt bridge (implemented for example when measuring the voltage of a DANIELL cell, see section 1.4.1.1). Here we will study the influence on the overall ionic junction voltage of the intermediate electrolyte's composition.

It is assumed in the numerical applications outlined in this section, that the molar conductivities are equal to their values at infinite dilution. These values are all listed in table 4.2 in section 4.2.2.4.

In the first example, the liquid junction voltage will be examined at quasi-steady-state conditions for the following electrochemical chain (which could be part of a reference electrode based on AgCl/Ag):

inner aqueous solution of reference (sol. α) | | HCl aqueous solution at $pH = 2$ (sol. β)

To fix the potential reference, one needs to fix the chloride ion concentration in the reference's inner solution (see section 1.5.1.2). However, this concentration is not the only ruling factor to be taken into account designing a high-quality reference electrode, as shown when comparing the four examples outlined below (the ideal reference electrode should have a zero ionic junction voltage). The nature of the solution β being studied (here it is HCl at $pH = 2$) also has an impact on the junction voltage. However, in an experimental situation it is much easier to adapt the composition of solution α.

- Solution α: 1 mol L^{-1} KCl aqueous solution

$$\varphi_\beta - \varphi_\alpha = 0.059 \frac{34.98 \times 10^{-2} - 7.35 + 7.63 \times 0.99}{34.98 \times 10^{-2} - 7.35 + 7.63 \times 0.99} \log \frac{7.35 + 7.63}{34.98 \times 10^{-2} + 7.35 \times 10^{-2}}$$
$$= -3.5 \text{ mV}$$

- Solution α: 1 mol L^{-1} NaCl aqueous solution

$$\varphi_\beta - \varphi_\alpha = -20.6 \text{ mV}$$

- Solution α: 1 mol L^{-1} LiCl aqueous solution

$$\varphi_\beta - \varphi_\alpha = -30.9 \text{ mV}$$

- Solution α: 10^{-2} mol L^{-1} KCl aqueous solution

$$\varphi_\beta - \varphi_\alpha = -26.8 \text{ mV}$$

These results underline the fact that in order to minimise the junction voltage, one needs to choose a highly concentrated electrolyte containing anions and cations whose molar conductivities are very close. Therefore, a KCl electrolyte is a much better choice than LiCl or NaCl when the anion is Cl^-.

The second example deals with a DANIELL cell, and shows to what extent the solution that is contained within the salt bridge has an impact on the overall ionic junction voltage. Here the voltage is the algebraic sum of two liquid junction voltages, illustrated by the following electrochemical chain:

10^{-1} mol L^{-1} $CuSO_4$ aqueous solution (sol. α) | | solution in the saline bridge (sol. β) | | 10^{-3} mol L^{-1} $ZnSO_4$ aqueous solution (sol. γ)

Due to their chemical nature, solutions α and γ must be slightly acidic in order to prevent hydroxides from forming. Let us fix $pH = 4$ using H_2SO_4, which is completely dissociated into H^+ and SO_4^{2-} at this pH value.

- Solution β: solution α (only one liquid junction)

$$\varphi_\gamma - \varphi_\alpha = -11.0 \text{ mV}$$

- Solution β: 10^{-3} mol L^{-1} KNO_3 aqueous solution

$$\varphi_\gamma - \varphi_\alpha = (-13.0 - 3.6) \text{ mV} = -16.6 \text{ mV}$$

- Solution β: 1 mol L^{-1} KNO_3 aqueous solution

$$\varphi_\gamma - \varphi_\alpha = (-1.7 + 2.2) \text{ mV} = +0.5 \text{ mV}$$

- Solution β: 1 mol L^{-1} HNO_3 aqueous solution

$$\varphi_\gamma - \varphi_\alpha = (-50.3 + 120.1) \text{ mV} = +69.8 \text{ mV}$$

As previously highlighted, it is better to select a concentrated electrolyte solution involving ions with very close molar conductivity values. Note that the very fact of inserting this solution (salt bridge) triggers a significant decrease in the overall junction voltage. This is particularly important from an experimental point of view, when this type of electrochemical chain is involved when measuring thermodynamic parameters such as standard potentials, activities, etc.

BASIC ELEMENTS FOR DEMONSTRATING THE HENDERSON EQUATION

Qualitatively speaking, when two solutions made up of different compositions are brought into contact in the same solvent, then quasi-instantaneously a small number of ions are exchanged, as when establishing a thermodynamic equilibrium (see appendix A.3.4). This exchange process leads to (after about 10^{-9} s) a build-up of charge excess on both sides of the junction area, as in the case of a double layer at an electrochemical interface. For instance, when dealing with a single ionic junction directly between the two solutions in a DANIELL cell *via* a porous plug, a small number of Cu^{2+} ions move from the $CuSO_4$ solution into the $ZnSO_4$ solution and conversely some Zn^{2+} ions are transferred from the $ZnSO_4$ solution into the $CuSO_4$ solution. Here we are talking about extremely small quantities, however the resulting surface charge excess produces a significant and immediate potential difference between the two solutions. The concentration profiles within the porous material then continue to evolve until finally reaching a quasi-steady state with fixed concentrations on each side of the porous plug, which dramatically slows down the mixing of the two solutions (see section 4.4.2). During the time it takes to reach these profiles (a process that may last up to several hours depending on the nature and thickness of the porous material), the fact that

electroneutrality prevails in the solutions (although it does not strictly apply) has the effect of forcing the migration and diffusion fluxes of the anions and cations to occur in a combined manner (see appendix A.4.1).

When giving a quantitative description, the first step is to write that the overall current resulting from the ionic fluxes (without convection) is zero at all times (see section 4.2.1.4):

$$0 = -\sum_i D_i\, z_i\, \mathscr{F}\, C_i\, \mathbf{grad}\,(\ln a_i) + \sum_i \lambda_i\, C_i\, \mathbf{E}$$

or:

$$\mathbf{E} = -\,\mathbf{grad}\,\varphi = \sum_i \frac{D_i\, z_i\, \mathscr{F}\, C_i}{\sum_j \lambda_j\, C_j}\,\mathbf{grad}\,(\ln a_i)$$

The NERNST-EINSTEIN equation describes the link between the molar conductivity and the diffusion coefficient in an ideal case. However, the equation can also be stretched to apply to other cases, provided that one remembers that D_i is the true diffusion coefficient and not the apparent one (first FICK's law, see section 4.2.1.4):

$$\lambda_i = D_i\, z_i^{\,2}\, \frac{\mathscr{F}^2}{\mathrm{R}T}$$

hence:

$$-\,\mathbf{grad}\,\varphi = \frac{\mathrm{R}T}{\mathscr{F}} \sum_i \frac{\lambda_i\, C_i}{z_i \sum_j \lambda_j\, C_j}\,\mathbf{grad}\,(\ln a_i) = \frac{\mathrm{R}T}{\mathscr{F}} \sum_i \frac{t_i}{z_i}\,\mathbf{grad}\,(\ln a_i)$$

and:

$$\varphi_\beta - \varphi_\alpha = \frac{\mathrm{R}T}{\mathscr{F}} \int_\beta^\alpha \left[\sum_i \frac{t_i}{z_i}\,\mathbf{grad}\,(\ln a_i) \right] \mathrm{d}x$$

The common version of the HENDERSON equation is then easily reached using the following approximations: concentrations are used instead of activities, the molar conductivities (or mobilities) are constant and the concentration profiles are considered as being linear.

If referring to usual applications, then the most questionable of all the simplifications listed above is the assumption that the activities are equal to the molar concentrations. Nevertheless, it should be pointed out that only the ratios appear in the final equation, which ends up minimising the impact of such systematic errors.

As for linear concentration profiles, it should be emphasised that the thickness of the zone where these profiles develop does not appear in the calculation result. Therefore it is easy to show that the ionic junction voltage which is reached at quasi-steady state (with a linear profile extending throughout the separator material) is identical to the voltage that is rapidly reached (about 10^{-9} s) before any modifications occur in the bulk concentrations. More complex models even show that the ensuing outcome, known as the HENDERSON equation, can be applied more widely than one would expect when one considers its usual demonstration (the equation can be applied at all times while the quasi-steady state is being reached). It is even possible to use a similar equation when there is a current flowing through the system, though this time the ohmic drop is included.

A.1.2 - POTENTIOSTAT AND GALVANOSTAT

POTENTIOSTAT

A potentiostat is an electronic instrument designed to control the potential difference applied to an electrochemical cell, between the working electrode (WE) where there is a current flow and a reference electrode (Ref) where there is no current flow. A potentiostat needs the use of a 3-electrode device: a working electrode, a reference electrode and a counter-electrode, or auxiliary electrode (CE). This type of instrument must be distinguished from a DC voltage supply, which imposes and controls in an electric circuit the potential difference between two terminals with a current flowing between them, namely the working and counter-electrodes in an electrochemical cell. The potentiostat is a crucial instrument when performing analytical studies in electrochemistry, because in order to properly understand, analyse and distinguish between the different phenomena at play at each interface, one needs more than simply information on the overall cell voltage.

In order to properly carry out this function, a particular type of software can be used that is driven by a microprocessor. However, here one would need to use electronic interface components (analogue/digital and digital/analogue converters) with extremely short conversion times so as to ensure that the servo-control is fast and accurate, and such converters are particularly expensive.

Alternatively, another possibility would be to use an electronic device with an operational amplifier mounted in servo-control, as illustrated in figure A.1.

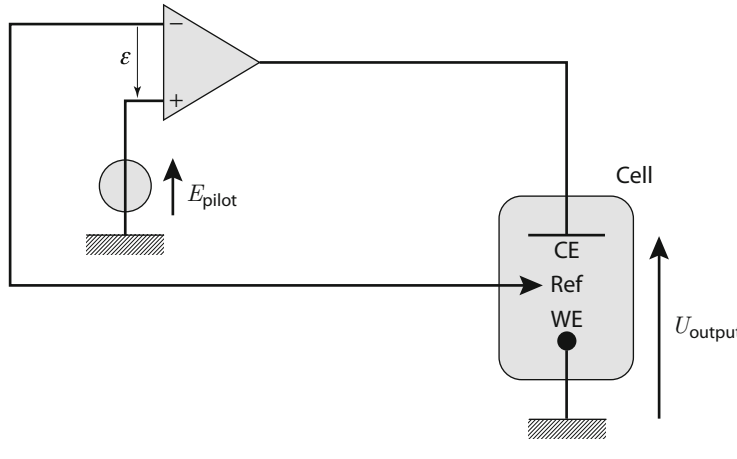


Figure A.1 - Diagram showing the basic principles of an analogue potentiostat

Here is a brief overview of the main theoretical features of an operational amplifier: the voltage gain (G) is infinite between the input and output connections (in practice higher than 10^5), the response time is very short (less than 10^{-6} s), the output impedance is low and the input impedance is infinite (in practice higher than 10^6 Ω, or even 10^{12} to 10^{14} Ω when using field effect transistor technology). Therefore the leakage current is extremely low between the amplifier's – and + input connections, and the pilot generator delivers practically no current.

In this case the voltage can be written as:

$$U_{\text{output}} = G\,(E_{\text{applied}} - E_{\text{Ref}}) \quad \text{or} \quad \varepsilon = E_{\text{applied}} - E_{\text{Ref}} = U_{\text{output}}/G \approx 0$$

In this example above, given that the working electrode is connected to the ground, the following equation can be applied at all times:

$$U_{\text{WE/Ref}} = -E_{\text{applied}}$$

Therefore, this type of device controls the voltage value between the working electrode and the reference electrode that has no current flowing through it. However, the voltage between the counter-electrode and the reference electrode may fluctuate due to experimental factors (for example, bubbles or a passive layer forming, etc.) while leaving the $E_{\text{WE/Ref}}$ value unaffected. The imposed voltage E_{applied} can be continuous or it can be modulated by a signal generator (triangular, square or sinusoidal).

It must be pointed out that the U_{output} value is limited by the power supply of the operational amplifier ($+V_{cc}$, $-V_{cc}$, which are not indicated on the diagram in figure A.1). Therefore, a small laboratory potentiostat matching the simple diagram in figure A.1 has its output power limited by the electronic components being used. More complex devices can drive electrochemical cells that need higher power values. Moreover, some potentiostats are equipped with a device compensating for the ohmic drop that occurs between the reference and the working electrodes.

GALVANOSTAT

A galvanostat is an instrument that controls the current intensity flowing through an electrochemical cell. For this application, one can use the electric setup indicated in figure A.2, which controls the voltage between the resistance connections (R).

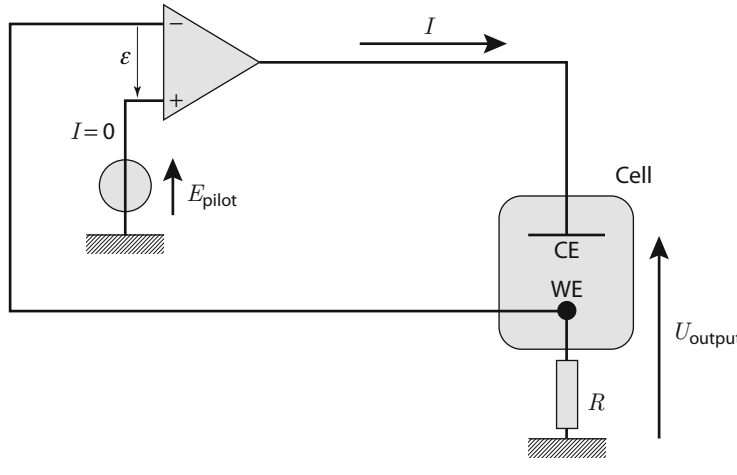


Figure A.2 - Diagram showing an analogue galvanostat

A calculation can be made that is similar to the one applied in the case of the potentiostat, which shows that $E_{\text{applied}} - RI \approx 0$. Here, the current flowing through the resistance, which is identical to the current flowing through the cell connected in series, is controlled by the operational amplifier. However, the voltage between the working and the counter-electrodes is not controlled and can fluctuate due to unpredictable experimental factors.

In a setup that uses a galvanostat, it is possible to not use a reference electrode. However, if there is a reference electrode, then it is only used to monitor the voltage between the working electrode and the reference electrode.

A potentiostat can also be used for an experiment that is set up in galvanostat mode. In this case, all that is needed is to insert a resistance in series with the electrochemical cell. The potentiostat is then connected to the assembly by linking the potentiostat's Ref output to the cell's working electrode and linking the WE output (the ground) to the other end of the resistance. The counter-electrode is connected in the usual manner, as shown in figure A.3.

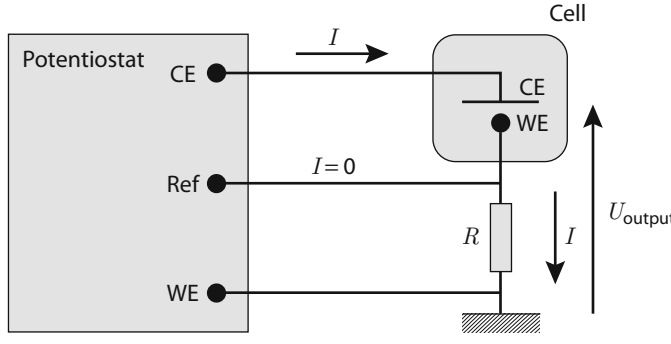


Figure A.3 - Diagram of a galvanostatic setup using a potentiostat

However, for this function to work there is no need to use a high-performance potentiostat. A mere DC current supply can be used, provided that it has adequate capacities (power, rise time, etc.). Some instruments offer the opportunity to use both functions (potentiostat and galvanostat).

A.2.1 - GENERAL SHAPE OF THE CURRENT-POTENTIAL CURVE FOR REDUCING WATER OR PROTONS: THE ROLE OF MASS TRANSPORT KINETICS

When dioxygen and dihydrogen are formed the reactions involved are complex in several ways. However, if they are simplified to a certain degree, then it is possible to define the shape of the current-potential curves corresponding to aqueous solutions with different pH values. The following analysis is confined to situations where the limiting process is the mass transport of electroactive species *via* diffusion. In other words, it only applies when the kinetics of the various steps of the reduction mechanism is much faster than that of mass transport (i.e., mass transport control). To fully grasp the following analysis, the key notions are outlined in the preceding chapters, and a thorough understanding of chapter 4 is particularly essential.

In this section we will first look at dihydrogen production in an acidic aqueous solution, whereby argon is continuously bubbled inside. Here, assuming unidirectional geometry, the steady states are described by the NERNST model: due to convection, the composition remains homogeneous throughout the bulk of the electrolyte, i.e., in the area beyond the thickness layer δ. This composition is identical to the initial composition: the pH is

fixed and no dihydrogen is dissolved. Moreover, a supporting electrolyte is added, which has the effect of minimising the migration of electroactive species. It is assumed that the diffusion coefficients are identical, which makes the calculations much easier, yet without limiting in any way the scope of the results that are presented below.

The first difficulty stems from the very nature of the product being formed. To simplify, here we will assume that the dissolved dihydrogen is the only reaction product, even if the solubility limit is often reached in experiments. Since only fast reduction reactions are being considered here, the potential of the inert electrode can be written using the reversibility hypothesis:

$$E = E^\circ + \frac{0.06}{-2}\log\left(\frac{a_{H_{2\text{dissolved}}}}{(a_{H^+})^2}\right)_{\text{interface}} = E^\circ - 0.06\ pH_{\text{interface}} - 0.03\log a_{H_{2\text{interface}}}$$

It must be emphasized that in the above equation for reversible proton reduction, the standard potential is not equal to 0 $V_{/SHE}$, since the couple in question, $H^+/H_{2_{dissolved}}$, is different from the usual $H^+/H_{2_{gaz}}$ couple. The link between these values calls into play the HENRY constant for dihydrogen, which leads to a solubility $s_{H_2} = 8\times10^{-4}$ mol L^{-1} for a partial pressure of 1 bar. The standard potential is therefore:

$$E^\circ = 0 - 0.03\log s_{H_2} = +0.093\ V_{/SHE}$$

Moreover, again for the sake of simplicity, the values of the activity and concentration for each of the species involved are considered here as being equal.

The second difficulty stems from the autoprotolysis equilibrium of the water or, in other words, from the fact that dihydrogen may form at the interface between the electrode and the electrolyte due to the reduction of H^+ and/or of H_2O (see section 2.1.2.3). In some operating conditions, *a priori* this leads to non-linear concentration profiles for the H^+ and OH^- ions throughout the diffusion layer, unlike the typical situation found for unidirectional-diffusion steady states.

This phenomenon looks like an anomaly when compared to the conventional case, for example the Fe^{3+}/Fe^{2+} couple, but in electrochemistry the occurrence of chemical equilibrium inside the solution cannot be considered as being exceptional. So, a specific term for volume production must be taken into account in the mass balance for the species involved in this equilibrium. At steady state, the mass balance of the electroactive species can be written as follows (see section 4.1.2):

$$0 = -\operatorname{div}\mathbf{N}_{H^+} + w_{H^+} = -\operatorname{div}\mathbf{N}_{OH^-} + w_{OH^-} = -\operatorname{div}\mathbf{N}_{H_2} + 0$$

The concentration profile for dissolved H_2 is therefore linear (i.e., the molar flux density inside the diffusion layer is constant), though this is not the case *a priori* for H^+ and OH^-.

However, given that the following water autoprotolysis reaction:

$$H_2O \rightleftharpoons H^+ + OH^-$$

involves H^+ and OH^- with identical stœchiometric numbers, their local production rates per volume unit are equal as written here:

$$w_{H^+} = w_{OH^-}$$

The volume production term can therefore be eliminated by subtracting the first two equations. A linear profile is therefore to be expected throughout the diffusion layer for the quantity $[H^+] - [OH^-]$.

Since the equilibrium constant is very low, it can be shown that H^+ and OH^- do not co-exist in significant quantities. Except for pH values close to 7, the following inequalities always apply:

$$\text{either } [H^+] \gg [OH^-] \qquad \text{or } [H^+] \ll [OH^-]$$

Therefore, depending on the working point in question, the diffusion layer can be divided into two adjoining zones: an alkaline zone and an acidic zone, each showing linear concentration profiles. This can be illustrated by studying the concentration profiles for different working points on the current-potential curve: let us consider the case of an acidic aqueous solution at $pH^* = 4$ in the cathodic domain [1].

- When the current is lower than the limiting current related to the simple reduction of H^+, then it suffices to consider that this reduction reaction is the only significant phenomenon at play. The OH^- concentration remains negligible in the diffusion layer. The concentration profile of dissolved dihydrogen is related to the proton concentration profile, taking into account the stœchiometric coefficients.

  The limiting current can be expressed by: $I_{lim} = -D\,\mathcal{F}\,S\,\dfrac{[H^+]^*}{\delta}$

  In this zone ($|I| < |I_{lim}|$), the interfacial concentrations can be expressed as a function of I:

$$[H^+]_{interface} = [H^+]^* \left(1 - \frac{I}{I_{lim}}\right) \qquad [H_2]_{interface} = [H^+]^* \frac{I}{2\,I_{lim}}$$

Figure A.4 depicts the concentration profiles for two working points that have been selected in this zone: at the half-wave ($I = I_{lim}/2$; $pH_{interface} = 4 + \log 2 = 4.3$) and for $pH_{interface} = 5$, i.e., $I = 0.9\ I_{lim}$.

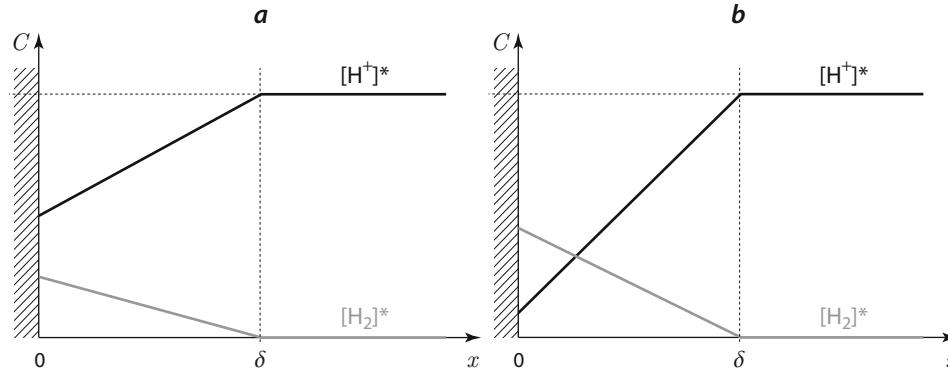


Figure A.4 - Concentration profiles of H^+ (black) and H_2 (grey) in an aqueous solution, with $pH^* = 4$, for (a) $I = I_{lim}/2$ and (b) $I = 0.9\ I_{lim}$
The OH^- concentration is not indicated: it is negligible throughout the solution.

[1] As mentioned in chapter 4, the bulk values are denoted by, and are equal to the initial values before the current is switched on.*

The equation for the current-potential curve for $|I| < |I_{lim}|$, that is plotted in figure A.5, is:

$$E = 0.093 - 0.03\ pH^* - 0.03 \log\left[\frac{I}{2\ I_{lim}}\left(\frac{I_{lim}}{I_{lim} - I}\right)^2\right]$$

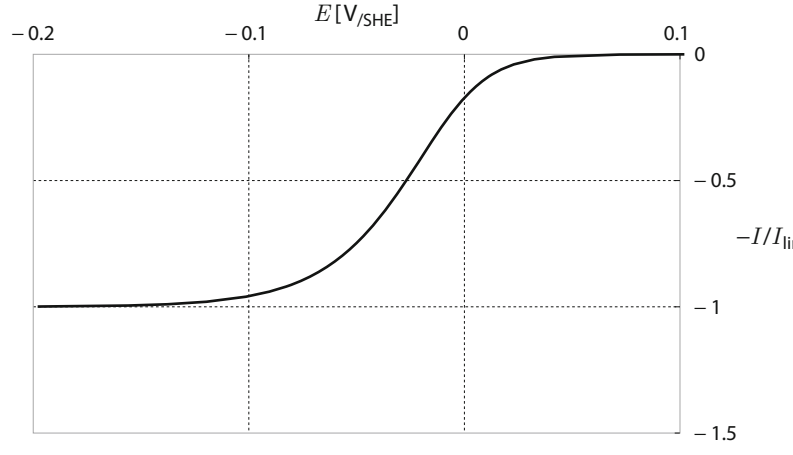


Figure A.5 - Current-potential curve for reducing an aqueous solution with $pH^* = 4$ for working points with $I/I_{lim} < 0.99$ (i.e., $pH_{interface} < 6$)

- If H_2O is reduced together with H^+, then it is possible to outstrip the limiting current previously defined. The water reduction leads to dihydrogen and hydroxide ions being produced (linked to water autoprotolysis). Therefore, it leads to a high $pH_{interface}$ value. As previously specified, the diffusion layer is divided into two zones. The first one, next to the electrode, is an alkaline zone where the proton concentration is negligible. The second zone is an intermediate zone, where the proton concentration is once again much larger than that of the hydroxide ions. In this intermediate zone, the pH decreases progressively until the point of reaching its initial value at a distance δ from the interface. Since the difference in concentrations $[H^+] - [OH^-]$ varies in a linear manner, then the values of the slopes of the concentration profiles for H^+ and OH^- must be opposite in each zone. As the current increases (in absolute value), then the thickness of the alkaline zone also increases and tends towards δ, while the thickness of the acidic zone decreases to insignificant values. This feature is illustrated in figure A.6 for working points corresponding to 2 I_{lim} and 4 I_{lim}.

  In this zone ($|I| > |I_{lim}|$), the interfacial concentrations can be expressed as a function of the current:

$$[OH^-]_{interface} = [OH^-]^* + [H^+]^*\left(\frac{I}{I_{lim}} - 1\right) \approx [H^+]^*\left(\frac{I}{I_{lim}} - 1\right)$$

$$[H^+]_{interface} = \frac{10^{-14}}{[OH^-]_{interface}}$$

$$[H_2]_{interface} = [H^+]^* \frac{I}{2\ I_{lim}}$$

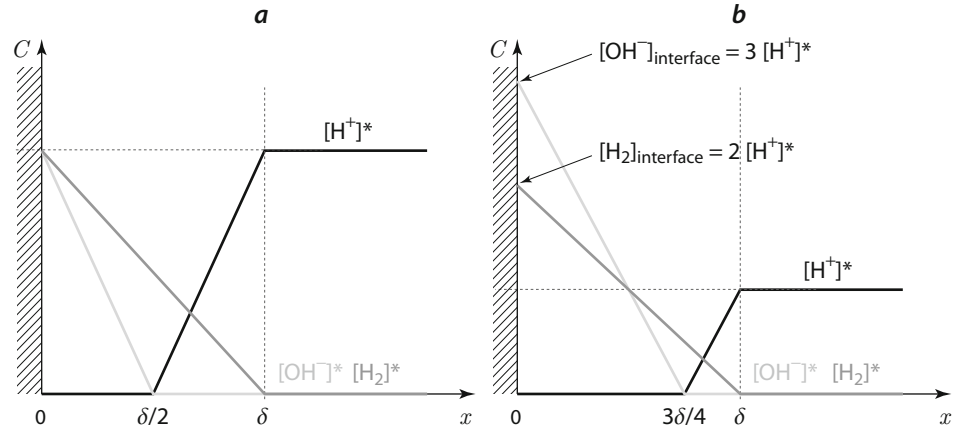


Figure A.6 - Concentration profiles of H^+ (black), OH^- (clear grey) and H_2 (dark grey) for an aqueous solution with $pH^* = 4$ for (a) $I = 2\ I_{lim}$ and (b) $I = 4\ I_{lim}$ (with a contracted concentration scale)

The equation for the corresponding part of the current-potential curve ($|I| > |I_{lim}|$), plotted in figure A.7, can be deduced from above and is written as the following:

$$E = 0.093 + 0.09\ pH^* - 0.06 \times 14 - 0.03 \log\left[\frac{I}{2\ I_{lim}}\left(\frac{I_{lim} - I}{I_{lim}}\right)^2\right]$$

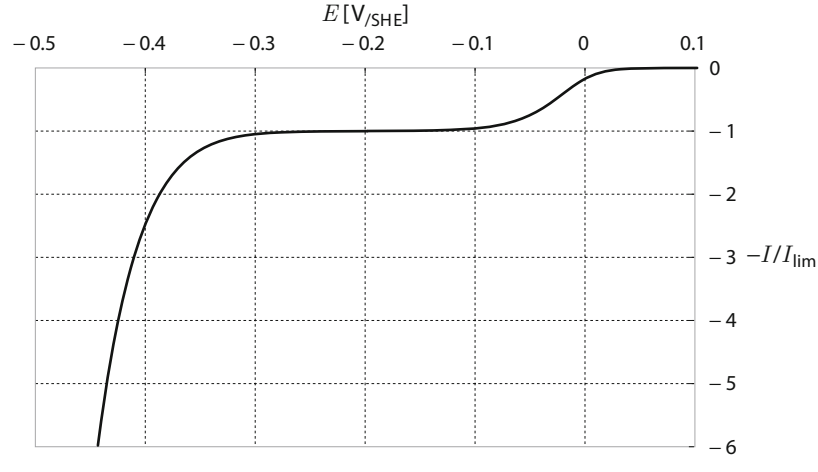


Figure A.7 – Shape of the current-potential curve for reducing an aqueous solution with $pH^* = 4$

In this slightly acidic type of solution, the steady-state current-potential curve shows two distinct reaction zones which can be ascribed to a low $pH_{interface}$ value (H^+ is reduced) or to a high $pH_{interface}$ value (H_2O is reduced). Let us recall it is assumed that the interfacial reactions kinetics plays no part here.

Figure A.8 shows the shape of the steady-state current-potential curves obtained for different values of the pH of the initial solution, pH*.

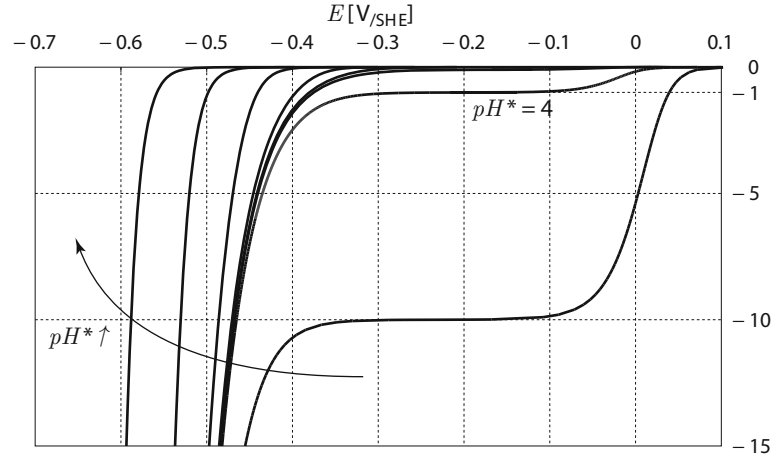


Figure A.8 - Shape of current-potential curves for reducing aqueous solutions with pH* = 3, 4, 5, 9, 10, 11, 12 and 13

The current scale is expressed with an arbitrary unit: –1 corresponds to the limiting current at pH = 4.*

As to be expected from a redox couple, the limiting current changes with the pH* value in the acidic solutions, since this current is proportional to the proton concentration in the solution. However, the corresponding potential changes are more complex. At low pH* values, the half-wave potential varies as – 0.03 pH* (see figure A5 and the equation just above it). The curves corresponding to pH* values between 5 and 9 are only barely distinguishable. Only at high pH* values can the position of the electrochemical window's cathodic boundary be easily linked to the apparent standard potential, which varies as – 0.06 pH*. This simplified example, assuming that it involves fast redox kinetics, shows how difficult it is to use the apparent standard potential for positioning the current-potential curves of water redox couples. Therefore, it is particularly inadvisable to apply such a concept with intermediate pH* values.

A.2.2 - DIFFERENT WORKING POINTS FOR AN ELECTROCHEMICAL SYSTEM

This appendix highlights an important case found in systems where the short-circuit current is extremely low. In such systems, almost all the operating conditions with significant currents are in electrolyser mode. For example, imagine a deaerated acidic aqueous electrolyte, with two inert electrodes (platinum and carbon) immersed within. One can assume that proton reduction kinetics is the only characteristic that distinguishes the interfaces. Therefore, the anodic branches of the current-potential curves are viewed as being the same, as long as the water oxidation into dioxygen occurs in the same way. The system's open-circuit voltage equals the difference between two mixed potentials. As presented in figure A.9, platinum is the positive electrode at open circuit.

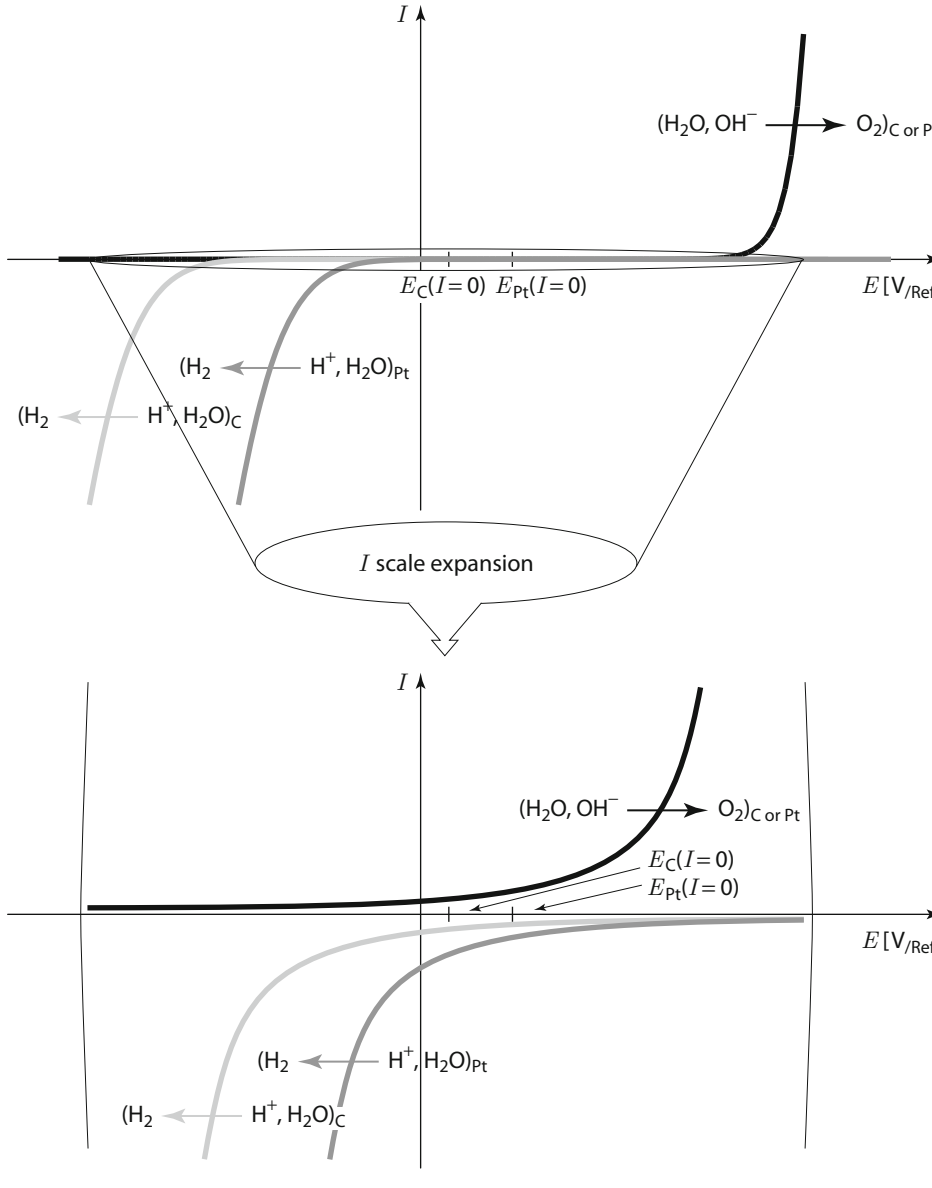


Figure A.9 - Superimposed anodic and cathodic branches of the current-potential curves of a carbon electrode and a platinum electrode immersed in a deaerated acidic aqueous solution

In this system, a slight current variation around 0 causes a sudden voltage variation. This variation reflects the change occurring between an electrolyser mode, where the anode is platinum (the dotted line in figure A.10-a), and another electrolyser mode where the platinum electrode plays the role of cathode (the dashed and dotted line in figure A.10-b).

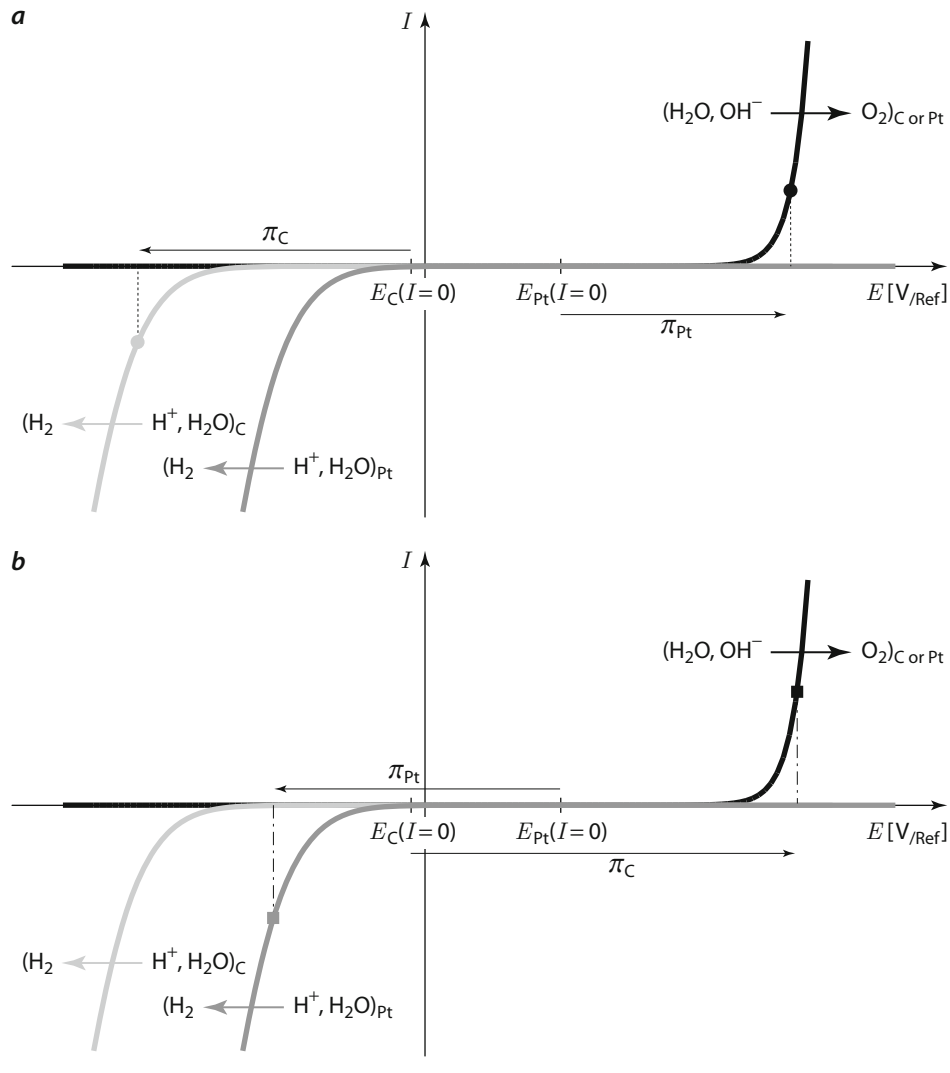


Figure A.10 - Superimposed anodic and cathodic branches of the current-potential curves of a carbon electrode and a platinum electrode immersed in a deaerated acidic aqueous solution
*Two different working points are indicated in the figures (**a :** ●) and (**b :** ■).*

However, within a certain voltage range the system works as a power source, yet with an insignificant current, as shown in figure A.11. Here, by convention, the working electrode is the electrode that is positive at open circuit, i.e., the platinum electrode. Over and above the particular examples of short circuit and open circuit (points ($U = 0$, I_{sc}) and ($U(I = 0)$, $I = 0$), the two working points depicted in figure A.10 (the dotted line in figure A.10-a and the dashed and dotted line in figure A.10-b) are also indicated in figure A.11.

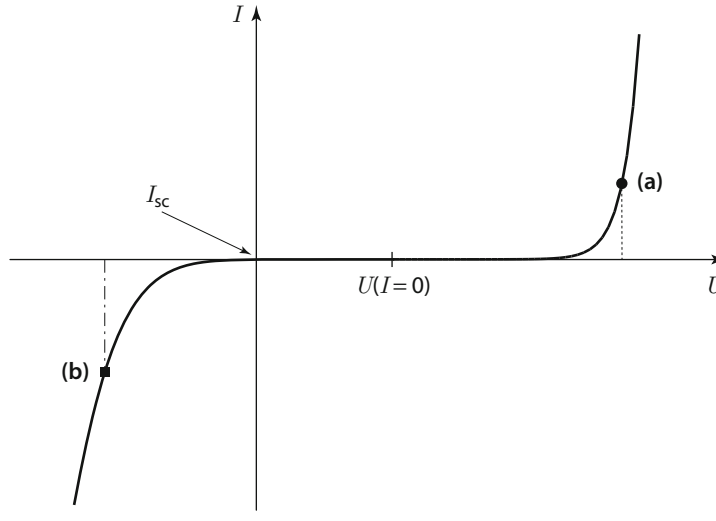


Figure A.11 - I(U) curve showing the working points of a system with a carbon electrode and a platinum electrode immersed in a deaerated acidic aqueous solution

A.3.1 - ELECTRIC POTENTIAL: VOLTA AND GALVANI POTENTIALS

Using a simple example to illustrate the concept of VOLTA and GALVANI potentials, let us consider a charged spherical conductor (radius r_0) in equilibrium and in vacuum. As depicted in figure A.12, only the surface is charged: the volume charge density, ρ_{ch}, is zero. It is assumed that the surface charges, $Q_{surface,}$ are uniformly distributed in the form of a thin, spherical crown, with a thickness of δ_{ch}[2]. Inside the crown, the volume charge density is not zero, with the following equation:

$$Q_{surface} = 4\,\pi\,\rho_{ch}\,\delta_{ch}\,r_0^{\,2}$$

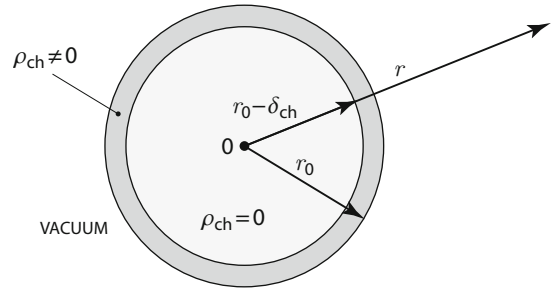


Figure A.12 - Conducting sphere with its charged surface

[2] *For electronic conductors, notably semiconductors, this volume is called a ' space charge zone '. It is equivalent to the double layer for an electrochemical interface.*

The laws of electrostatics can be applied to show the equations for the equilibrium electric field $\mathbf{E}$ and potential V. The electric field, which is radial (modulus denoted by E_r), and the potential V are expressed as a function of the distance from the origin:

- Applying the GAUSS theorem for the electric field profile gives: $4\,\pi\,r^2\,E_r = \frac{Q_{inner}}{\varepsilon_0}$.

$$0 \le r \le r_0 - \delta_{ch} \qquad E_r = 0$$

$$r_0 - \delta_{ch} \le r \le r_0 \qquad E_r = \frac{\rho_{ch}}{\varepsilon_0}\left[r - (r_0 - \delta_{ch})\right]$$

$$r \ge r_0 \qquad E_r = \frac{\rho_{ch}}{\varepsilon_0}\,\delta_{ch}\left(\frac{r_0}{r}\right)^2$$

- The potential profile is obtained by integration of $E_r = -\frac{dV}{dr}$, with $V = 0$ at infinite distance and continuity at the interfaces, which gives.

$$r \ge r_0 \qquad V = \frac{\rho_{ch}}{\varepsilon_0}\,\delta_{ch}\,\frac{r_0^2}{r} = \frac{Q_{surface}}{4\,\pi\,\varepsilon_0\,r}$$

$$r_0 - \delta_{ch} \le r \le r_0 \qquad V = -\frac{\rho_{ch}}{2\,\varepsilon_0}\left\{\left[r - (r_0 - \delta_{ch})\right]^2 - 2\,r_0\,\delta_{ch} - \delta_{ch}^2\right\}$$

$$0 \le r \le r_0 - \delta_{ch} \qquad V = \frac{\rho_{ch}}{\varepsilon_0}\,\delta_{ch}\,r_0\left(1 + \frac{\delta_{ch}}{2\,r_0}\right)$$

The corresponding profiles are illustrated in figures A.13 and A.14. The two graphs on the right (electric field and potential) are plotted on a dilated scale compared to those on the left. In addition, in figure A.14 the ordinate scales are different for χ and ψ. Consequently, this leads to a break in the slope for r_0, which has no physical meaning since the following equation applies:

$$\chi = \psi\,\frac{\delta_{ch}}{2\,r_0} \ll \psi$$

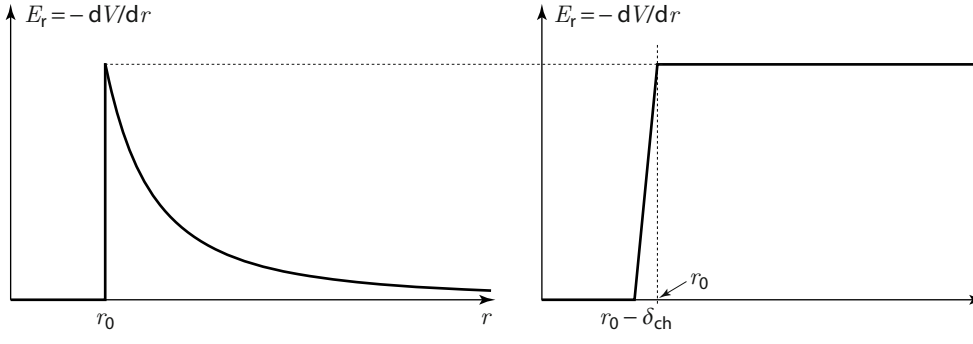


Figure A.13 - Radial component profile of the electric field ($\rho_{ch} > 0$)
In the figure on the right, the r scale is considerably dilated.

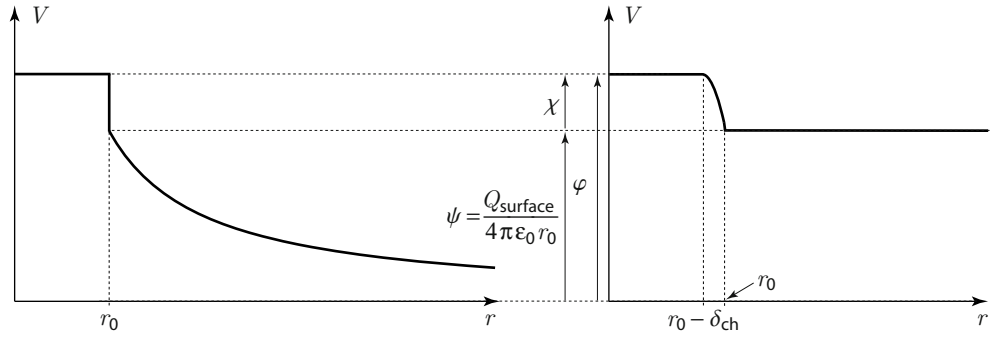


Figure A.14 - Electric potential profile ($\rho_{ch} > 0$)
In the figure on the right, the r scale is considerably dilated.

A.3.2 - MEAN ACTIVITY OF A SOLUTE IN AN ELECTROLYTE

Strictly speaking, it is possible to measure electrochemical potential and activity for any neutral species, though not for an ion: one cannot add a single type of ion to an electrolyte medium because such a modification would not preserve electroneutrality (see section 3.1.2.2). That said, it has to be recognised that the electrochemical potential and the activity of an ion are both conceivable notions. Indeed, they are so widely used in electrochemistry (and especially in this book), that it is easy to forget that, technically speaking, they are non-measurable quantities. This may seem inconsistent with other conventional concepts in electrochemistry, especially with the notion of selective electrodes, which are commonly used as indicators for a specific ion activity. The most famous of these selective electrodes is the pH electrode, although pH is, by definition, impossible to measure from a strictly thermodynamic point of view. The following appendix addresses this apparent contradiction by examining the thermodynamic equilibrium or the quasi-steady state of different electrochemical chains at open circuit.

The first group of examples illustrated deals with electrochemical chains with no ionic junction. In this case the thermodynamic voltage is always written in a straightforward way using an equation that includes the activities of neutral species (in particular the mean activities of electrolytes, see section 3.2.1.1). The second group of examples deals with electrochemical chains with at least one ionic junction. In this case, the equation for the open-circuit voltage usually shows the ion activity as a separate entity. In this section we will show how it is only possible to write the equation in this way when the ionic junction voltage has been disregarded. Let us recall that, in the latter case, the electrochemical interfaces are in thermodynamic equilibrium, whereas the liquid junction are at quasi-steady state (see section 3.3.5 and appendix A.1.1).

ELECTROCHEMICAL CHAINS WITH NO IONIC JUNCTION

It is a hard task to find a realistic example of an electrochemical chain that is both in true thermodynamic equilibrium and with no ionic junction. However, the two examples laid out below come relatively close to this case, provided that an additional assumption is made, which is specified in each case.

▸▸ The first example is the following chain:

Ag' | Pt, H_2 | aqueous solution containing HCl and KCl | AgCl | Ag

Here it has to be assumed that dihydrogen is not in contact with AgCl, otherwise it would spontaneously react. Remember that in order to write the correct equation for the voltage that is measured by a voltmeter, the electrochemical chain needs to end with two materials of an identical nature. As a result, it is only their VOLTA potentials which differ (see section 3.3.4.1). By writing equations for the electrochemical equilibrium of all the interfaces, one ends up with the following chain voltage (see section 3.4.1.1):

$$\begin{aligned}\varphi_{Ag} - \varphi_{Ag'} &= \frac{1}{2\mathcal{F}}(2\mu_{AgCl} + \mu_{H_2} - 2\mu_{Ag} - 2\mu_{H^+} - 2\mu_{Cl^-}) \\ &= U^\circ + \frac{RT}{\mathcal{F}}\ln\sqrt{a_{H_2}} - \frac{RT}{\mathcal{F}}\ln(a_{H^+}a_{Cl^-}) \\ &= U^\circ + \frac{RT}{\mathcal{F}}\ln\sqrt{a_{H_2}} - \frac{2RT}{\mathcal{F}}\ln a_\pm\end{aligned}$$

Therefore the thermodynamic voltage of this cell is mainly a function of the mean activity of HCl, whereas the activities of H^+ or Cl^- do not play any part when taken separately. Here, it must be underlined that because the solution contains three types of ions (H^+, K^+ and Cl^-), one therefore needs to include the different H^+ and Cl^- concentrations when calculating the mean activity coefficient of HCl.

▸▸ The second example that illustrates a lead-acid battery, presents the following electrochemical chain:

Pb' | $PbSO_4$ | H_2SO_4 aqueous solution | $PbSO_4$ | PbO_2 | Pb

Here, it is assumed that the solvent decomposition reactions (release of dihydrogen and dioxygen) are immeasurably slow. The battery voltage in equilibrium is obtained by writing the electrochemical equilibrium of all the interfaces:

$$\begin{aligned}\varphi_{Pb} - \varphi_{Pb'} &= \frac{1}{2\mathcal{F}}\left(\mu_{PbO_2} + \mu_{Pb} + 2\mu_{H^+} - 2\mu_{HSO_4^-} - 2\mu_{H_2O} - 2\mu_{PbSO_4}\right) \\ &= U^\circ - \frac{RT}{\mathcal{F}}\ln a_{H_2O} + \frac{RT}{\mathcal{F}}\ln(a_{H^+}a_{HSO_4^-}) \\ &= U^\circ - \frac{RT}{\mathcal{F}}\ln a_{H_2O} + \frac{2RT}{\mathcal{F}}\ln a_\pm\end{aligned}$$

Therefore the overall battery voltage gives access to the mean activity of H_2SO_4. Indeed, it can be noted that the data are often expressed in terms of mean activity coefficients. Depending on which author, the results take into consideration either the species H^+ and HSO_4^- or H^+ and SO_4^{2-}. In fact $a_\pm$ is the only experimental datum.

ELECTROCHEMICAL CHAINS WITH AN IONIC JUNCTION

▸▸ Let us first consider a chain involving the same electrochemical interfaces as in the first example with no ionic junction, yet this time introducing two aqueous solutions with different compositions which are placed in contact through a porous material:

Ag' | Pt, H_2 | HCl solution (sol. α) | | KCl solution (sol. β) | AgCl | Ag

The following shows the open-circuit voltage that is obtained by writing the electrochemical equilibria of all the interfaces, with the ionic junction excluded (see section 3.4.1.1):

$$\varphi_{Ag} - \varphi_{Ag'} = \frac{1}{2\mathscr{F}}(2\,\mu_{AgCl} + \mu_{H_2} - 2\,\mu_{Ag} - 2\,\mu_{H^+} - 2\,\mu_{Cl^-}) + \varphi_\beta - \varphi_\alpha$$
$$= U^\circ + \frac{RT}{\mathscr{F}} \ln \sqrt{a_{H_2}} - \frac{RT}{\mathscr{F}} \ln(a_{H^+_\alpha} a_{Cl^-_\beta}) + U_{junction}$$

Using the values in appendix A.1.1, with a solution of $pH = 2$ for α and a 1 mol L^{-1} KCl solution for β, the ionic junction voltage is very small in numerical terms (3.5 mV). Therefore, it would not be incongruous to write[3]:

$$\varphi_{Ag} - \varphi_{Ag'} \approx U^\circ + \frac{RT}{\mathscr{F}} \ln \sqrt{a_{H_2}} - \frac{RT}{\mathscr{F}} \ln(a_{H^+_\alpha} a_{Cl^-_\beta})$$

In this equation, there appears no clear thermodynamic parameter involving ions, the reason being that parameters for the ions belonging to phases α and β are mixed. Yet, this type of equation is commonly found in electrochemistry. In order to gain a full understanding of what is being measured, it is nonetheless worth describing the ionic junction term in precise detail, even though its value is small in numerical terms. By reusing the results from appendix A.1.1, the junction voltage can be written as being an integral over the thickness of the porous material:

$$\varphi_\beta - \varphi_\alpha = \frac{RT}{\mathscr{F}} \int_\beta^\alpha \left(t_{H^+}\, \mathbf{grad}\,(\ln a_{H^+}) + t_{K^+}\, \mathbf{grad}\,(\ln a_{K^+}) - t_{Cl^-}\, \mathbf{grad}\,(\ln a_{Cl^-}) \right) \mathrm{d}x$$

Since the sum of the transport numbers is equal to 1 at any point, one can also write:

$$U_{junction} = \frac{RT}{\mathscr{F}} \int_\beta^\alpha \left(t_{H^+}\, \mathbf{grad}\,(\ln(a_{H^+} a_{Cl^-})) + t_{K^+}\, \mathbf{grad}\,(\ln(a_{K^+} a_{Cl^-})) - \mathbf{grad}\,(\ln a_{Cl^-}) \right) \mathrm{d}x$$
$$= \frac{RT}{\mathscr{F}} \ln \frac{a_{Cl^-_\beta}}{a_{Cl^-_\alpha}} + \frac{RT}{\mathscr{F}} \int_\beta^\alpha \left(t_{H^+}\, \mathbf{grad}\,(\ln(a_{H^+} a_{Cl^-})) + t_{K^+}\, \mathbf{grad}\,(\ln(a_{K^+} a_{Cl^-})) \right) \mathrm{d}x$$

and finally:

$$\varphi_{Ag} - \varphi_{Ag'} = U^\circ + \frac{RT}{\mathscr{F}} \ln \sqrt{a_{H_2}} - \frac{RT}{\mathscr{F}} \ln(a_{H^+_\alpha} a_{Cl^-_\alpha})$$
$$+ \frac{RT}{\mathscr{F}} \int_\beta^\alpha \left(t_{H^+}\, \mathbf{grad}\,(\ln(a_{H^+} a_{Cl^-})) + t_{K^+}\, \mathbf{grad}\,(\ln(a_{K^+} a_{Cl^-})) \right) \mathrm{d}x$$

Therefore, one can see that in this more thorough version of the equation, the cell's open-circuit voltage (at quasi-steady state) does not show any isolated ionic activity. Instead, it shows the mean activities of the neutral species HCl and KCl: $\sqrt{a_{H^+} a_{Cl^-}}$ and $\sqrt{a_{K^+} a_{Cl^-}}$ respectively.

▸▸ The case of an ion-selective electrode for a given ion i, produces the same type of equation. If one disregards the ionic junction voltage, due to the fact that a reference

[3] *When dealing with a cell with a salt bridge, it would be all the more legitimate to disregard the junction voltage.*

electrode is completing the electrochemical sensor for example, the following type of equation emerges:

$$U \approx \text{Cst} + \frac{\nu_i \mathrm{R}T}{\nu_\mathrm{e}\,\mathscr{F}} \ln a_i$$

This equation, which is the most common, could indicate that the activity of ion i is a measurable quantity, though this is not strictly exact. The correct expression to give the accurate voltage, with the ionic junction voltages taken into account, always includes the mean activities and their spatial variations.

▸▸ The final example, which also deals with aqueous solutions, gives a result that is commonly found in electrochemistry, when it is not possible to disregard the cell's ionic junction voltage. In this case, there is only one correct way of writing the equation, which involves mean activities as it should be. This applies to a particular type of cell that is sometimes called a ' concentration cell ':

$$\text{Pt', } \mathrm{H_2} \mid \text{HCl solution (sol. } \alpha) \mid \mid \text{HCl solution (sol. } \beta) \mid \mathrm{H_2}\text{, Pt}$$

$$\varphi_{\mathrm{Pt}} - \varphi_{\mathrm{Pt'}} = \frac{\mathrm{R}T}{\mathscr{F}} \ln \frac{a_{\mathrm{H^+}\beta}}{a_{\mathrm{H^+}\alpha}} + \varphi_\beta - \varphi_\alpha$$

In this electrolyte with only two ions with identical concentrations, the equation for the junction voltage gets even simpler if one can assume that the ionic transport numbers are identical at all points throughout the system:

$$\begin{aligned}
\varphi_\beta - \varphi_\alpha &= \frac{\mathrm{R}T}{\mathscr{F}} \int_\beta^\alpha \left(t_{\mathrm{H^+}}\ \mathbf{grad}\,(\ln a_{\mathrm{H^+}}) - t_{\mathrm{Cl^-}}\ \mathbf{grad}\,(\ln a_{\mathrm{Cl^-}}) \right) \mathrm{d}x \\
&= \frac{\mathrm{R}T}{\mathscr{F}} \int_\beta^\alpha \left(t_{\mathrm{H^+}}\ \mathbf{grad}\,(\ln(a_{\mathrm{H^+}} a_{\mathrm{Cl^-}})) - \mathbf{grad}\,(\ln a_{\mathrm{Cl^-}}) \right) \mathrm{d}x \\
&= \frac{\mathrm{R}T}{\mathscr{F}}\, t_{\mathrm{H^+}} \ln \frac{a_{\mathrm{H^+}\alpha}\, a_{\mathrm{Cl^-}\alpha}}{a_{\mathrm{H^+}\beta}\, a_{\mathrm{Cl^-}\beta}} - \frac{\mathrm{R}T}{\mathscr{F}} \ln \frac{a_{\mathrm{Cl^-}\alpha}}{a_{\mathrm{Cl^-}\beta}}
\end{aligned}$$

and finally:

$$\varphi_{\mathrm{Pt}} - \varphi_{\mathrm{Pt'}} = \frac{\mathrm{R}T}{\mathscr{F}}\, t_{\mathrm{Cl^-}} \ln \frac{a_{\mathrm{H^+}\beta}\, a_{\mathrm{Cl^-}\beta}}{a_{\mathrm{H^+}\alpha}\, a_{\mathrm{Cl^-}\alpha}}$$

This equation for the open-circuit voltage (at quasi-steady state) of a concentration cell is commonly found in electrochemistry, and effectively involves the mean activity of HCl in each compartment. By analogy with the HITTORF mass balance (see section 4.4.2.3), it can also be demonstrated in terms of a thermodynamic energy balance. The energy change that occurs when an extremely low amount of charge flows through the cell is expressed as a function of the transport numbers and of the ionic activities. Therefore, this type of cell is one way of determining transport numbers in an experiment.

A.3.3 - DEBYE-HÜCKEL'S MODEL

Here we will briefly summarise the basic elements that are needed for demonstrating the DEBYE-HÜCKEL laws as a means of estimating the ionic activity coefficients in a solution.

The electrostatic potential φ is the combined result of an individual ion with a charge of z_k that is placed at the origin ($r = 0$) and all the other surrounding ions, including those of the same nature. The solution's average potential is chosen as the reference value ($\varphi_{sol} = 0$). In this case, the following laws and equations are used:

- the laws of electrostatics (POISSON's equation in spherical coordinates):

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \varphi}{\partial r}\right) = -\frac{\rho_{ch}}{\varepsilon} \qquad \text{with } \rho_{ch} = \sum_i n_i z_i |e|$$

  where n_i is the concentration of ion i (expressed in the number of ions i per unit volume, i.e., in m^{-3}) and ρ_{ch} is the charge density (expressed in $C\,m^{-3}$) at a distance r from the centre;

- the BOLTZMANN statistics, indicating how the species concentration is distributed based on their potential energy:

$$n_i = n_i^* e^{-\frac{z_i |e| \varphi}{kT}}$$

  where n_i^* is the mean concentration of ions i;

- the electroneutrality equation (based on mean values):

$$\sum_i z_i n_i^* = 0$$

If one adopts the assumptions underlying this model (see section 3.2.1.3), since $|z_i e \varphi| \ll kT$, then it is possible to use the TAYLOR expansion around zero of the preceding n_i expression coming from the BOLTZMANN statistics:

$$n_i \approx n_i^*\left(1 - \frac{z_i |e| \varphi}{kT}\right)$$

The equation describing the charge distribution with the potential then becomes:

$$\rho_{ch} = -\sum_i z_i^2 n_i^* \frac{e^2}{kT}\varphi$$

Using the following parameter L_D, which has the dimension of a length and is called the DEBYE length (see the physical analogy below):

$$L_D = \sqrt{\frac{\varepsilon kT}{\sum_i z_i^2 n_i^* e^2}}$$

the POISSON-BOLTZMANN equation can be written in the following form:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \varphi}{\partial r}\right) = \frac{\varphi}{L_D^2}$$

By introducing the function $g = r\varphi$, the equation is made much easier to integrate, thus becoming:

$$\frac{\partial^2 g}{\partial r^2} = \frac{g}{L_D^2}$$

with the following boundary conditions:

$$r \to \infty \qquad g \to 0$$

$$r \to 0 \qquad g \to \frac{z_k \,|\mathrm{e}|}{4\,\pi\,\varepsilon}$$

The latter condition relates to a dilute electrolyte solution, whose charges are considered to be point charges. In the area closely surrounding the central ion (r tends towards zero) the only potential that prevails is the one created by the central charge. All the other ions are too far away to have any bearing on the potential.

By integration, one obtains: $g = A_1\ \mathrm{e}^{-\frac{r}{L_\mathrm{D}}} + A_2\ \mathrm{e}^{+\frac{r}{L_\mathrm{D}}}$

with the following equations taking into account the limiting conditions:

$$\begin{cases} A_1 = \dfrac{z_k \,|\mathrm{e}|}{4\,\pi\,\varepsilon} \\ A_2 = 0 \end{cases}$$

A TAYLOR expansion around zero, i.e., for a short distance to the central ion when compared to the DEBYE length, then gives the following equation:

$$\varphi = \frac{z_k \,|\mathrm{e}|}{4\,\pi\,\varepsilon\, r} - \frac{z_k \,|\mathrm{e}|}{4\,\pi\,\varepsilon\, L_\mathrm{D}}$$

In this equation, the first term corresponds to the potential that is produced by the point charge of the central ion. The second term corresponds to the potential produced by all the other ions. The parameter L_D, which has the dimension of a length, corresponds to the radius of a sphere whose charge is opposite to that of the central ion (counter-ion). However, it has no direct physical meaning since there is no real charge $-\,z_k\,|\,\mathrm{e}\,|$ placed on this virtual sphere.

By introducing the concept of ionic strength I_s, as defined in section 3.2.1.2, and by using molar notations for the concentrations, the equation for the DEBYE length becomes:

$$L_\mathrm{D} = \sqrt{\frac{\varepsilon\,\mathrm{R}\,T}{2 I_\mathrm{s}\,\mathscr{F}^2}}$$

For example, for an aqueous solution at 25 °C (dielectric permittivity of pure water: $\varepsilon = \varepsilon_\mathrm{r} / (36\times10^9\pi)$ with $\varepsilon_\mathrm{r} = 78$) of ionic strength 10^{-3} mol L^{-1} (= 1 mol m^{-3}), the DEBYE length is about 100 Å, or 10 nm. This means that the previous equation that illustrates the potential surrounding the central ion only applies when dealing with a distance of less than a few Å from this ion, because it stems from a TAYLOR expansion around zero (i.e., for small values of r compared to L_D). However, this suffices to be able to determine the equation for the activity coefficient, as shown in the following reasoning.

From an energy point of view, the deviation from ideality that is caused by the surrounding ions interacting with the central ion, equates to the same value as the energy required to gradually generate a charge of $z_k\,|\,\mathrm{e}\,|$ at the point of the central ion, while keeping the place of the other ions:

$$\Delta W_{\text{interactions}} = \mathrm{k}T \ln \gamma_k = -\int_0^{z_k|\mathrm{e}|} \frac{q}{4\,\pi\,\varepsilon\,L_\mathrm{D}}\,\mathrm{d}q = -\frac{(z_k\,\mathrm{e})^2}{8\,\pi\,\varepsilon\,L_\mathrm{D}}$$

so:
$$\log \gamma_k = -A\,{z_k}^2\sqrt{I_\mathrm{s}}$$

with:
$$A = \frac{\mathscr{F}^3\sqrt{2}}{8\,\pi\,\mathscr{N}(\varepsilon\,\mathrm{R}T)^{3/2}\ln 10}\sqrt{10^3} \qquad \text{in } \mathrm{L}^{1/2}\,\mathrm{mol}^{1/2}$$

For example, using the dielectric permittivity of pure water at 25°C, the value of A is 0.509 $\mathrm{L}^{1/2}\,\mathrm{mol}^{1/2}$, which is close to the experimental value determined from the mean activity coefficients in aqueous solutions.

When the ionic strength is higher than 10^{-3} mol L^{-1}, then the following extended DEBYE-HÜCKEL equation can be used:

$$\log \gamma_k = -A\,{z_k}^2\sqrt{I_\mathrm{s}}\,\frac{L_\mathrm{D}}{L_\mathrm{D}+a} = -\frac{A\,{z_k}^2\sqrt{I_\mathrm{s}}}{1+a\,B\sqrt{I_\mathrm{s}}}$$

with:
$$B = \sqrt{\frac{2\,\mathscr{F}^2}{\varepsilon\,\mathrm{R}T}}$$

This equation is based on a calculation similar to the previous one, but in this particular case the volume of the charges is no longer disregarded. The parameter a, which has the dimension of a length, is the minimum distance by which the ions can approach the central ion. The function $g = r\varphi$ is then integrated between a (instead of 0) and the infinite distance. The parameter a is determined experimentally by adjusting the experimental points to fit the specific law in question. For a single solute, a is close to the sum of the two radii of the solvated ions. In reality, its value is slightly lower: there is an intermingling that occurs between the two solvated ions when they are brought into contact. For single-solute electrolytes, the sum of the parameters given for each of the two ions is often used (see the data tables provided in scientific literature: the order of magnitude is a few Å). The value of parameter B for aqueous solutions at 25 °C using the dielectric permittivity of pure water is 3.3 $\mathrm{L}^{1/2}\,\mathrm{mol}^{1/2}\,\mathrm{nm}^{-1}$. The product aB is then always close to 1. Most often for aqueous solutions at room temperature, a simplified equation is used which is deduced from the previous equation:

$$\log \gamma_k \approx -A\,{z_k}^2\,\frac{\sqrt{I_\mathrm{s}}}{1+\sqrt{I_\mathrm{s}}}$$

that is to say, for a solute:
$$\log \gamma_\pm \approx A\,z_+\,z_-\,\frac{\sqrt{I_\mathrm{s}}}{1+\sqrt{I_\mathrm{s}}}$$

Such a law is commonly used for ionic strengths that are lower than 10^{-2} mol L^{-1} (and exceptionally 10^{-1} mol L^{-1}). For instance, it leads to a corrective term compared to the limiting law, of about 10% on the logarithm for an ionic strength of 10^{-3} mol L^{-1}.

A.3.4 - THERMODYNAMIC EQUILIBRIUM AT A REACTIVE INTERFACE INVOLVING A SINGLE REACTION BETWEEN CHARGED OR NEUTRAL SPECIES

The aim of this section is to compare the different consequences entailed when a state of thermodynamic equilibrium is established between two conducting media. For this purpose we will focus on the case of three different types of reactive interfaces:

- the junction between two materials of the same nature, when only neutral molecules M can be exchanged;
- the junction between two materials of the same nature, when a single type of charged species can be exchanged: for instance an exchange of cations M^+;
- the electrochemical interface between an inert electrode and an electrolyte containing two elements of a redox couple: for example an equimolar mixture of M^{2+} and M^{3+}.

Let us consider two samples of conducting condensed material with identical volumes (two cubes with $\ell = 1$ cm) at room temperature (25°C). In their initial state, they are placed at a distance from each other, and neither their surface nor volume is charged. In the first two cases, both materials are of the same nature and therefore have equal standard chemical potentials. However the initial concentrations of M or M^+ are different:

$$C_{0\alpha} = 10^{-1}\ \text{mol L}^{-1} \quad \text{and} \quad C_{0\beta} = 10^{-3}\ \text{mol L}^{-1}$$

The last case involves a metal, with an initial electron concentration of $C_{0\alpha} = 100\ \text{mol L}^{-1}$, that is in contact with an equimolar mixture of M^{2+} and M^{3+} in a solution with an initial concentration of $C_{0\beta} = 10^{-3}\ \text{mol L}^{-1}$.

In the simplified reasoning applied here, the concentrations are used instead of the activities, except in the case of metals where the electron activity is always equal to 1. Moreover, when the equilibrium is established, it is assumed that the surface charges that emerge as a result, are distributed in such a way that a parallel plate capacitor is formed (area is $S = 1\ \text{cm}^2$) [4]. The distance between the planes is $\delta = 1$ nm, with a relative dielectric permittivity $\varepsilon_r = 10$. This capacitor corresponds to the electrochemical double layer.

Therefore, we end up with a first phase α (with a thickness $\ell = 1$ cm perpendicular to the interface) with a surface charge excess σ_{ch}. This interface forms the first plate of the plate capacitor. The second plate, with an excess of opposite charge, is located at $\delta = 1$ nm inside the second phase β (volume thickness $\ell = 1$ cm):

$$\text{phase } \alpha, \text{ charge} + \sigma_{ch} \mid \text{interfacial zone } \delta = 1\ \text{nm} \mid \text{charge} - \sigma_{ch}, \text{ phase } \beta$$

Moreover, the difference between the surface electric voltages in the two phases is overlooked (see section 3.1.1.2, $\chi_\alpha = \chi_\beta$). Therefore, the VOLTA and GALVANI potential differences between the two phases are considered as being equal ($\varphi_\beta - \varphi_\alpha = \psi_\beta - \psi_\alpha$).

---

[4] This means that the boundary effects are disregarded: the surface charge density is zero on five faces and uniform on the sixth face which is in contact with the other phase. This system can be also represented as part of a system with unidirectional geometry (two conducting volumes with an infinite section and a thickness ℓ).

EXCHANGE OF NEUTRAL SPECIES M

Once both phases have been brought into contact, molecules M are exchanged between them until thermodynamic equilibrium has been reached. The chemical potential of M, expressed by $\mu_M = \mu^\circ_M + RT \ln C$, is higher at the initial state in phase α than in phase β, therefore molecules M move from phase α to phase β until equilibrium is reached.

▸▸ *Variations in concentration and in the amount of substance required to reach equilibrium*

At thermodynamic equilibrium, the equality of chemical potentials leads to the equality of M activities (= concentrations) in both phases:

$$C_{eq_\alpha} = C_{eq_\beta} = \frac{C_{0_\alpha} + C_{0_\beta}}{2} = \frac{0.1 + 0.001}{2} \approx 0.05 \text{ mol L}^{-1}$$

Once the volume of each phase is taken into account, this concentration variation corresponds to the following amount of substance exchanged:

$$\Delta n = n_{eq_\beta} - n_{0_\beta} = -(n_{eq_\alpha} - n_{0_\alpha}) = \frac{C_{0_\alpha} - C_{0_\beta}}{2} \ell^3 = 5 \times 10^{-5} \text{ mol} = 3 \times 10^{19} \text{ molecules}$$

▸▸ *Variations in chemical potential linked to the process of reaching equilibrium*

Between the two phases, the initial difference in chemical potential for M is:

$$\mu_{0_\alpha} - \mu_{0_\beta} = RT \ln \frac{C_{0_\alpha}}{C_{0_\beta}} = +11.4 \text{ kJ mol}^{-1}$$

In each phase, between the equilibrium state and the initial state, the variation in chemical potential for M is:

$$\Delta\mu_\alpha = \mu_{eq_\alpha} - \mu_{0_\alpha} = RT \ln \frac{C_{eq_\alpha}}{C_{0_\alpha}} = -1.7 \text{ kJ mol}^{-1}$$

$$\Delta\mu_\beta = \mu_{eq_\beta} - \mu_{0_\beta} = RT \ln \frac{C_{eq_\beta}}{C_{0_\beta}} = +9.7 \text{ kJ mol}^{-1}$$

EXCHANGE OF CATION M^+

After contact, M^+ ions are exchanged between both phases until thermodynamic equilibrium has been reached. Let us recall that initially there is no surface charge, and that the difference in surface voltages is overlooked. In the initial state, the difference in electrochemical potentials is therefore identical to that of chemical potentials, and the electrochemical potential is higher in phase α than in phase β. Therefore, in order to reach the equilibrium state, M^+ ions move from phase α to phase β.

▸▸ *Variations in concentration and in the amount of substance required to reach equilibrium*

The movement of ions M^+ from phase α to phase β creates a charge excess in phase β and charge depletion in phase α. In equilibrium, such opposite charge excesses are located on the surface (remember that it is assumed here that they form a plate capacitor).

The related potential difference is given by the following equation:

$$(\psi_{\mathrm{eq}\beta} - \psi_{\mathrm{eq}\alpha})\,\frac{\varepsilon_0\,\varepsilon_\mathrm{r}\,S}{\delta} = (n_{\mathrm{eq}\beta} - n_{0\beta})\,\mathscr{F} = -(n_{\mathrm{eq}\alpha} - n_{0\alpha})\,\mathscr{F}$$

Moreover, with the VOLTA and GALVANI potential differences being taken as equal, the equality of electrochemical potentials yields the following:

$$\mathrm{R}T\ln\frac{C_{\mathrm{eq}\alpha}}{C_{\mathrm{eq}\beta}} = (\psi_{\mathrm{eq}\beta} - \psi_{\mathrm{eq}\alpha})\,\mathscr{F}$$

This equation can therefore be written using a single unknown $\Delta n = n_{\mathrm{eq}\beta} - n_{0\beta}$:

$$\mathrm{R}T\ln\frac{C_{0\alpha} - \Delta n/\ell^3}{C_{0\beta} + \Delta n/\ell^3} = \frac{\delta}{\varepsilon_0\,\varepsilon_\mathrm{r}\,\ell^2}\,\Delta n\,\mathscr{F}^2 = \frac{\ell\delta\,\mathscr{F}^2}{\varepsilon_0\,\varepsilon_\mathrm{r}}\,\frac{\Delta n}{\ell^3}$$

Solving this equation gives:

$$\Delta C = \frac{\Delta n}{\ell^3} = 1.1\times10^{-8}\ \mathrm{mol\ L^{-1}} \ll C_{0\beta}$$

or: $\Delta n = n_{\mathrm{eq}\beta} - n_{0\beta} = -(n_{\mathrm{eq}\alpha} - n_{0\alpha}) = 1.1\times10^{-11}$ mol $= 6.5\times10^{12}$ molecules

which corresponds to a surface charge excess of 1.0 μC cm^{-2}.

Therefore, what has been demonstrated here is that when a charged species is exchanged, there are only minor variations in concentration and chemical potential in each phase, between the equilibrium and initial states [5]:

$$\begin{cases} C_{\mathrm{eq}\alpha} \approx C_{0\alpha} & \text{and} \quad C_{\mathrm{eq}\beta} \approx C_{0\beta} \\ \mu_{\mathrm{eq}\alpha} \approx \mu_{0\alpha} & \text{and} \quad \mu_{\mathrm{eq}\beta} \approx \mu_{0\beta} \end{cases}$$

▸▸ *Variations in the GALVANI potential difference linked to the process of reaching equilibrium*

In equilibrium, the two phases do not have the same GALVANI potential:

$$\varphi_{\mathrm{eq}\beta} - \varphi_{\mathrm{eq}\alpha} = \frac{\delta}{\varepsilon_0\,\varepsilon_\mathrm{r}\,S}\,\Delta n\,\mathscr{F} \approx \frac{\mathrm{R}T}{\mathscr{F}}\ln\frac{C_{0\alpha}}{C_{0\beta}} = 118\ \mathrm{mV}$$

with an equal distribution: $\varphi_{\mathrm{eq}\beta} = -\varphi_{\mathrm{eq}\alpha} = 59$ mV.

▸▸ *Variations in electrochemical potential linked to the process of reaching equilibrium*

Between the two phases, the initial difference in electrochemical potential for M^+ is:

$$\widetilde{\mu}_{0\alpha} - \widetilde{\mu}_{0\beta} = \mu_{0\alpha} - \mu_{0\beta} = \mathrm{R}T\ln\frac{C_{0\alpha}}{C_{0\beta}} = +11.4\ \mathrm{kJ\ mol^{-1}}$$

---

[5] This calculation enables one to predict that such an approximation will cease to apply if δ and/or ℓ are strongly decreased: if the product $\ell\,\delta$ decreases, then $\Delta C = \Delta n/\ell^3$ increases and may become significant in comparison to the initial concentrations.

Between the equilibrium and the initial states, the variation in electrochemical potential for M^+ in each phase is:

$$\Delta\widetilde{\mu}_\alpha = \widetilde{\mu}_{eq_\alpha} - \widetilde{\mu}_{0_\alpha} \approx (\varphi_{eq_\alpha} - \varphi_{0_\alpha})\,\mathcal{F} = -5.7 \text{ kJ mol}^{-1}$$
$$\Delta\widetilde{\mu}_\beta = \widetilde{\mu}_{eq_\beta} - \widetilde{\mu}_{0_\beta} \approx (\varphi_{eq_\beta} - \varphi_{0_\beta})\,\mathcal{F} = +5.7 \text{ kJ mol}^{-1}$$

REDOX EQUILIBRIUM AT AN ELECTROCHEMICAL INTERFACE

In order to address this issue, one firstly needs to add an assumption related to the numerical values of the standard potential of various species. It will therefore be assumed here that:

$$\mu^\circ_{M^{2+}} - \mu^\circ_{M^{3+}} - \mu^\circ_e = +100 \text{ kJ mol}^{-1}$$

Although this value has been picked arbitrarily, it nonetheless depicts a realistic order of magnitude for a chemical GIBBS energy of reaction [6].

Once the phases have been brought into contact, the redox reaction can proceed in one direction or in the other, until thermodynamic equilibrium is reached. Given that there is no surface charge in the initial state and that the difference in surface voltages has been overlooked, the GALVANI potential difference is therefore zero and the electrochemical GIBBS energy of reaction is equal to the GIBBS energy of reaction ($\Delta_r\widetilde{G} = \Delta_r G + \mathcal{F}(\varphi_\beta - \varphi_\alpha) = \Delta_r G$). Moreover, since the initial mixture of electroactive species is equimolar, the GIBBS energy of reaction is equal to its standard value. Therefore, in the initial state, the following can be written: $(\mu_{M^{2+}} - \mu_{M^{3+}} - \mu_e)_0 > 0$. To conclude, in order for the equilibrium state to be reached, the redox half-reaction proceeds in the direction of oxidation.

▸▸ *Variations in concentration and in the amount of substance required to reach equilibrium*

The oxidation of M^{2+} ions to M^{3+} leads to an excess of positive charge in phase β and negative charge in phase α (metal). In equilibrium, these charge excesses, which are exact opposites, are located on the surface. Reaching the state of thermodynamic equilibrium leads to the fact that Δn mol of additional electrons appear on the metal surface, together with the transformation of Δn mol of M^{2+} ions into the same amount of M^{3+} ions in the electrolyte.

---

[6] In the case of a M^{3+}/M^{2+} couple this value can be estimated by combining the couple's standard potential value ($E°$), with the absolute potential of the SHE (estimated as 4.45 $V_{/vacuum}$, see section 1.5.1.1) and the electron work function of platinum (5.32 eV, see section 3.2.2.3). The following combination can therefore be written:

$$\begin{array}{rcl} M^{3+}_{aq} + \tfrac{1}{2}\,H_{2,gaz} & \rightleftharpoons & M^{2+}_{aq} + H^+_{aq} \\ e^-_{gaz} + H^+_{aq} & \rightleftharpoons & \tfrac{1}{2}\,H_{2,gaz} \\ e^-_{Pt} & \rightleftharpoons & e^-_{gaz} \\ \hline M^{3+}_{aq} + e^-_{Pt} & \rightleftharpoons & M^{2+}_{aq} \end{array} \qquad \begin{array}{r} -|e|E° \text{ eV} \\ -4.45 \text{ eV} \\ 5.32 \text{ eV} \\ \hline 5.32 - 4.45 - |e|E° \end{array}$$

Let us examine a few M^{3+}/M^{2+} couples in order to estimate the corresponding order of magnitude. For the Fe^{3+}/Fe^{2+} couple, $E = +0.77$ $V_{/SHE}$ and the estimated GIBBS energy is 0.10 eV = 10 kJ mol^{-1}. For the couple V^{3+}/V^{2+}, $E° = -0.26$ $V_{/SHE}$ and the estimated GIBBS energy is 1.13 eV = 107 kJ mol^{-1}. Finally for the couple Cr^{3+}/Cr^{2+}, $E = -0.41$ $V_{/SHE}$ and the estimated GIBBS energy is 1.28 eV = 122 kJ mol^{-1}. This explains how the numerical value of 100 kJ mol^{-1} was chosen when estimating the amount of substance variation required to reach equilibrium.

The resulting potential difference is given by the following equation:

$$(\psi_{\mathrm{eq}\beta} - \psi_{\mathrm{eq}\alpha})\,\frac{\varepsilon_0\,\varepsilon_\mathrm{r}\,S}{\delta} = \Delta n\,\mathscr{F} > 0$$

In equilibrium, the electrochemical GIBBS energy of reaction is equal to zero. So, assuming that the VOLTA and GALVANI potential differences are equal, the following is obtained:

$$\mu^\circ_{\mathrm{M}^{2+}} - \mu^\circ_{\mathrm{M}^{3+}} - \mu^\circ_\mathrm{e} + \mathrm{R}T\ln\frac{C_{\mathrm{eq}\beta}(\mathrm{M}^{2+})}{C_{\mathrm{eq}\beta}(\mathrm{M}^{3+})} = (\varphi_{\mathrm{eq}\beta} - \varphi_{\mathrm{eq}\alpha})\,\mathscr{F}$$

This equation can be written using a single unknown, Δn:

$$\mu^\circ_{\mathrm{M}^{2+}} - \mu^\circ_{\mathrm{M}^{3+}} - \mu^\circ_\mathrm{e} + \mathrm{R}T\ln\frac{C_{0\beta} - \Delta n/\ell^3}{C_{0\beta} + \Delta n/\ell^3} = \frac{\delta}{\varepsilon_0\,\varepsilon_\mathrm{r}\,\ell^2}\,\Delta n\,\mathscr{F}^2 = \frac{\ell\delta\,\mathscr{F}^2}{\varepsilon_0\,\varepsilon_\mathrm{r}}\,\frac{\Delta n}{\ell^3}$$

Solving this equation gives:

$$\Delta C = \frac{\Delta n}{\ell^3} = 9.5\times10^{-8}\ \mathrm{mol\ L^{-1}} \ll C_{0\beta}$$

or: $$\Delta n = 9.5\times10^{-11}\ \mathrm{mol} = 5.7\times10^{13}\ \mathrm{molecules}$$

which corresponds to an excess of surface charge of 9.2 μC cm^{-2}.

Therefore, what has been shown here is that when redox equilibrium is reached, there are only negligible variations in the concentration and chemical potential in each phase, between the equilibrium and initial states [5]:

$$\begin{cases} C_{\mathrm{eq}\alpha} \approx C_{0\alpha} & \text{and} \quad C_{\mathrm{eq}\beta} \approx C_{0\beta} \\ \mu_{\mathrm{eq}\alpha} \approx \mu_{0\alpha} & \text{and} \quad \mu_{\mathrm{eq}\beta} \approx \mu_{0\beta} \end{cases}$$

▸▸ *Variations in the GALVANI potential difference linked to the process of reaching equilibrium*

In equilibrium, the GALVANI potential in the two phases are not the same:

$$\varphi_{\mathrm{eq}\beta} - \varphi_{\mathrm{eq}\alpha} = \frac{\delta}{\varepsilon_0\,\varepsilon_\mathrm{r}\,S}\,\Delta n\,\mathscr{F} = 1.15\ \mathrm{V}$$

This difference is divided equally between the two phases: $\varphi_{\mathrm{eq}\beta} = -\varphi_{\mathrm{eq}\alpha} = 0.58$ V.

▸▸ *Variations in electrochemical potential linked to the process of reaching equilibrium*

Between the equilibrium and initial states, the electrochemical potential variation for each species in its particular phase is:

$$\Delta\widetilde{\mu}_{\mathrm{e}_\alpha} = \widetilde{\mu}_{\mathrm{eq,e}_\alpha} - \widetilde{\mu}_{0,\mathrm{e}_\alpha} \approx -(\varphi_{\mathrm{eq}\alpha} - \varphi_{0\alpha})\,\mathscr{F} = +55.7\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta\widetilde{\mu}_{\mathrm{M}_\beta{}^{2+}} = \widetilde{\mu}_{\mathrm{eq,M}_\beta{}^{2+}} - \widetilde{\mu}_{0,\mathrm{M}_\beta{}^{2+}} \approx 2\,(\varphi_{\mathrm{eq}\beta} - \varphi_{0\beta})\,\mathscr{F} = +111.4\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta\widetilde{\mu}_{\mathrm{M}_\beta{}^{3+}} = \widetilde{\mu}_{\mathrm{eq,M}_\beta{}^{3+}} - \widetilde{\mu}_{0,\mathrm{M}_\beta{}^{3+}} \approx 3\,(\varphi_{\mathrm{eq}\beta} - \varphi_{0\beta})\,\mathscr{F} = +167.0\ \mathrm{kJ\ mol^{-1}}$$

with: $$\Delta\widetilde{\mu}_{M_\beta^{3+}} - \Delta\widetilde{\mu}_{M_\beta^{2+}} = 55.7\ \text{kJ mol}^{-1} = \Delta\widetilde{\mu}_{e_\alpha}$$

We can conclude this appendix by stressing that when the equilibrium state is being reached, the process triggers modifications at the level of a reactive interface which are strongly dependent on whether the reactions involve molecules (neutral species) or charged species (ion exchange or redox reaction). This is a key consideration in electrochemical systems, which can be stretched to apply to most cases[7]:

- for an interfacial reaction occurring between molecules (e.g., exchange or reaction between molecules) the equilibrium state is reached when a large amount of substance has reacted at the interface, therefore triggering a change in composition on both sides:

$$\begin{cases} C_{eq_\alpha} \neq C_{0_\alpha} & \text{and} \quad C_{eq_\beta} \neq C_{0_\beta} \\ \mu_{eq_\alpha} \neq \mu_{0_\alpha} & \text{and} \quad \mu_{eq_\beta} \neq \mu_{0_\beta} \end{cases}$$

- for an interfacial reaction involving charged species (e.g., ion exchange or redox reaction), the equilibrium state is reached once an extremely small amount of substance has reacted, therefore triggering no change in the volume composition:

$$\begin{cases} C_{eq_\alpha} \approx C_{0_\alpha} & \text{and} \quad C_{eq_\beta} \approx C_{0_\beta} \\ \mu_{eq_\alpha} \approx \mu_{0_\alpha} & \text{and} \quad \mu_{eq_\beta} \approx \mu_{0_\beta} \end{cases}$$

In these cases, the equilibrium state is reached by adjusting the GALVANI potential differences between the two phases in contact with each other.

A.4.1 - HIGHLIGHTING THE ROLE OF THE SUPPORTING ELECTROLYTE IN MASS TRANSPORT AND ITS IMPACT ON AN ELECTROLYSIS CELL

This appendix sets out to illustrate the following concepts, using two simple examples to which one can apply almost all of the reasoning in analytical terms:

- steady-state concentration and potential profiles, including estimating the ohmic drop,
- distribution of the diffusion and migration mass transport modes, assuming that the NERNST-EINSTEIN equation applies[8],
- process of reaching the steady state,
- validity limit for the electrolyte electroneutrality.

---

[7] In experimental situations, one needs to call this equation into question mainly in cases where the ratio of phase volumes to the interface area is very low (reflecting a dramatic decrease in the ℓ value in our calculation).

[8] Let us recall here (see section 4.2.1) that it is only possible to split the migration and diffusion contributions in quantitative terms if one first draws up a hypothesis based on their respective properties. The simplest assumption is that the two phenomena have an identical microscopic mechanism, and that the activity and concentration values are equal. This leads to the NERNST-EINSTEIN equation, as used here.

The two examples that have been selected both relate to a case of electrolysis involving two simple and opposite redox reactions [9]. On the one hand a single 1-1 solute is used as electrolyte, and on the other hand the same solute but with a supporting electrolyte. They are dealt with one after the other, but the interest of this exercise also lies in comparing the two situations.

Imagine a parallelepipedic cell (with unidirectional geometry), comprising two planar, parallel, silver electrodes with a surface area of $S = 1$ cm^2, separated by a distance of $L = 2$ mm. They are both successively immersed in one of the two aqueous solutions S_1 or S_2 being studied, and connected to a constant current supply:

solution S_1 : silver nitrate, $AgNO_3$, with the concentration $C^* = 10^{-3}$ mol L^{-1}

solution S_2 : silver nitrate, $AgNO_3$, with the concentration $C^* = 10^{-3}$ mol L^{-1}
+ potassium nitrate, KNO_3, with the concentration 10^{-1} mol L^{-1} = 100 C^*

The pH is adjusted in both solutions to prevent any silver oxide from precipitating, and the protons and hydroxide ions are assumed to play only a minor role in the mass transport.

At the anode, one can observe the dissolution of the silver sheet: $Ag \longrightarrow Ag^+ + e^-$

At the cathode, one can observe silver deposition: $Ag^+ + e^- \longrightarrow Ag$

The origin of the x axis, which is normal to the electrodes, is chosen as the anode plane, as illustrated in figure A.15. In order to build up a comprehensive definition, one needs to choose a unique origin and a unique orientation of the normal axis, and therefore pay particular attention to the signs in the equations.

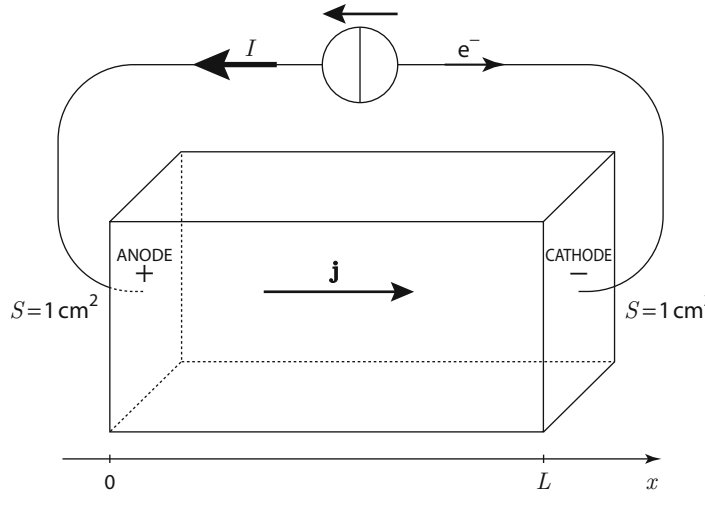


Figure A.15 - Diagram showing the electrolysis cell in question

[9] The advantage of choosing an electrolysis reaction with no overall chemical change is that steady states can be obtained with non zero current. Such steady states are easy to describe in analytical terms. These conditions correspond to an electrolyte whose composition is non-homogeneous, with the diffusion phenomena applying throughout the entire volume, and with a single diffusion layer that measures the same as the inter-electrode distance L.

Assuming that the charge transfer reactions are very fast in comparison to the mass transport phenomena, one can conclude that the charge transfer kinetics plays no part in the voltage value between the electrolysis cell terminals. The voltage is wholly governed by the mass transport phenomena in the electrolyte. The concentration and activity values are considered as equal. It is assumed that both the natural and forced convection phenomena are negligible: only migration and diffusion are taken into account in this analysis [10]. Moreover, the NERNST-EINSTEIN equation is assumed to apply in the system in question. In addition, the characteristic mass transport parameters (diffusion coefficients and mobilities or electrical conductivities) are taken as being independent of the concentration and equal to their values at infinite dilution:

$\lambda_{Ag^+} = \lambda_+ = 6.19\ \text{mS mol}^{-1}\ \text{m}^2$ and $D_{Ag^+} = D_+ = 1.65\times10^{-9}\ \text{m}^2\ \text{s}^{-1}$

$\lambda_{NO_3^-} = \lambda_- = 7.14\ \text{mS mol}^{-1}\ \text{m}^2$ and $D_{NO_3^-} = D_- = 1.90\times10^{-9}\ \text{m}^2\ \text{s}^{-1}$

$\lambda_{K^+} = 7.35\ \text{mS mol}^{-1}\ \text{m}^2$ and $D_{K^+} = 1.96\times10^{-9}\ \text{m}^2\ \text{s}^{-1}$

SOLUTION WITH NO SUPPORTING ELECTROLYTE (SOLUTION S_1)

THE EQUATIONS FOR THE SYSTEM

- The electroneutrality of the solution at all points throughout the volume leads to (see the section further on in this appendix dealing with the validity limit of this equation):

$$C_+ = C_- \qquad (\neq C^* \textit{ a priori})$$

- Because the system is in unidirectional geometry, the molar flux density vectors are all parallel to the x axis and N_i is the algebraic projection on this axis. The volume mass balance in the electrolyte is written in the following way for species i (see section 4.1.2 without homogeneous reaction):

$$\frac{\partial C_i}{\partial t} = -\frac{\partial N_i}{\partial x}$$

and in particular, at steady state: $\dfrac{\mathrm{d}N_i}{\mathrm{d}x} = 0$

In other words, the molar flux densities become homogeneous in the overall electrolyte volume at steady state.

- The system is also defined in terms of the interfacial mass balance. In this case, NO_3^- does not react at the anode, yet silver is oxidized. Therefore, at this interface the mass balance is written with the anodic current taken as being positive, as usual (see FARADAY's law in section 4.1.4):

$$\begin{cases} (N_+)_{x=0} = \dfrac{I}{\mathscr{F} S} \\ (N_-)_{x=0} = 0 \end{cases}$$

---

[10] If a distance of 2 mm is chosen in an experiment, then a polymer or a gel electrolyte needs to be used in order to eliminate natural convection. In fact, the influence of natural convection cannot be wholly disregarded in a liquid solution. The term 'thin film cell' is sometimes used to describe such a device.

When the FARADAY law is applied at the cathode, the same equations emerge. One must then bear in mind that the conventions usually applied in electrochemistry for a given electrode are not followed when forming the equations for a complete system, since the axis normal to the surface is oriented here at the cathode interface from the electrolyte towards the metal (i.e., outside the system, see figure A.15)[11]. The FARADAY law for the cation should be written as follows:

$$(N_+)_{x=L} = \frac{I}{\mathscr{F} S} < 0$$

with an axis oriented towards the electrolyte. For the same example, yet keeping the same axis orientation for the complete system and specifying $I > 0$ for the current measured in the circuit, we therefore have to write here:

$$(N_+)_{x=L} = \frac{I}{\mathscr{F} S} > 0$$

- Each different molar flux density can be written as the sum of two terms (diffusion and migration, see section 4.2.1.4):

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

Using the NERNST-EINSTEIN equation: $\dfrac{u_i}{D_i} = \dfrac{|z_i| \mathscr{F}}{\mathsf{R} T}$

we can write:

$$\begin{cases} N_+ = -D_+ \dfrac{\partial C_+}{\partial x} - D_+ \dfrac{\mathscr{F}}{\mathsf{R} T} C_+ \dfrac{\partial \varphi}{\partial x} \\ N_- = -D_- \dfrac{\partial C_-}{\partial x} + D_- \dfrac{\mathscr{F}}{\mathsf{R} T} C_- \dfrac{\partial \varphi}{\partial x} \end{cases}$$

STEADY-STATE CONCENTRATION PROFILES

At steady state, the molar flux densities, N_+ and N_-, are constant throughout the whole electrolyte volume and equal to their interfacial values[12].

- By combining the previous equations so as to eliminate the term showing the electric field, one gets:

$$D_- C_- N_+ + D_+ C_+ N_- = - D_- C_- D_+ \frac{\partial C_+}{\partial x} - D_+ C_+ D_- \frac{\partial C_-}{\partial x}$$

and finally, with $C_+ = C_-$ and $N_- = 0$:

$$N_+ = -2 D_+ \frac{\partial C_+}{\partial x} = \frac{I}{\mathscr{F} S}$$

---

[11] See the illustrated board entitled ' Sign convention for current '.

[12] In fact, having two opposite interfacial reactions means that non-zero current steady states can exist in this type of system (see section 4.4.1.2).

that is to say : $$\frac{\partial C_+}{\partial x} = -\frac{I}{2D_+ \mathcal{F} S} = \text{Cst}$$

Therefore the profiles of C_+ and C_- are linear:

$$C_+ = C_- = (C_-)_{x=L/2} + \frac{I}{2D_+ \mathcal{F} S}\left(\frac{L}{2} - x\right)$$

- The integration constant (here the concentration at the central plane of the electrolyte, i.e., $x = L/2$) is determined by writing the mass preservation for the Ag^+ or NO_3^- ions. For the nitrate ions, which are neither consumed nor produced at the electrodes, we can write in the volume V:

$$\iiint C_- \mathrm{d}V = C^* V$$

The Ag^+ ion preservation leads to an identical equation, because the overall mass balance is also zero: the amount of substance produced at the anode is exactly compensated by the amount consumed at the cathode.

Whatever the current value is, the integration produces the following:

$$(C_-)_{x=L/2} = C^*$$

Therefore, the equation for the concentration profiles (which is identical for both species) is:

$$\frac{C_+}{C^*} = \frac{C_-}{C^*} = 1 + \frac{I}{2D\,\mathcal{F} S\,C^*}\left(\frac{L}{2} - x\right) = 1 + \frac{I}{I_{\text{lim}_{S_1}}}\left(1 - \frac{2x}{L}\right)$$

by introducing $I_{\text{lim}_{S_1}}$ with the following definition:

$$I_{\text{lim}_{S_1}} = \frac{4D_+ \mathcal{F} S\,C^*}{L}$$

This quantity corresponds to the limiting current (see section 4.3.3.1, with a thickness of $L/2$ and a diffusion coefficient equal to $2D_+$). Using the numerical data chosen in this example, it is equal to 31.8 µA. Figure A.16 represents the steady-state concentration profile for a current equal to 90% of the limiting current (i.e., 28.6 µA), which gives a slope of -0.9×10^{-3} mol L^{-1} mm^{-1}.

When the current gets very close to the limiting current, the ion concentration in the area next to the cathode becomes very low. Therefore, the solution in this area can no longer be considered as a good conductor. The equations generally used in electrochemistry cannot be applied because the deviations from electroneutrality are too wide. In this case, the equation for expressing electroneutrality cannot be used to make a correct calculation of the concentration profiles in the zone next to the cathode (see section 3.1.1.1). It becomes more complex when one has to describe the system, which will not be addressed here. In short, in order to define the link between the potential and the concentration, one needs to make the same type of calculation, yet this time including the POISSON equation. It is important to keep in mind that the calculation given here no longer applies in quantitative terms once the current value gets close to value of the limiting current.

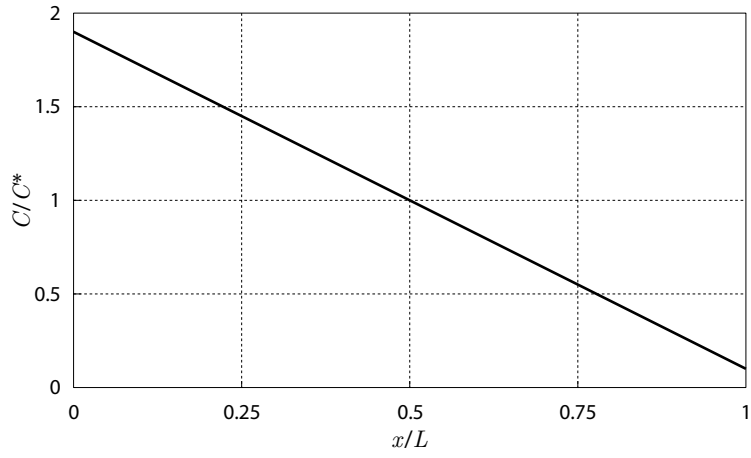
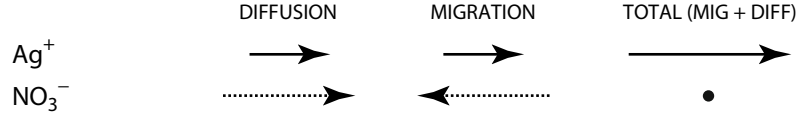


Figure A.16 - Steady-state concentration profile in the solution with no supporting electrolyte for $I = 0.9\ I_{lim_{S_1}}$

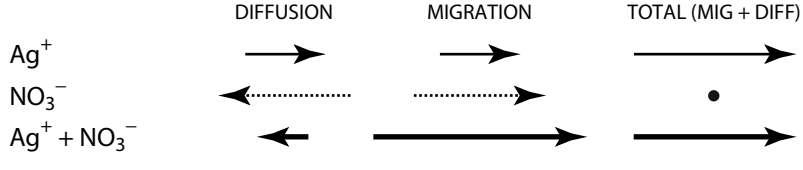
For lower currents, there is also a deviation from electroneutrality when the current flows, though it is very minute in terms of concentration values. This aspect will be examined again after having first dealt with the description of the steady state in the following section.

MOLAR FLUX AND CURRENT DENSITIES AT STEADY STATE

It is possible to depict the diffusion and migration contributions to molar flux densities. Remember that the diffusion flux goes from the most concentrated zone towards the least concentrated (see figure A.16). Keep in mind that the molar flux of the Ag^+ ions is divided into two equal parts between diffusion and migration (see factor 2 D_+ above, at steady state, assuming that the NERNST-EINSTEIN equation applies). Finally, since the diffusion coefficient of the NO_3^- ions is higher than that of the Ag^+ ions, the following diagram is obtained:



The current densities are in the opposite direction to the molar flux for the nitrate ion because it is an anion:



The nitrate ions are electroinactive and do not move macroscopically at steady state. However this is not the case in a transient state, since the steady-state concentration profile has yet to be reached. The interfacial molar flux of nitrate ions is always zero but the transient flux is not constant throughout the whole electrolyte volume, as explained further on.

The overall diffusion current is not zero because of the difference between the anion and cation diffusion coefficients. As shown in an example already described in section 4.2.1.5 the calculation gives:

$$j_{\text{migration}} = \frac{I}{2t_+ S} = 1.08\ j$$

$$j_{\text{diffusion}} = 1 - j_{\text{migration}} = -0.08\ j$$

It should be noted that such a distribution between diffusion and migration fluxes remains formal, i.e., based on the assumption that the NERNST-EINSTEIN equation applies.

Given that the molar flux of NO_3^- anion is zero at steady state:

$$\widetilde{t}_+ = 1$$

This means that, at steady state, all of the current is carried by the cations, with a half/half distribution of migration and diffusion contributions. This example underlines the difference between the electrochemical transport number and the usual transport number, when the different migration phenomena can be assumed as the only significant phenomena:

$$t_+ = t_{Ag^+} = \frac{\sigma_{Ag^+}}{\sigma} = \frac{\lambda_+}{\lambda_- + \lambda_+} = 0.46$$

In this particular case, whereas the electrochemical transport number has a physical meaning, the migration transport number is only a virtual parameter which is simply the result of a calculation. It does not match the real contributions in the mass transport.

STEADY-STATE POTENTIAL PROFILES

- Here, by returning to the equations for molar flux densities and combining them together so as to eliminate the term showing the concentration variations, one gets:

$$D_- N_+ - D_+ N_- = -2D_+ D_- \frac{\mathcal{F}}{RT} C_+ \frac{\partial \varphi}{\partial x}$$

Therefore, when using the equations for molar flux densities at steady state, $N_- = 0$ and $N_+ = I/(\mathcal{F} S)$, one obtains:

$$\frac{\partial \varphi}{\partial x} = -\frac{RT}{\mathcal{F}} \frac{I}{2\,\mathcal{F}\,S\,D_+} \frac{1}{C_+}$$

Given that the concentration is a function of the distance to the electrodes, this equation does not match a linear potential profile. One ends up with:

$$\frac{\partial C_+}{\partial x} = -\frac{I}{2D_+ \mathcal{F} S} \quad \Rightarrow \quad \frac{\partial \varphi}{\partial C_+} = \frac{RT}{\mathcal{F}} \frac{1}{C_+}$$

- By integrating the previous equation between the abscissa x plane and the middle of the electrolyte $x = L/2$, where the origin of the potential values is taken arbitrarily, one obtains the following:

$$\varphi = \frac{RT}{\mathcal{F}} \ln \frac{C_+}{C^*} = \frac{RT}{\mathcal{F}} \ln \left[1 + \frac{I}{I_{\lim_{S_1}}} \left(1 - \frac{2x}{L} \right) \right]$$

When the current is low compared to the limiting current, the profile is quasi-linear, as in the case of pure migration phenomena:

$$\varphi \approx \frac{RT}{\mathcal{F}} \frac{I}{I_{lim_{S_1}}} \left(1 - \frac{2x}{L}\right)$$

As far as the interfacial voltages are concerned, since the redox couple is considered fast, one can write the following (see section 4.3.2.4):

$$\varphi_{metal} - \varphi_{solution} = Cst + \frac{RT}{\mathcal{F}} \ln [Ag^+]_{interface}$$

Figure A.17 depicts the steady-state potential profile for a current equal to 90% of the limiting current (i.e., 28.6 µA).

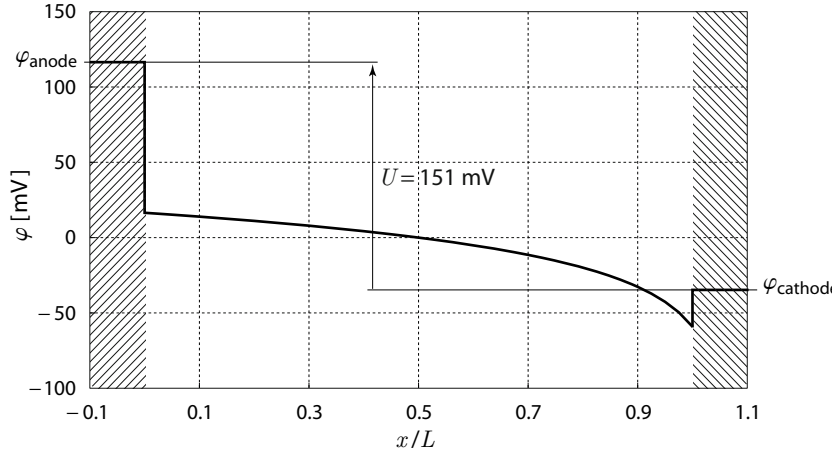


Figure A.17 - Potential profile in the solution with no supporting electrolyte for $I = 0.9\ I_{lim_{S_1}}$
The value of the anode potential is fixed arbitrarily.
Yet the value of the cathode potential is deduced from that of the anode.

The electrolysis voltage is therefore equal to:

$$U = \varphi_{anode} - \varphi_{cathode} = \varphi_{x=0} - \varphi_{x=L} + \frac{RT}{\mathcal{F}} \ln \frac{[Ag^+]_{x=0}}{[Ag^+]_{x=L}} = 2\frac{RT}{\mathcal{F}} \ln \frac{1 + \dfrac{I}{I_{lim_{S_1}}}}{1 - \dfrac{I}{I_{lim_{S_1}}}}$$

In the example shown in figure A.17 ($I = 0.9\ I_{lim_{S_1}}$) the electrolysis voltage is equal to 151 mV (the ohmic drop is 76 mV).

RESISTANCE OF THE ELECTROLYTE AT STEADY STATE

The calculation for the electrolyte's overall resistance is worked out directly using the values of the potential at $x = 0$ and $x = L$:

$$U_{ohmic\ drop} = \varphi_{x=0} - \varphi_{x=L} = R\,I$$

with:
$$R = \frac{\mathrm{R}T}{I\mathscr{F}} \ln \frac{1 + \dfrac{I}{I_{\mathrm{lim}_{S_1}}}}{1 - \dfrac{I}{I_{\mathrm{lim}_{S_1}}}}$$

Figure A.18 illustrates the variations in the overall electrolyte resistance as being a function of the current flowing through the cell.

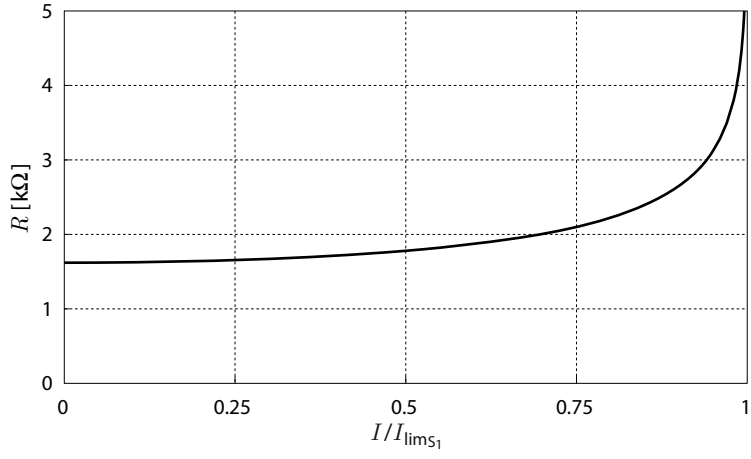


Figure A.18 - Overall resistance of the solution without a supporting electrolyte for different current values

The overall resistance depends on the current value. Therefore, the ohmic drop term is not proportional to the current, as would be the case in a conventional OHM law (for example if there were a supporting electrolyte, as in the case of solution S_2 which is dealt with further on in this section). The overall resistance becomes extremely high when the current approaches the limiting current value, as explained previously.

When I is small compared to $I_{\mathrm{lim}_{S_1}}$, a TAYLOR expansion around zero of the general equation can be written, which leads to:
$$R_{I\to 0} \approx \frac{\mathrm{R}T}{\mathscr{F}} \frac{2}{I_{\mathrm{lim}_{S_1}}} = \frac{L}{S(2\,\lambda_+)\,C^*} = 1.62\ \mathrm{k\Omega}$$

If the electrolyte were to have a homogeneous composition the value of R would be:
$$R_{\text{pure migration}} = \frac{L}{S\,\sigma} = \frac{L}{S(\lambda_- + \lambda_+)\,C^*} = 1.50\ \mathrm{k\Omega}$$

and finally:
$$R_{I\to 0} = \frac{R_{\text{pure migration}}}{2\,t_+}$$

This is to be compared to the equation linking the migration current and the overall current, which is demonstrated above. Indeed, in whatever situation, the OHM law can be written as follows at the local level:
$$j_{\text{migration}} = -\,\sigma \frac{\partial \varphi}{\partial x}$$

Due to the difference between the diffusion coefficients, the migration current is slightly higher than the overall current. Therefore the resistance calculated from the potential profile and the overall current (which are the only experimental data available) is slightly higher than the resistance obtained from a calculation using the solution's conductivity.

DEVIATIONS FROM ELECTRONEUTRALITY

In this case ($I/I_{\text{lim}S_1} = 0.9$), the fact that the electrolyte's potential profile is not linear indicates that there is a deviation from electroneutrality within the solution. In fact, there would be a linear potential profile if the electroneutrality equation were to be strictly applied using the LAPLACE law. In the unidirectional system in question, the POISSON equation gives a mean to estimate this deviation from electroneutrality:

$$\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} = -\frac{\rho_{\text{ch}}}{\varepsilon} = \frac{\mathscr{F}}{\varepsilon}(C_- - C_+)$$

$$C_- - C_+ = -\frac{\varepsilon}{\mathscr{F}}\frac{\mathrm{R}T}{\mathscr{F}}\left(\frac{I}{I_{\text{lim}S_1}}\right)^2 \frac{1}{L^2}\frac{1}{\left(1-\frac{x}{L}\frac{I}{I_{\text{lim}S_1}}\right)^2}$$

For example, with a current of 28.6 µA ($I/I_{\text{lim}S_1} = 0.9$):

$$\text{for } x = L \quad C_- - C_+ = -2\times10^{-11} \text{ mol L}^{-1}$$

whereas we have calculated $C_+ = 10^{-4}$ mol L^{-1} at the cathode surface ($x = L$)

$$\text{for } x = 0 \quad C_- - C_+ = -4\times10^{-14} \text{ mol L}^{-1}$$

whereas we have calculated $C_+ = -2\times10^{-3}$ mol L^{-1} at the anode surface ($x = 0$).

Therefore, it is proved *a posteriori* that it is legitimate to use electroneutrality to calculate the concentration profiles. However, the LAPLACE law is too approximate in numerical terms to give a correct value for the potential. Therefore, to determine this profile one needs to use the concentration profiles, as already described above.

When the current gets even closer to the limiting current, the Ag^+ and NO_3^- concentrations become very minute in the area next to the cathode. As a result, the deviations from electroneutrality need to be taken into account when simultaneously defining both the concentration and potential profiles (using POISSON's law). Moreover, one also needs to consider the influence of H^+ and OH^- ions in the aqueous solution (concentrations about 10^{-7} mol L^{-1}). In this light, the example previously outlined therefore no longer holds true. However, given that the electrolyte is very resistant, the shape of the curve depicting the resistance related to the current still stands in qualitative terms, showing an abrupt increase when I tends towards the limiting current.

CHARACTERISING THE TRANSIENT PERIOD LEADING TO THE STEADY STATE

If we do not confine ourselves to studying the steady states, then we can no longer assume that the molar flux densities are constant in the electrolyte, nor that the electroinactive ions are immobile. Nevertheless, by using the electroneutrality of the electrolyte, we are then able to go back to the general equations described at the beginning of the appendix (same kind of calculation as in section 4.2.1.2):

$$\begin{cases} \dfrac{\partial C}{\partial t} = -\dfrac{\partial N_+}{\partial x} = -\dfrac{\partial N_-}{\partial x} \\ D_- N_+ + D_+ N_- = -2D_- D_+ \dfrac{\partial C}{\partial x} \end{cases}$$

The same type of calculation as in section 4.2.1.2 gives the following equation:

$$(D_- + D_+)\frac{\partial C}{\partial t} = 2D_- D_+ \frac{\partial^2 C}{\partial x^2}$$

The progression towards the steady state therefore correlates with the $AgNO_3$ diffusion (i.e., the coupled diffusion of both anions and cations), with a mean diffusion coefficient:

$$D_\pm = \frac{2D_- D_+}{D_- + D_+} = 2\,t_- D_+ = 2\,t_+ D_-$$

The characteristic time, τ, required for establishing the steady state, is defined by:

$$\tau = \frac{L^2}{4D_\pm}$$

Here, with the numerical data for the example in question ($D_+ = 1.77 \times 10^{-9}$ m^2 s^{-1}), it gives $\tau = 566$ s.

Figure A.19 illustrates how the concentration profiles develop during the transient period while the steady-state profile is being established. It depicts a chronopotentiometry experiment for a constant current equal to 90% of the limiting current, i.e., 28.6 µA.

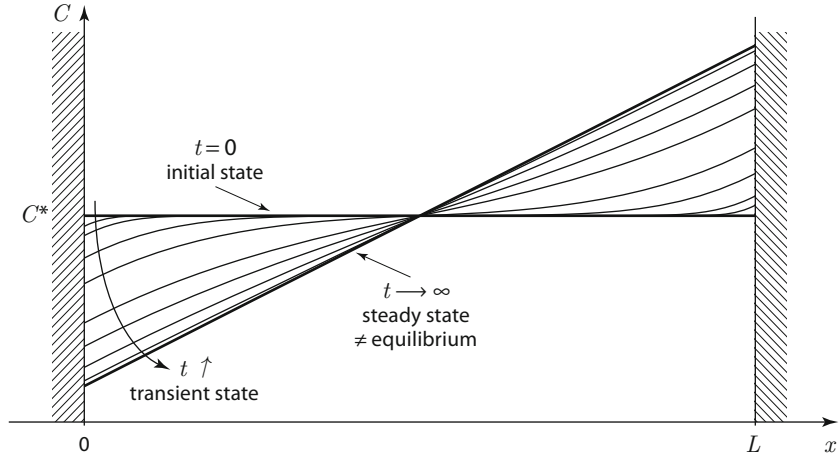


Figure A.19 - Concentration profile change with time towards the steady-state profile during a chronopotentiometry experiment

One must keep in mind that the steady characteristics only depend on parameters of the electroactive ion (here D_+). However, the changes that occur with time during the transient period depend on a parameter, $D_\pm$, which is linked to the properties of both the ions.

The transient period also denotes a change in the distribution between the migration and diffusion processes. At steady state, an equal distribution has been achieved, as already demonstrated above based on the assumption that the NERNST-EINSTEIN equation applies. Figure A.20 illustrates this phenomenon by showing the changing curves for the diffusion and migration molar flux densities ratio for Ag^+, throughout the electrolyte.

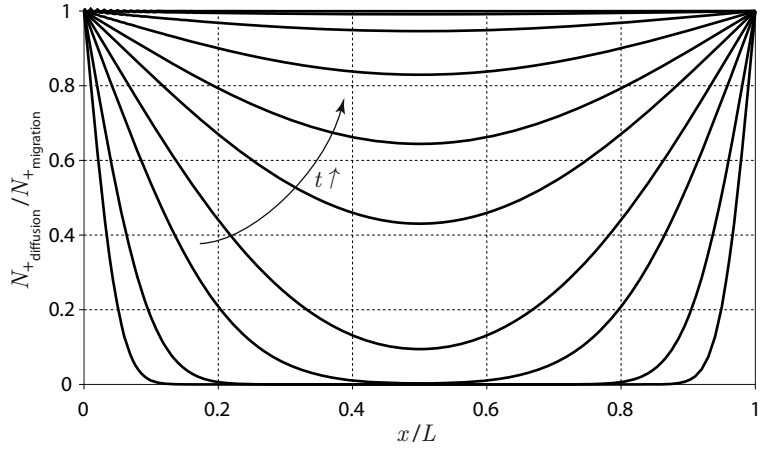


Figure A.20 - Change with time of the diffusion/migration flux densities ratio for Ag^+

The concentration changes in the central part of the electrolyte only appear after a certain time delay. At the beginning of the transient period, the current in this zone is totally due to migration. The diffusion contribution gradually increases, and comes into play later in the process.

To extend even further beyond this example where there is no supporting electrolyte, it is worth examining the limiting case where the anion diffusion coefficient becomes negligible when compared to the cation. What happens in this limiting case is that it takes an extremely long time to reach the steady state. Therefore, on a usual experimental time scale, the experiment always ends at the beginning of the transient period, namely the stage where the diffusion phenomenon is insignificant throughout the electrolyte. Whatever the fixed current, there is no noticeable change in the electrolyte composition in these particular systems. The voltage follows the simple OHM law, which only applies when migration phenomena are involved, such as in metals or in many ionic solids with a single type of charge carrier. These systems are developed by research groups investigating lithium batteries by using polymers where the negative charge is on the polymer chain. Here, the power limitations which are usually due to the diffusion phenomena in the electrolyte may be overcome in such electrolytes.

SOLUTION WITH A SUPPORTING ELECTROLYTE (SOLUTION S_2)

This second part investigates the electrolysis of solution S_2 with a supporting electrolyte. The composition is the following, as indicated at the beginning of this appendix: 10^{-3} mol L^{-1} $AgNO_3$ + 10^{-1} mol L^{-1} KNO_3 aqueous solution.

In the following, the subscripts + and – design Ag^+ and NO_3^- respectively.

THE EQUATIONS FOR THE SYSTEM

- The equation for expressing electroneutrality throughout the solution volume is:

$$C_+ + C_{K^+} = C_-$$

- In the case examined here, there is no reaction in the homogeneous phase and the system has unidirectional geometry. The volume mass balance for each species is:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial N_i}{\partial x}$$

Therefore at steady state we have: $\dfrac{\mathrm{d}N_i}{\mathrm{d}x} = 0$

In other words, at steady state the molar flux densities become constant throughout the electrolyte volume.

- At the anode, K^+ and NO_3^- do not react, whereas Ag becomes oxidized:

$$\begin{cases} (N_+)_{x=0} = \dfrac{I}{\mathscr{F} S} \\ (N_-)_{x=0} = 0 \\ (N_{K^+})_{x=0} = 0 \end{cases}$$

The same equations can be obtained by applying the FARADAY law at the cathode (being careful about the signs used; see the previous case).

- The different molar flux densities can be written as the sum of two terms (diffusion and migration) :

$$N_+ = -D_+ \frac{\partial C_+}{\partial x} - u_+ C_+ \frac{\partial \varphi}{\partial x}$$
$$N_- = -D_- \frac{\partial C_-}{\partial x} + u_- C_- \frac{\partial \varphi}{\partial x}$$
$$N_{K^+} = -D_{K^+} \frac{\partial C_{K^+}}{\partial x} - u_{K^+} C_{K^+} \frac{\partial \varphi}{\partial x}$$

or by applying the NERNST-EINSTEIN equation:

$$\begin{cases} N_+ = -D_+ \dfrac{\partial C_+}{\partial x} - D_+ \dfrac{\mathscr{F}}{\mathrm{R}T} C_+ \dfrac{\partial \varphi}{\partial x} \\ N_- = -D_- \dfrac{\partial C_-}{\partial x} + D_- \dfrac{\mathscr{F}}{\mathrm{R}T} C_- \dfrac{\partial \varphi}{\partial x} \\ N_{K^+} = -D_{K^+} \dfrac{\partial C_{K^+}}{\partial x} - D_{K^+} \dfrac{\mathscr{F}}{\mathrm{R}T} C_{K^+} \dfrac{\partial \varphi}{\partial x} \end{cases}$$

STEADY-STATE CONCENTRATION PROFILES

At steady state, the molar flux densities N_+, N_- and N_{K^+} are constant throughout the electrolyte volume and are equal to their interfacial values.

- When the previous equations are combined, the diffusion terms are eliminated to give the following:

$$\frac{N_+}{D_+} + \frac{N_{K^+}}{D_{K^+}} - \frac{N_-}{D_-} = -\frac{\mathcal{F}}{RT}(C_+ + C_{K^+} + C_-)\frac{\partial \varphi}{\partial x}$$

and finally, with $C_+ + C_{K^+} = C_-$ and $N_- = N_{K^+} = 0$,

$$N_+ = -2D_+ \frac{\mathcal{F}}{RT} C_- \frac{\partial \varphi}{\partial x}$$

therefore: $$N_+ = -D_+ \frac{\partial C_+}{\partial x} - D_+ \frac{\mathcal{F}}{RT} C_+ \frac{\partial \varphi}{\partial x} = -D_+ \frac{\partial C_+}{\partial x} + \frac{C_+}{2C_-} N_+$$

Due to the fact that there is a supporting electrolyte, this gives $C_+ \ll C_-$, and therefore:

$$N_+ \approx -D_+ \frac{\partial C_+}{\partial x}$$

In other words, with a supporting electrolyte present, the migration of the Ag^+ electroactive ions is negligible when compared to their diffusion.

- By using the equation coming from the FARADAY law (see above) to express the molar flux densities of Ag^+, it can be shown that the C_+ profile is linear:

$$\frac{\partial C_+}{\partial x} = -\frac{I}{D_+ \mathcal{F} S} = \text{Cst}$$

Linear profiles also emerge for the electroinactive ions, again when using the equations involving the molar flux densities. However the slopes are twice as small as those obtained for the electroactive ions, in accordance with the electroneutrality. The equation then becomes:

$$\frac{\partial C_{K^+}}{\partial x} = -\frac{\partial C_-}{\partial x} = \frac{I}{2D_+ \mathcal{F} S}$$

- The integrated mass balance for each type of ion gives the integration constant of the concentration profiles by writing the following:

$$(C_+)_{x=L/2} = C^* \qquad (C_{K^+})_{x=L/2} = 100\ C^* \qquad (C_-)_{x=L/2} = 101\ C^*$$

The new equation for the limiting current in this case can then be introduced (see section 4.3.3.1, with a thickness equal to $L/2$ and a diffusion coefficient equal to D_+):

$$I_{lim_{S_2}} = \frac{2D_+ \mathcal{F} S C^*}{L}$$

The limiting current is twice as small as the one obtained with no supporting electrolyte.

The equations for the concentration profiles are the following:

$$\begin{cases} \dfrac{C_+}{C^*} = 1 + \dfrac{I}{I_{\text{lim}_{S_2}}}\left(1 - \dfrac{2\,x}{L}\right) \\ \dfrac{C_{K^+}}{C^*} = 100 - \dfrac{I}{2\,I_{\text{lim}_{S_2}}}\left(1 - \dfrac{2\,x}{L}\right) \\ \dfrac{C_-}{C^*} = 101 + \dfrac{I}{2\,I_{\text{lim}_{S_2}}}\left(1 - \dfrac{2\,x}{L}\right) \end{cases}$$

In both solutions S_1 and S_2, the slope of the concentration profile for the electroactive species Ag^+ is proportional to I/I_{lim}. However we must remember that the limiting current is twice as small when there is a supporting electrolyte. Consequently, for a given value of the current I, the fact that there is a supporting electrolyte present causes this slope to increase by a factor of 2, as illustrated in figure A.21. The figure shows the steady-state profiles of Ag^+ for a current equal to 90% of the new limiting current (i.e., 14.3 μA). A slope of -0.9×10^{-3} mol L^{-1} mm^{-1} is obtained for the solution S_2, with a supporting electrolyte, while the slope is twice as small for the solution S_1 with the same current.

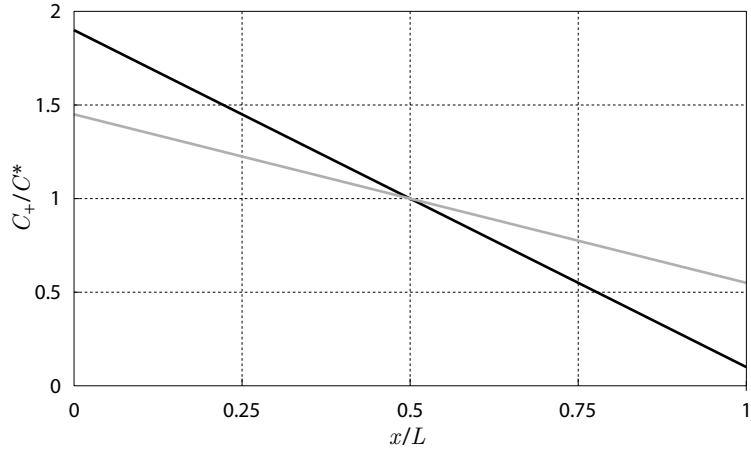


Figure A.21 - Steady-state concentration profiles for Ag^+ in the electrolyte for $I = 0.9\ I_{lim_{S_2}}$
Comparing solution S_1 (without a supporting electrolyte, grey curve) with S_2 (with a supporting electrolyte, black curve), using the same current.

This difference in behaviour can be explained in qualitative terms. When there is a supporting electrolyte present the current is totally due to diffusion, whereas when there is no supporting electrolyte, half of the steady-state current is carried by migration. One must keep in mind the fact that these distributions between diffusion and migration produce the same total current, i.e., the same amount of substance is transformed per time unit at the electrodes whether they be with or without a supporting electrolyte.

The concentration profiles of electroinactive ions are given in figure A.22 for the same current 14.3 μA.

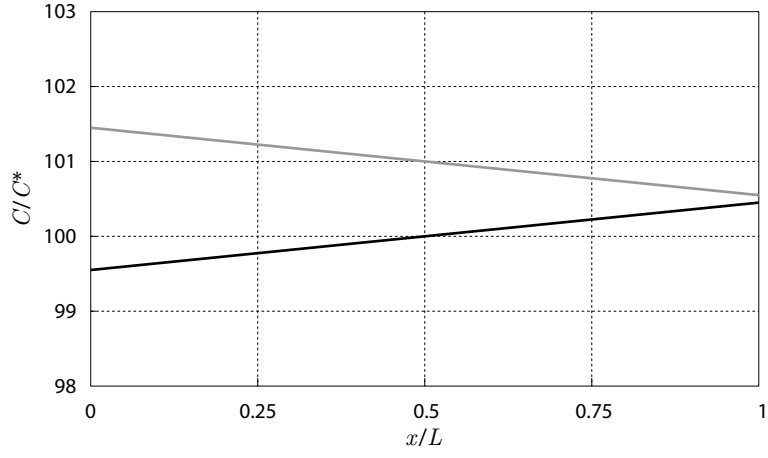
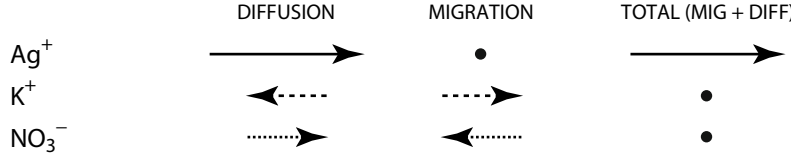


Figure A.22 - Steady-state concentration profiles for the supporting electrolyte ions: K^+ (black) and NO_3^- (grey) in the solution S_2 for $I = 0.9\ I_{lim_{S_2}}$

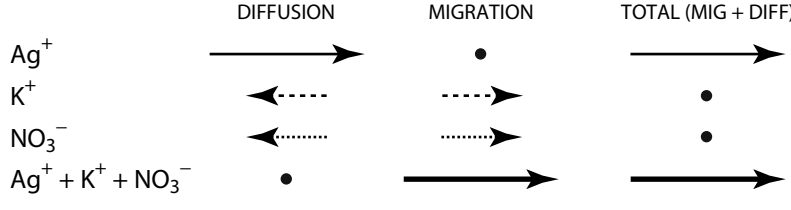
For these electroinactive ions, the slopes of the concentration profiles share the same order of magnitude as those of the electroactive ion (twice as small). Nevertheless, since the mean value of their concentrations is at least one hundred times higher, then their relative changes are very small. This is why such profiles are not generally described, even if their magnitudes are just as great as those belonging to electroactive species.

MOLAR FLUXES AND CURRENT DENSITIES AT STEADY STATE

Using figures A.21 and A.22, and remembering that diffusion fluxes are oriented from the most concentrated towards the least concentrated zones, the different contributions of the molar flux densities can be represented as follows:



As far as the current densities are concerned, the directions are opposite to the molar flux density in the case of the nitrate ion because it is an anion:



⏩ Since the molar fluxes of NO_3^- and K^+ are zero at steady state:

$$\widetilde{t}_+ = 1$$

This means that the entire current is carried by the Ag^+ ions, as in the case with no supporting electrolyte. In the example studied here almost all of the current is due to diffusion. This value corresponds to the electrochemical transport number. If it were possible to consider the migration phenomena as being the only relevant one, then usual transport numbers would be obtained:

$$t_+ = t_{Ag^+} = \frac{\sigma_{Ag^+}}{\sigma} = \frac{\lambda_+}{101\,\lambda_- + 100\,\lambda_{K^+} + \lambda_+} = 0.004$$

and $$t_{NO_3^-} = 0.49 \qquad t_{K^+} = 0.50$$

STEADY-STATE POTENTIAL PROFILES

- Previously the following relationship was obtained:

$$\frac{\mathscr{F}}{RT}\frac{\partial \varphi}{\partial x} = -\frac{N_+}{2D_+C_-} = -\frac{I}{2D_+\,C\,\mathscr{F}\,S}$$

- Strictly speaking, because the anion concentration is a function of the distance to the electrodes, then the following equation does not relate to a linear potential profile. One has:

$$\frac{\partial \varphi}{\partial C_-} = \frac{RT}{\mathscr{F}}\frac{1}{C_-}$$

- By integrating the previous equation between the two planes with x and $x = L/2$ abscissae, and with the potential origin being taken arbitrarily at $x = L/2$, one obtains the following:

$$\varphi = \frac{RT}{\mathscr{F}}\ln\left(\frac{C_-}{101\,C^*}\right) = \frac{RT}{\mathscr{F}}\ln\left[1 + \frac{1}{101}\frac{I}{2\,I_{lim_{S_2}}}\left(1 - \frac{2\,x}{L}\right)\right]$$

Given that there is a supporting electrolyte, even for a current close to the limiting current, then the term $I/(101\ I_{lim_{S_2}})$ remains low compared to 1 and the profile is almost linear:

$$\varphi \approx \frac{RT}{2\,\mathscr{F}}\frac{I}{101\,I_{lim_{S_2}}}\left(1 - \frac{2\,x}{L}\right)$$

This example shows that due to the fact that there is a supporting electrolyte, the potential profile is almost linear even for a current close to the limiting current.

- Since the redox couple is considered as being fast, the interfacial voltage can be written as follows (see section 4.3.2.4):

$$\varphi_{metal} - \varphi_{solution} = Cst + \frac{RT}{\mathscr{F}}\ln[Ag^+]_{interface}$$

Figure A.23 depicts the steady-state potential profile for a current equal to 90% of the limiting current (i.e., 14.3 µA).

The electrolysis voltage is then equal to:

$$U = \varphi_{anode} - \varphi_{cathode} = \varphi_{x=0} - \varphi_{x=L} + \frac{RT}{\mathscr{F}}\ln\frac{[Ag^+]_{x=0}}{[Ag^+]_{x=L}}$$

$$U \approx \frac{\mathrm{R}T}{\mathscr{F}} \ln \frac{[\mathrm{Ag}^+]_{x=0}}{[\mathrm{Ag}^+]_{x=L}} = \frac{\mathrm{R}T}{\mathscr{F}} \ln \frac{1+\dfrac{I}{I_{\mathrm{lim}_{S_2}}}}{1-\dfrac{I}{I_{\mathrm{lim}_{S_2}}}}$$

In the example shown in figure A.23 ($I = 0.9\ I_{\mathrm{lim}_{S_2}}$) the electrolysis voltage is equal to 76 mV (the ohmic drop value is 0.2 mV).

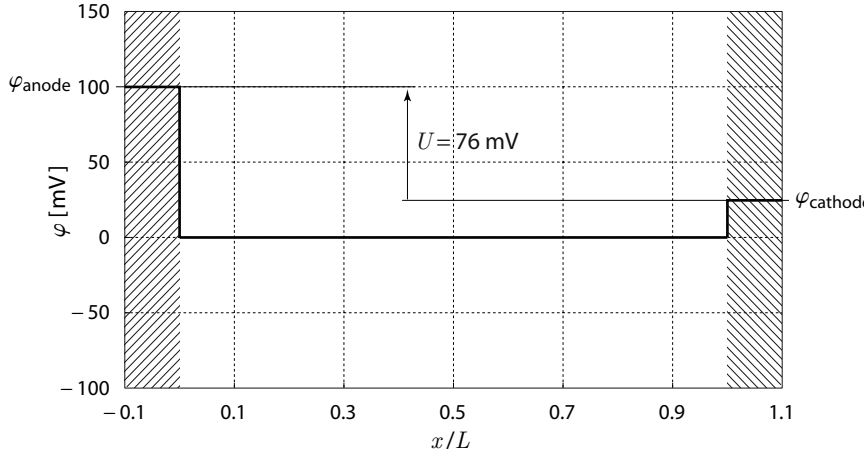


Figure A.23 - Potential profile within the electrolyte for $I = 0.9\ I_{lim_{S_2}}$
The anode potential value is arbitrarily fixed.
Yet the cathode potential is deduced from that of the anode.

ELECTROLYTE RESISTANCE AT STEADY STATE

The overall electrolyte resistance is calculated from the potential values at $x = 0$ and $x = L$: $U_{\text{ohmic drop}} = \varphi_{x=0} - \varphi_{x=L} = R\,I$.

$$R = \frac{\varphi_{x=0} - \varphi_{x=L}}{I} = \frac{\mathrm{R}T}{I\,\mathscr{F}} \ln \left(\frac{1+\dfrac{1}{101}\dfrac{I}{2\,I_{\mathrm{lim}_{S_2}}}}{1-\dfrac{1}{101}\dfrac{I}{2\,I_{\mathrm{lim}_{S_2}}}} \right)$$

A TAYLOR expansion around zero of the previous equation gives, even for a current close to $I_{\mathrm{lim}_{S_2}}$:

$$R \approx \frac{\mathrm{R}T}{\mathscr{F}} \frac{1}{101\,I_{\mathrm{lim}_{S_2}}} = \frac{L}{S(2\,\lambda_+)\,101\,C^*} = 16.0\ \Omega$$

If the composition of the electrolyte were homogeneous, then the resistance would be:

$$R_{\text{pure migration}} = \frac{L}{S\,\sigma} = \frac{L}{S(101\,\lambda_- + 100\,\lambda_{K^+} + \lambda_+)\,C^*} = 13.7\ \Omega$$

and finally,

$$R \approx \frac{R_{\text{pure migration}}}{2\,t_+} \frac{C_+^*}{C_-^*}$$

The resistance remains almost constant when the current varies when there is a supporting electrolyte. Moreover it is much lower than in the previous case, i.e., with no supporting electrolyte. However, the voltage between the system's terminals also tends towards infinity when the current approaches the limiting current: since the Ag^+ concentration tends towards zero, the interfacial voltage at the cathode tends towards infinity.

CHARACTERISING THE TRANSIENT PERIOD LEADING TO THE STEADY STATE

If we do not confine ourselves here to studying the steady states, then the molar flux densities can no longer be considered as constant in the electrolyte, and the electroinactive ions can no longer be considered as immobile. Nevertheless, by using the expression for electroneutrality, one can reuse the general equations previously written:

$$\frac{\partial C_+}{\partial t} = -\frac{\partial N_+}{\partial x} \approx D_+ \frac{\partial^2 C}{\partial x^2}$$

The progression towards the steady state therefore relates to the Ag^+ diffusion, with a characteristic time, τ, defined by:

$$\tau = \frac{L^2}{4\,D_+}$$

In the particular case examined here, by putting $D_+ = 1.65 \times 10^{-9}$ m^2 s^{-1}, one ends up with $\tau = 606$ s.

At this point, the fact that there is a supporting electrolyte or not has no significant impact, provided that D_+ and D_- share the same order of magnitude.

A.4.2 - CONCENTRATION PROFILES AT AN INTERFACE

Concentration profiles are very useful for understanding electrochemical phenomena. Yet it should be kept in mind that they make up only one part of those phenomena, since only diffusion is visualized. For example, in the case described in appendix A.4.1, the profile of the NO_3^- anion does not appear flat, although this ion is not consumed at the electrodes. Indeed, even if diffusion has a tendency to carry this species from anode to cathode, the migration compensates for this phenomenon in exact terms. Finally, at steady state, there is no overall mass transport for these ions. Another difficulty arises from the different interpretations of these concentration profiles, in terms of mass consumption or production in transient or steady states.

To illustrate this difference, let us consider the example of a system with Fe^{2+} and Fe^{3+} ions, a supporting electrolyte, two inert electrodes, in unidirectional geometry (see figure A.15 in appendix A.4.1). As in the example chosen in appendix A.4.1, both redox reactions are exact opposites (with the same reaction in both forward and reverse directions):

- at the anode ($x = 0$), the reaction is:

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

- at the cathode ($x = L$), the reaction is:

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

The migration fluxes of the electroactive ions can be disregarded, and the supporting electrolyte's ions are not examined here either. The mass transport parameters of the two electroactive ions involved are considered as being constant and equal to [13]:

$$D_{Fe^{2+}} = 0.72\times10^{-9}\ m^2\ s^{-1} \qquad D_{Fe^{3+}} = 0.40\times10^{-9}\ m^2\ s^{-1}$$

Here, a chronopotentiometry experiment is studied in the successive conditions below:

- semi-infinite unidirectional diffusion (with no convection nor migration of the electroactive species, and with the two electrodes set far apart from each other),
- steady-state unidirectional diffusion (with no convection nor migration of the electroactive species, and with the two electrodes set close to each other),
- diffusion-convection as defined using the NERNST model (with no migration of the electroactive species).

Finally, to complete the study, a detailed description is given to specify the interfacial conditions involved in chronoamperometry, in the case where there are unidirectional diffusion conditions with a fast redox couple (a reversible reaction) and where there are different diffusion coefficients for the electroactive species.

CHRONOPOTENTIOMETRY WITH SEMI-INFINITE UNIDIRECTIONAL DIFFUSION

The first case has already been described in qualitative terms in section 4.3.1.2. In this section, we will complete figure 4.15 by returning to the analysis given in section 4.3.1.3, figure 4.19. At a given time t, one is able to calculate the concentration profiles as they appear in figure A.24 on the anodic side, and in figure A.25 on the cathodic side. The FARADAY law produces an equation for the interfacial concentrations at the anode:

$$-\frac{I}{\mathcal{F}\,S} = -D_{Fe^{2+}}\left(\frac{\partial[Fe^{2+}]}{\partial x}\right)_{x=0} = -D_{Fe^{2+}}\,\frac{[Fe^{2+}]^* - [Fe^{2+}]_{x=0}}{2\sqrt{\dfrac{D_{Fe^{2+}}t}{\pi}}}$$

$$[Fe^{2+}]_{x=0} = [Fe^{2+}]^* - \frac{2I}{\mathcal{F}\,S}\sqrt{\frac{t}{D_{Fe^{2+}}\pi}}$$

and similarly:

$$[Fe^{3+}]_{x=0} = [Fe^{3+}]^* + \frac{2I}{\mathcal{F}\,S}\sqrt{\frac{t}{D_{Fe^{3+}}\pi}}$$

As described in section 4.3.1.2, the two grey surfaces are identical in absolute value: they represent the amount of substance produced or consumed between the initial time and time t. Equally, the same result can be reached by using the equations previously established. Indeed, one can even determine the order of magnitude of these two areas by building a calculation based on the algebraic area of triangles that is bounded by the interfacial slopes at time t.

---

[13] For Fe^{2+}, the value is taken from table 4.2 in section 4.2.2.4, using the NERNST-EINSTEIN law, and the value for Fe^{3+} is underestimated (since its real value is $0.60\times10^{-9}\ m^2\ s^{-1}$, deduced from the values in table 4.2), so as to make it easier to visualize the impact made by the difference between these two values.

These are given below:

$$A_{Fe^{2+}} = \frac{1}{2}\left([Fe^{2+}]_{x=0} - [Fe^{2+}]^*\right) 2\sqrt{\frac{D_{Fe^{2+}}t}{\pi}} = -\frac{2I}{\mathcal{F}S}\frac{t}{\pi}$$

$$A_{Fe^{3+}} = \frac{1}{2}\left([Fe^{3+}]_{x=0} - [Fe^{3+}]^*\right) 2\sqrt{\frac{D_{Fe^{3+}}t}{\pi}} = +\frac{2I}{\mathcal{F}S}\frac{t}{\pi} = -A_{Fe^{2+}}$$

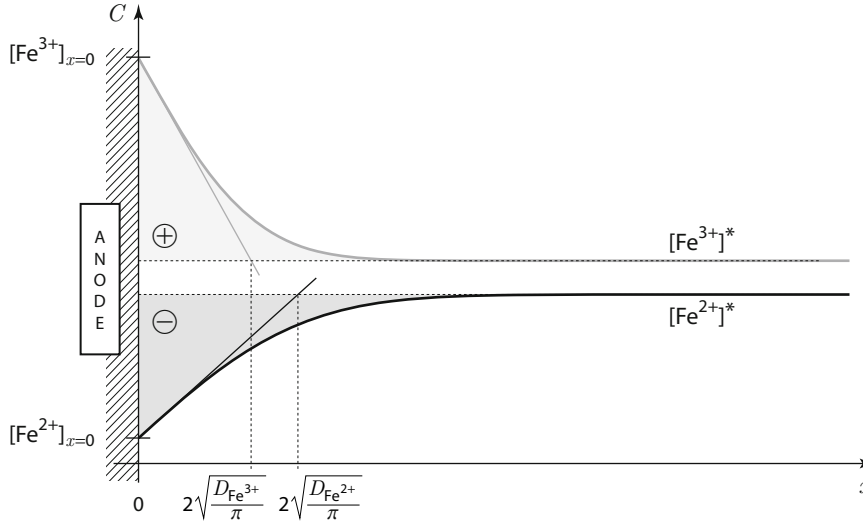


Figure A.24 - Concentration profiles for Fe^{3+} (grey) and Fe^{2+} (black) on the anodic side

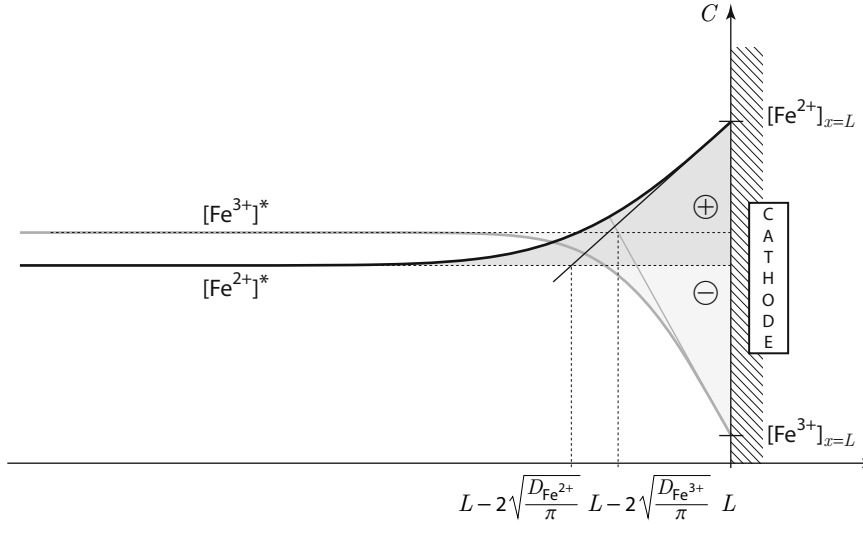


Figure A.25 - Concentration profiles for Fe^{3+} (grey) and Fe^{2+} (black) on the cathodic side

It is also possible to visualize the mass preservation (equal amounts of species produced and consumed in this particular example) by plotting the curve that shows the profile of the sum $[Fe^{2+}] + [Fe^{3+}]$. At the interface this quantity is greater than the sum $[Fe^{2+}]^* + [Fe^{3+}]^*$.

It then decreases to lower than $[Fe^{2+}]^* + [Fe^{3+}]^*$, before reaching a minimum, whereupon it increases again, tending towards $[Fe^{2+}]^* + [Fe^{3+}]^*$. If the two diffusion coefficients were equal, then the sum $[Fe^{2+}] + [Fe^{3+}]$ would remain constant and equal to $[Fe^{2+}]^* + [Fe^{3+}]^*$ throughout the whole electrolyte, reflecting a local application of the mass balance. However, when the two diffusion coefficients are different, then mass preservation can no longer apply at all points. Nonetheless, an overall preservation applies throughout the whole diffusion layer, as defined in section 2.2.1.1: the algebraic area of the surface bounded by the curves ($[Fe^{2+}]^* + [Fe^{3+}]^*$) and ($[Fe^{2+}] + [Fe^{3+}]$) is zero.

CHRONOPOTENTIOMETRY WITH STEADY-STATE UNIDIRECTIONAL DIFFUSION

When the two electrodes are very close to each other, a steady state is reached after a transient period, which itself is as described above during its initial moments. Figure A.26 shows the concentration profiles for the electroactive species at steady state.

They relate to the following equations:

$$D_{Fe^{2+}} \frac{\partial [Fe^{2+}]}{\partial x} = \frac{I}{\mathcal{F}\, S} = -D_{Fe^{3+}} \frac{\partial [Fe^{3+}]}{\partial x}$$

hence:

$$[Fe^{2+}] = [Fe^{2+}]^* + \frac{I}{D_{Fe^{2+}} \mathcal{F}\, S\, L} \left(x - \frac{L}{2} \right)$$

$$[Fe^{3+}] = [Fe^{3+}]^* - \frac{I}{D_{Fe^{3+}} \mathcal{F}\, S\, L} \left(x - \frac{L}{2} \right)$$

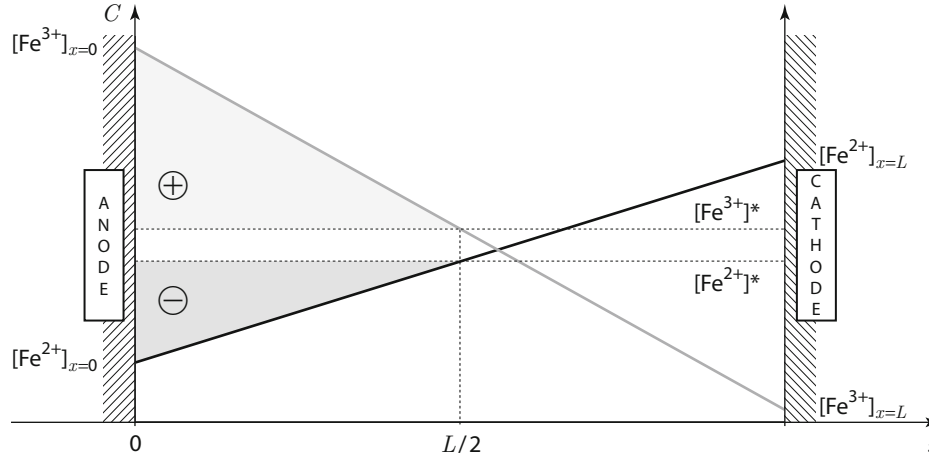


Figure A.26 - Steady-state concentration profiles for Fe^{3+} (grey) and Fe^{2+} (black)

Given that the two redox reactions are opposite, the average concentration for each ion in the electrolyte remains equal to the initial value. As illustrated in figure A.26, this means that the average concentration value is found at the exact middle of the cell, at $x = L/2$. The grey surfaces have different areas because they no longer represent the amounts of substance consumed between two specific moments in time. This disparity observed at steady state is explained by the fact that Fe^{2+} and Fe^{3+} ions do not take the same time to reach steady state, because their diffusion coefficients are different.

CHRONOPOTENTIOMETRY WITH DIFFUSION-CONVECTION ACCORDING TO THE NERNST MODEL

The concept of forced convection is introduced here in simple terms. The steady state that emerges is defined by using the NERNST model (see section 4.3.1.4), and the corresponding concentration profiles are shown in figure A.27.

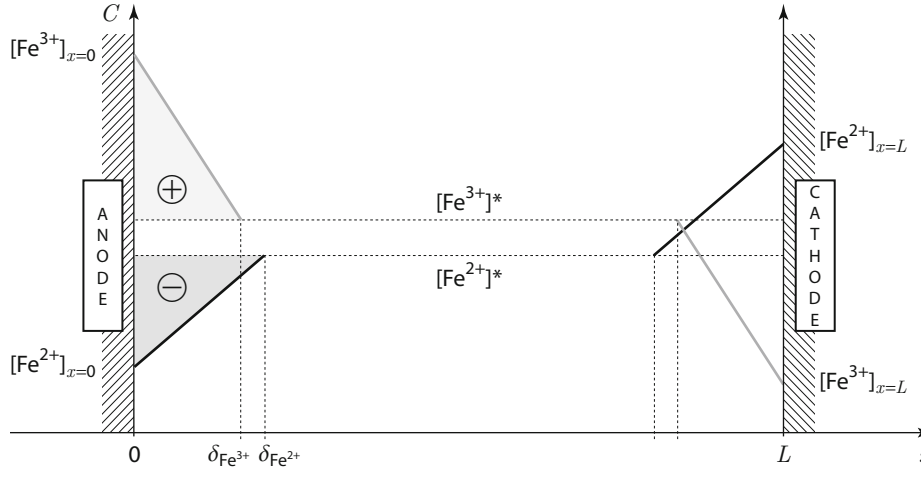


Figure A.27 - Steady-state concentration profiles for Fe^{3+} (grey) and Fe^{2+} (black) for a diffusion-convection mode according to the NERNST model

The concentration profiles on the anodic side are described by the following equations:

$$[Fe^{2+}] = [Fe^{2+}]^* + \frac{I}{D_{Fe^{2+}} \mathcal{F} S}\left(\frac{x}{\delta_{Fe^{2+}}} - 1\right)$$

$$[Fe^{3+}] = [Fe^{3+}]^* - \frac{I}{D_{Fe^{3+}} \mathcal{F} S}\left(\frac{x}{\delta_{Fe^{3+}}} - 1\right)$$

To give an even more precise description, the LEVICH law can be applied to express the thickness of the NERNST layer in experiments using a rotating disk electrode:

$$\delta_i = 1.611\, D_i^{1/3}\, \nu^{1/6}\, \Omega^{-1/2}$$

with : δ_i thickness of the NERNST layer [m]
D_i diffusion coefficient [$m^2\ s^{-1}$]
ν kinematic viscosity of the electrolyte[14] [$m^2\ s^{-1}$]
Ω rotating speed of the electrode[15] [$rad\ s^{-1}$]

Therefore, as shown in figure A.27, the NERNST layer for Fe^{2+} ions is thicker than that for Fe^{3+} ions.

---

[14] Be careful not to mix up kinematic viscosity ν (in $m^2\ s^{-1}$) with dynamic viscosity η (in Pa s), as used for example in the case of the STOKES law (see section 4.2.2.4). The link between these two parameters is expressed as: $\nu = \eta / \rho$, where ρ is the density of the medium.

[15] 1 rpm = $(2\pi/60)$ rad s^{-1}

The following gives the algebraic areas of the triangles bounded by the steady state and the initial profiles:

$$A_{Fe^{2+}} = \frac{1}{2}\left([Fe^{2+}]_{x=0} - [Fe^{2+}]^*\right)\delta_{Fe^{2+}} = -\frac{I(\delta_{Fe^{2+}})^2}{2D_{Fe^{2+}}\mathcal{F}\,S} = -\frac{1.611^2 I}{2\,\mathcal{F}\,S\,\Omega}\left(\frac{\nu}{D_{Fe^{2+}}}\right)^{1/3}$$

$$A_{Fe^{3+}} = \frac{I(\delta_{Fe^{3+}})^2}{2D_{Fe^{3+}}\mathcal{F}\,S} = \frac{1.611^2 I}{2\,\mathcal{F}\,S\,\Omega}\left(\frac{\nu}{D_{Fe^{3+}}}\right)^{1/3} \neq -A_{Fe^{2+}}$$

These two areas are not equal in absolute value, because they do not represent the amount of substance consumed between two precise moments in time.

CHRONOAMPEROMETRY WITH STEADY-STATE UNIDIRECTIONAL DIFFUSION

In a chronoamperometry experiment, the concentration profiles next to the working electrode at any given time have the same shape as those described above in the case of a chronopotentiometry experiment (see figure A.24). Yet there is a difference in the concentration profile changes at different times, and especially in the way in which the diffusion layer thickness evolves, as described in section 4.3.1.3. The later section highlights the fact that fixing the working electrode potential for a fast couple (chronamperometry in a potential range where the reaction is reversible) is tantamount to fixing the interfacial concentration values of the electroactive species (see figure 4.18).

It is easy to demonstrate this result when the two diffusion coefficients are equal. In fact, by combining the equations for Fe^{3+} and Fe^{2+} (mass balance, initial and boundary conditions), the following system can be obtained:

$$\frac{\partial}{\partial t}\left([Fe^{3+}] + [Fe^{2+}]\right) = D\frac{\partial^2}{\partial x^2}\left([Fe^{3+}] + [Fe^{2+}]\right)$$

with $t \leq 0$ $\quad [Fe^{3+}] + [Fe^{2+}] = [Fe^{3+}]^* + [Fe^{2+}]^*$

$t > 0, x = 0$ $\quad D\frac{\partial}{\partial x}\left([Fe^{3+}] + [Fe^{2+}]\right) = 0$

$t > 0, x = L$ $\quad D\frac{\partial}{\partial x}\left([Fe^{3+}] + [Fe^{2+}]\right) = 0$

The unique solution of this system is:

$\forall t, \forall x$ $\quad [Fe^{3+}] + [Fe^{2+}] = [Fe^{3+}]^* + [Fe^{2+}]^*$

This equation applies in particular at the working electrode surface. By combining it with the reversibility hypothesis for the interfacial reaction:

$$\frac{[Fe^{3+}]_{x=0}}{[Fe^{2+}]_{x=0}} = e^{\xi}$$

one can obtain equations that give the interface concentrations, showing that they are not time-dependent:

$$[Fe^{2+}]_{x=0} = \frac{[Fe^{3+}]^* + [Fe^{2+}]^*}{1 + e^{\xi}}$$

$$[Fe^{3+}]_{x=0} = \left([Fe^{3+}]^* + [Fe^{2+}]^*\right)\frac{e^{\xi}}{1 + e^{\xi}}$$

The fact that the interfacial concentrations for a fast couple are determined by the electrode potential still applies when the diffusion coefficients are different, however the demonstration then becomes much more complicated [16]. In this case the equations are:

$$[Fe^{3+}] + [Fe^{2+}] \neq [Fe^{3+}]^* + [Fe^{2+}]^*$$

and

$$[Fe^{2+}]_{x=0} = \frac{[Fe^{3+}]^* + \sqrt{\frac{D_{Fe^{2+}}}{D_{Fe^{3+}}}}[Fe^{2+}]^*}{\sqrt{\frac{D_{Fe^{2+}}}{D_{Fe^{3+}}}} + e^{\xi}}$$

$$[Fe^{3+}]_{x=0} = e^{\xi}[Fe^{2+}]_{x=0}$$

Therefore, in a chronamperometry experiment, the interface concentrations are fixed, though this rule does not apply for a slow redox couple.

[16] The results given here can be demonstrated using the LAPLACE transformation.

SUMMARY TABLES

1 - BASIC NOTIONS

2 - SIMPLIFIED DESCRIPTION OF THE ELECTROCHEMICAL SYSTEMS

3 - THERMODYNAMIC FEATURES

4 - CURRENT FLOW: A NON-EQUILIBRIUM PROCESS

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

1 - BASIC NOTIONS

WHAT NEEDS TO BE KNOWN	RESPONSE ELEMENTS

Introduction

Definition of ***electrochemistry***	**1.1.1** Exchange of electric and chemical energies
Principal types of electrochemical applications	**1.1.3** Electrosynthesis - Surface treatments - Energy storage and conversion Analysis and measurements - Environment - Corrosion - Bioelectrochemistry

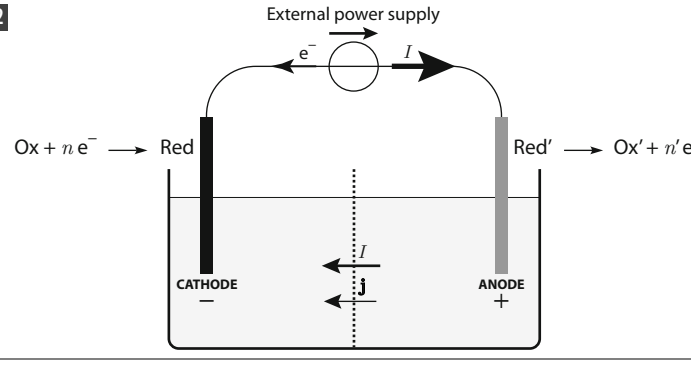
Oxidation-reduction

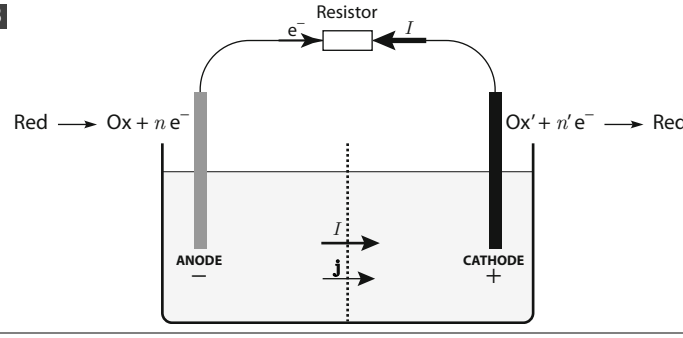
Definition of: ***oxidant, reductant, oxidation, reduction***	**1.2.1** **Oxidant** (or oxidized form, written Ox): form able to **fix electrons** **Reductant** (or reduced form, written Red): form able to **give electrons** $\mathrm{Red} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \mathrm{Ox} + n\,\mathrm{e}^-$
Calculating an ***oxidation number***	**1.2.2** The usual o.n. of **H** is equal to **+I**. The usual o.n. of **O** is equal to **−II**. The usual o.n. of **X** (**halogen**) is equal to **−I**. The usual o.n. of **M** (**alkaline**) is equal to **+I**.
Writing a balanced ***redox half-reaction***	**1.2.3** Preserving the amounts of elements and charge The number of exchanged electrons results from the difference of o.n. in Ox and Red

Current

Different types of conductors and interfaces	**1.3.2** Electronic, ionic, mixed conductors Electronic, ionic junctions, electrochemical and mixed interfaces
Definition of : ***anode***, ***cathode***	**1.3.3** Electrochemical system: heterogeneous system including at least two electrodes and one electrolyte: at **anode**, **oxidation** at **cathode**, **reduction**

Electrochemical chain

Sign convention for the current	**1.4.1** At anode: $I > 0$ at cathode: $I < 0$ (this comes down to having the normal vector to the interface oriented from the metal to the electrolyte)
Use of the property of conservative current	**1.4.1** Conservative current flux resulting from the electroneutrality of the conducting media: $\lvert I \rvert = \langle j_{\mathrm{an}} \rangle S_{\mathrm{an}} = -\langle j_{\mathrm{cat}} \rangle S_{\mathrm{cat}}$ j: current density (A m^{-2})
Representing an electrochemical system in ***electrolyser*** mode (or for a ***recharging battery***)	**1.4.2** 

WHAT NEEDS TO BE KNOWN		RESPONSE ELEMENTS
Representing an electrochemical system in ***power source*** mode (or for a ***discharging battery***)	1.4.3	

Potential - Voltage - Polarisation

Defining the ***standard hydrogen electrode***	1.5.1	SHE is a virtual half-cell (which cannot be achieved by experiment) used as potential reference. It corresponds to the H^+/H_2 couple in its standard state
Knowing the main experimental ***reference*** systems	1.5.1	▸ HE, NHE, ▸ Silver chloride electrode (AgCl /Ag couple) or calomel electrode (Hg_2Cl_2/Hg couple): the potential relative to SHE depends on the chloride ion activity in the electrolyte, ▸ SCE: calomel electrode with a KCl-saturated solution
Definition of ***polarisation*** and ***overpotential***	1.5.2	$\pi_+ = E_{+/\text{Ref}} - E_{+/\text{Ref}}(I=0)\ldots$ Polarisation (π) is the general term. Overpotential (η) is used when the system at zero current is in equilibrium

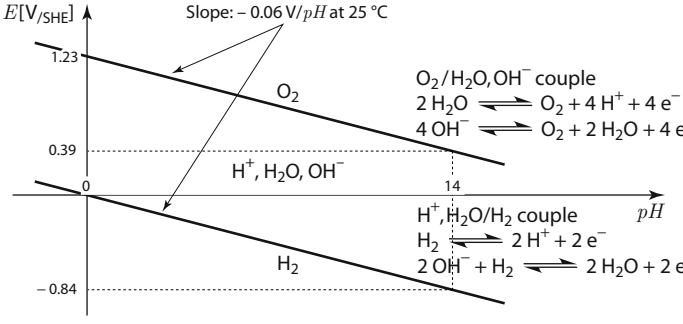
Experiments

Types of ***control***	1.6.2	Potentiometry: I is imposed (possibly $I=0$) and U or E is measured. Amperometry: U or E is imposed and I is measured.
Denomination of electrodes	1.6.2	▸ Working electrode (WE) ▸ Counter-electrode (or auxiliary electrode, CE) ▸ Reference electrode (Ref)
Defining principles of a ***potentiostat***	1.6.2	Laboratory device using 3 electrodes and enabling the control of the WE potential *vs* Ref (no current flows through the reference electrode)
Definition of a ***steady***, ***quasi-steady*** state	1.6.4	Quantities (I, U, concentrations…) independent of time ▸ strictly speaking, for a true steady state ▸ numerically, on the observation time scale, for a quasi-steady state

2 - SIMPLIFIED DESCRIPTION OF THE ELECTROCHEMICAL SYSTEMS

WHAT NEEDS TO BE KNOWN ***RESPONSE ELEMENTS***

Equilibrium

Writing and using the ***NERNST law***	**2.1.2** $E_{/\text{Ref}} = E^\circ_{/\text{Ref}} + \dfrac{0.06}{\nu_e} \log \prod_i a_i^{\nu_i}$ at 25 °C, ν_i and ν_e algebraic
E/pH diagram of ***water redox couples***	**2.1.2** 

Current

Main phenomena occurring when a current flows	**2.2.1** Transport within the volume: migration, diffusion (diffusion layer), convection At the interfaces: redox or chemical reaction, exchange, accumulation
Writing and using the ***FARADAY law***	**2.2.2** $\Delta n_i^{\text{farad}} = \dfrac{\nu_i}{\nu_e \mathcal{F}} Q^{\text{farad}} = \dfrac{\nu_i}{\nu_e \mathcal{F}} j^{\text{farad}} S \, \Delta t$ Δn_i, ν_i, ν_e, Q and j algebraic, $1\,\mathcal{F} = \mathcal{N} \lvert e \rvert \approx 96\,500$ C mol^{-1}
Defining and using the ***faradic yield***	**2.2.2** Faradic yield: proportion of current used for a given half-reaction Additivity of faradic currents if several simultaneous reactions occur at the same interface
Describing the ***potential profile*** in an electrochemical system	**2.2.3** $U(I \neq 0) = E_+ - E_- = U(I=0) + \pi_+ - \pi_- + \Sigma U_{\text{ohmic drop}}$ **2.4.3** **2.4.4** ▸ system in electrolyser mode: $U(I \neq 0) \geq U(I=0) + U_{\text{ohmic drop}} \geq U(I=0)$ ▸ system in power source mode : $U_{\text{supplied}} \leq U(I=0) - \lvert U_{\text{ohmic drop}} \rvert \leq U(I=0)$
Conduction by pure migration: ***conductivity***, ***transport number***	**2.2.4** $\mathbf{j} = \sigma \mathbf{E} = \dfrac{1}{\rho} \mathbf{E}$ or $U = RI$, if σ is homogeneous in the volume $\sigma = \sum_i \sigma_i = \sum_i \lambda_i C_i$ $\quad t_i = \dfrac{I_i}{I} = \dfrac{j_i}{j} = \dfrac{\sigma_i}{\sigma}$ λ_i molar ionic conductivity $\approx 10^{-2}$ S m^2 mol^{-1} $= 10^2$ S cm^2 mol^{-1} in aqueous solution σ_i ionic conductivity ≈ 1 S m^{-1} for a concentration of about 0.1 mol L^{-1} t_i transport number of species i: $0 < t_i < 1$
Definition of a ***supporting electrolyte***	**2.2.4** Non-electroactive ions in much higher concentrations than those of electroactive ions The migration current of electroactive species is then negligible compared to the overall migration current. Moreover, the ohmic drop is most often insignificant in this situation

WHAT NEEDS TO BE KNOWN		RESPONSE ELEMENTS
Current-potential curves		
Knowing the general shapes of ***(E,I) curves***	**2.3.1**	Curves normally increase, with $\pi I > 0$ or else: $\pi_{an} > 0$ ($I > 0$) and $\pi_{cat} < 0$ ($I < 0$) For a redox couple, there is only one branch if either the Red or Ox is absent in the system
Influence of the ***mass transport kinetics***	**2.3.2**	Existence of a limiting current, generally proportional to the consumed species concentration within the bulk electrolyte
Influence of the ***redox kinetics***	**2.3.3**	The absolute value of the overvoltage increases when the redox reaction kinetics gets slower
Definition of the ***electrochemical window***	**2.3.6**	Potential range of non-electroactivity of a half-cell when only the solvent and the supporting electrolyte are in contact with a given electrode; it is also called the redox stability window of this half-cell
Predicting reactions		
Predicting the ***spontaneous*** evolution of an electrode ***in open circuit***	**2.4.1**	Basing logic on the current-potential curves (including the kinetic and thermodynamic aspects) and not only on a thermodynamic potential scale A zero current in a non-equilibrium state is characterized by a mixed potential: at least two different half-reactions occur at the interface (oxidation and reduction)
Predicting the reactions during ***forced current flow***	**2.4.3**	When there are several possible reactions at an interface, the main half-reaction is that presenting the lowest polarisation (in absolute value) for the same current. The main overall reaction is therefore that which requires the lowest imposed voltage
Predicting the reactions during ***spontaneous current flow***	**2.4.4**	When there are several possible reactions at an interface, the main half-reaction is the one which presents the lowest polarisation (in absolute value) for the same current. The main overall reaction is therefore that which delivers the highest voltage, i.e., the greatest energy amount to an external circuit.

3 - THERMODYNAMIC FEATURES

WHAT NEEDS TO BE KNOWN	RESPONSE ELEMENTS

Potential

VOLTA and ***GALVANI*** potentials	**3.1.1** φ: internal or GALVANI potential, not measurable ψ: external or VOLTA potential, measurable
Writing the ***electrochemical potential*** and the ***activities***	**3.1.2** $\widetilde{\mu}_i = \mu_i + z_i \mathscr{F} \varphi$ with $\mu_i = \mu^\circ{}_i + \mathrm{R}T \ln a_i$ For a solution : $a_{\text{solvent}} \approx 1$ $a_i = \gamma_i \dfrac{C_i}{C^\circ}$
Conventions in thermodynamic tables	**3.1.2** For pure elements : the chemical potentials are zero To define $\mu^\circ{}_i$ of ion i in solution : $\forall T$ $\mu^\circ{}_{\mathrm{H}^+} = 0$ J mol^{-1}

Monophasic system

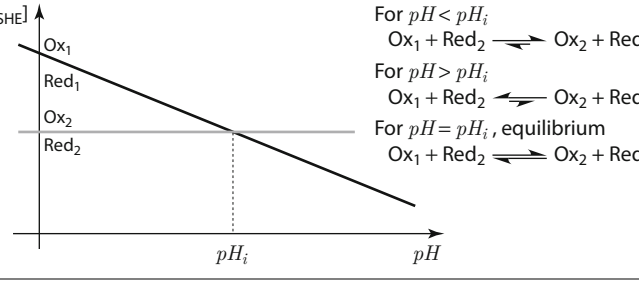
Use of the ***mass action law***	**3.2** $K_{\text{eq}}(T) = \prod_i a_i^{\nu_i}$ with $\Delta_{\text{r}}G^\circ + \mathrm{R}T \ln K_{\text{eq}} = 0$ K_{eq}, a_i and ν_i are dimensionless numbers (ν_i algebraic)
Use of the ***mean activity*** of a solute	**3.2.1** For a solute $A_{p_+}B_{p_-}$: $a = a_\pm^p = a_-^{p_-} a_+^{p_+}$ with $p = p_+ + p_-$ (for the simple case AB, $a_\pm = \sqrt{a_+ a_-}$ is measurable whereas a_+ and a_- are not individually measurable)
Defining and calculating the ***ionic strength*** of an electrolyte	**3.2.1** $I_{\text{s}} = \dfrac{1}{2}\sum_i C_i z_i^2$
Use of the ***DEBYE-HÜCKEL limiting law*** (including validity limits)	**3.2.1** $\log \gamma_\pm = A z_+ z_- \sqrt{I_{\text{s}}}$ with $A \approx 0.5$ L$^{1/2}$ mol$^{-1/2}$ (aqueous solutions at 25 °C) valid for $I_{\text{s}} < 10^{-3}$ to 10^{-2} mol L^{-1}

Interface

Describing the electrochemical ***double layer***	**3.3.1** The electrochemical double layer is the thin layer (about 10 Å thick) where electroneutrality does not apply due to charge accumulation on both sides of an electrochemical interface (comparable to a capacitor, this zone is also called the space charge zone). Separating this zone into two layers: HELMOLTZ's layer and diffuse layer
Describing the equilibrium at a ***reactive interface***	**3.3.2** $\Delta_{\text{r}}\widetilde{G} = \sum_i \nu_i \widetilde{\mu}_i = 0$ taking care to indicate which phase each species i belongs to
Describing the equilibrium at an ***ionic junction*** where only one charged species is exchanged	**3.3.4** The equilibrium corresponding to $\widetilde{\mu}_{i_\alpha} = \widetilde{\mu}_{i_\beta}$, is set by the exchange of a very low quantity of ions (there is an insignificant concentration difference between the initial and the equilibrium states) This results in a variation in the junction voltage
Describing the equilibrium at a reactive ***electrochemical interface***	**3.3.4** There is an interfacial voltage in equilibrium: $\varphi_{\text{metal}} - \varphi_{\text{electrolyte}} = \dfrac{1}{\mathscr{F}}\left(\mu_{\text{e}_{\text{metal}}} + \dfrac{1}{\nu_{\text{e}}}\sum_i \nu_i \mu_i\right) = \text{Cst} + \dfrac{\mathrm{R}T}{\nu_{\text{e}}\mathscr{F}} \ln \prod_i a_i^{\nu_i}$

WHAT NEEDS TO BE KNOWN	RESPONSE ELEMENTS

Electrochemical systems

Indicating the relationship between ***emf*** (in equilibrium) and ***thermodynamic data***	**3.4.1** $\Delta_r G = \nu_e \mathcal{F} U = \nu_e \mathcal{F} (\varphi_{WE} - \varphi_{CE})$ when ν_e represents the algebraic stoichiometric number of electrons involved in the half-reaction at the interface of the working electrode.
Making qualitative use of an ***E/pH diagram***	**3.4.2**  For $pH < pH_i$ $Ox_1 + Red_2 \rightleftharpoons Ox_2 + Red_1$ For $pH > pH_i$ $Ox_1 + Red_2 \rightleftharpoons Ox_2 + Red_1$ For $pH = pH_i$, equilibrium $Ox_1 + Red_2 \rightleftharpoons Ox_2 + Red_1$

4 - CURRENT FLOW: A NON-EQUILIBRIUM PROCESS

WHAT NEEDS TO BE KNOWN	RESPONSE ELEMENTS

Mass balance

Relationships between ***molar flux densities and current densities***	4.1.1	$\mathbf{j} = \sum_i z_i \mathscr{F} \mathbf{N}_i$
Writing the ***local mass balance in volume***, using the concept of a reaction rate	4.1.2	$\frac{\partial C_i}{\partial t} = -\,\mathrm{div}\,\mathbf{N}_i + w_i$ in unidirectional geometry : $\frac{\partial C_i}{\partial t} = -\frac{\partial N_{x,i}}{\partial x} + w_i$ $w_i = \sum_{\text{reactions}} \nu_{i_r}\, v_r$ with ν_{i_r} the algebraic stoichiometric number of the species i involved in the reaction r, with the rate v_r
Writing the ***interfacial mass balance***	4.1.3	$(N_i)_{\text{interface}_\beta} - (N_i)_{\text{interface}_\alpha} = -\frac{\partial \Gamma_i}{\partial t} + w_{S_i}$ normal oriented from α to β
Writing the mass balance at an electrochemical interface: ***capacitive and faradic currents***	4.1.3	For a species i, when it is mobile in the electrolyte (with the normal oriented from the metal to the electrolyte): $(N_i)_{\text{interface}} = \underbrace{-\frac{\partial \Gamma_i}{\partial t}}_{\substack{\text{capacitive term}\\ \text{(supporting electrolyte)}}} + \underbrace{w_{S_i}}_{\substack{\text{faradic term}\\ \text{(electroactive species)}}}$
Using the ***FARADAY law***	4.1.4	$j^{\text{farad}} = \mathscr{F} \frac{\nu_e}{\nu_i} (N_i^{\text{farad}})_{\text{interface}}$ for a species i mobile in the electrolyte

Mass transport

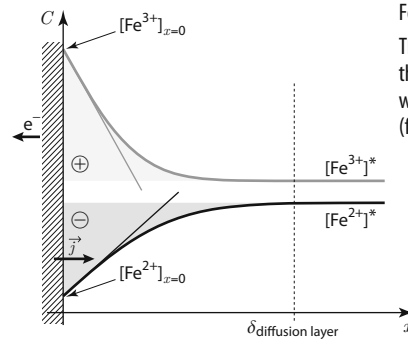
Writing the ***3 components of molar flux densities*** or of current densities	4.2.1	$\mathbf{j}_i = \underbrace{-\,D_i\, z_i\, \mathscr{F}\, \mathbf{grad}\, C_i}_{\mathbf{j}_{i\,\text{diffusion}}} + \underbrace{\lambda_i\, C_i\, \mathbf{E}}_{\mathbf{j}_{i\,\text{migration}}} + \underbrace{C_i\, z_i\, \mathscr{F}\, \boldsymbol{\omega}_{\text{medium}}}_{\mathbf{j}_{i\,\text{convection}}}$ $\mathbf{N}_i = \underbrace{-\,D_i\, \mathbf{grad}\, C_i}_{\mathbf{N}_{i\,\text{diffusion}}} + \underbrace{\frac{z_i}{\lvert z_i \rvert}\, u_i\, C_i\, \mathbf{E}}_{\mathbf{N}_{i\,\text{migration}}} + \underbrace{C_i\, \boldsymbol{\omega}_{\text{medium}}}_{\mathbf{N}_{i\,\text{convection}}}$ At a given point, the overall current density of convection is zero (electroneutrality) Moreover, if the diffusion coefficients of charge carriers have close values, then the overall current density of diffusion is insignificant and therefore the overall current is close to the migration current.
The ***NERNST-EINSTEIN*** equation	4.2.1	$D_i = \widetilde{u}_i\, \mathrm{R}T = \frac{u_i}{\lvert z_i \rvert \mathscr{F}} \mathrm{R}T$ or $\lambda_i = D_i\, z_i^2\, \frac{\mathscr{F}^2}{\mathrm{R}T}$ This equation results from the link made between migration and diffusion phenomena (assuming there are identical mechanisms at the microscopic level).
KOHLRAUSCH'S law	4.2.2	$\Lambda = \Lambda^0 - \mathrm{Cst}\,\sqrt{C}$

WHAT NEEDS TO BE KNOWN		RESPONSE ELEMENTS

Interface

Drawing the shape of the *concentration profiles* and defining the *diffusion layer*

4.3.1



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

The current is proportional to the slope of the concentration profile at the interface, when a supporting electrolyte is present (first Fick's law and FARADAY's law)

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

In the particular case of a limiting current, the interfacial concentration of the consumed species is negligible.

Writing the *rate laws* in the simplest case of the E redox mechanism

4.3.2

$$v_{\text{oxidation}} = k^\circ \exp\left[+\alpha\frac{n\mathcal{F}}{RT}(E-E^\circ)\right][\text{Red}]_{x=0} = k^\circ e^{\alpha\xi}[\text{Red}]_{x=0}$$

$$v_{\text{reduction}} = k^\circ \exp\left[-(1-\alpha)\frac{n\mathcal{F}}{RT}(E-E^\circ)\right][\text{Ox}]_{x=0} = k^\circ e^{-(1-\alpha)\xi}[\text{Ox}]_{x=0}$$

Definition of the concepts of *fast/slow* redox couples

4.3.2

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

k° is the standard redox reaction rate constant. It is intrinsic to the couple.
m characterizes the mass transport rate and therefore depends on the particular experimental conditions in each case.
For an experiment in steady state with an RDE in aqueous solution ($m = D/\delta$), a redox couple following an E mechanism is: fast if $k^\circ > 10^{-2}$ cm s^{-1} and slow if $k^\circ < 10^{-4}$ cm s^{-1}

Definition of the concepts of *reversible/irreversible* reactions

4.3.2

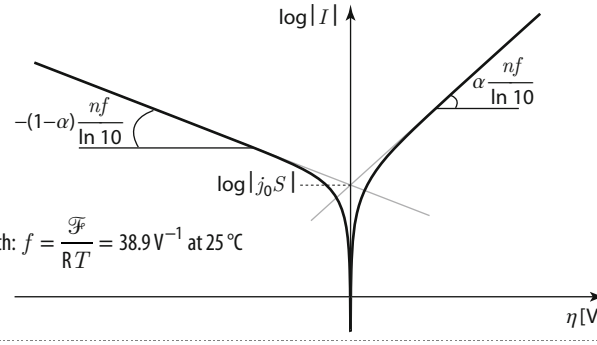
- A step is called **reversible** if, and only if, the overall reaction rate is very low in comparison to the forward and backward reaction rates: $v \ll v_{\rightarrow}$ and $v \ll v_{\leftarrow}$
  Consequently, the forward and backward reaction rates are almost equal: $v_{\rightarrow} \approx v_{\leftarrow}$
- A step is called **irreversible** in the forward direction (for example) if, and only if, the backward reaction rate is negligible compared to the forward reaction rate: $v_{\rightarrow} \gg v_{\leftarrow}$
  Consequently the overall rate is almost equal to the forward reaction rate: $v \approx v_{\rightarrow}$

Analytical expression of the steady-state current-potential curve of a *fast couple*

4.3.3

$E = E^\circ + \frac{RT}{n\mathcal{F}}\ln\frac{[\text{Ox}]_{x=0}}{[\text{Red}]_{x=0}}$ (nernstian system), thus $E = E_{1/2} + \frac{RT}{n\mathcal{F}}\ln\frac{I - I_{\lim_{\text{cat}}}}{I_{\lim_{\text{an}}} - I}$

with: $E_{1/2} = E^\circ + \frac{RT}{n\mathcal{F}}\ln\frac{m_{\text{Red}}}{m_{\text{Ox}}}$ and $I_{\lim} = -\frac{\nu_e}{\nu_i}\mathcal{F}S\,m_i\,C_i^*$ (i consumed species)

WHAT NEEDS TO BE KNOWN	RESPONSE ELEMENTS
The ***TAFEL*** plot of the steady-state current-potential curve of a ***slow couple***	**4.3.3**  with: $f = \frac{\mathscr{F}}{RT} = 38.9\ V^{-1}$ at 25 °C
Analytical expression of the steady-state current-potential curve of a ***slow couple*** with an E mechanism in the ***BUTLER-VOLMER zone***	**4.3.3** $I = n\mathscr{F} S k^\circ \left(e^{+\alpha\xi}[Red]^* - e^{-(1-\alpha)\xi}[Ox]^* \right)$ If Ox and Red are present: $I = S\, j_0 \left(e^{+\alpha n f \eta} - e^{-(1-\alpha) n f \eta} \right)$ with: $j_0 = n\mathscr{F} k^\circ ([Red]^*)^{(1-\alpha)} ([Ox]^*)^{\alpha}$
Characteristics of the steady-state current-potential curve of a ***slow couple*** in the ***irreversible zone***	**4.3.3** Half-wave potential in oxidation: $E_{1/2_{an}} = E^\circ - \frac{1}{\alpha} \frac{RT}{n\mathscr{F}} \ln \frac{k^\circ}{m_{Red}}$ Half-wave potential in reduction: $E_{1/2_{cat}} = E^\circ + \frac{1}{1-\alpha} \frac{RT}{n\mathscr{F}} \ln \frac{k^\circ}{m_{Ox}}$
Analytical expression of the steady-state current-potential curve of a couple with an E mechanism in a ***general case***	**4.3.3** $I = n\mathscr{F} S k^\circ \left(e^{+\alpha\xi}[Red]_{x=0} - e^{-(1-\alpha)\xi}[Ox]_{x=0} \right)$ or else: $\frac{1}{I} = \underbrace{\frac{1}{I_d}}_{\text{mass transport control}} + \underbrace{\frac{1}{I_{ct}}}_{\text{charge transfer control}}$

ANSWERS

1 - BASIC NOTIONS

1.2.1 1 - An anion is always negatively charged ✓ **true** false

1.2.1 2 - An oxidant is always a cation true ✓ **false**

1.2.1 **1.2.2** 3 - In the following half-reaction:

$$Co + 4\,Cl^- \longrightarrow CoCl_4^{2-} + 2\,e^-$$

indicate:

- the redox couple involved **$CoCl_4^{2-}/Co$**
- the oxidized species of the couple **$CoCl_4^{2-}$**
- the (algebraic) charge number of the oxidant **−2**
- the (algebraic) stoichiometric number of the reducing agent **−1**
- the element undergoing oxidation **Co**
- the oxidation number of the oxidized element **+II**
- the direction of the reaction ✓ **oxidation** reduction

1.2.1 **1.3.3** 4 - An anion can be reduced at the cathode ✓ **true** false

1.2.2 5 - What is the usual oxidation number of oxygen in a compound? **−II**

Among the following compounds, circle where oxygen features:

- at its usual oxidation number

H_2O **FeO** H_2O_2 **OH^-** **ClO_4^-** F_2O **CO_2** **CO**

- at a higher oxidation number

H_2O FeO **H_2O_2** OH^- ClO_4^- **F_2O** CO_2 CO

1.2.2 6 - What is the oxidation number of oxygen in O_3?

−III −I **0** +I +III

1.2.3 7 - Write the redox half-reaction of the SiO_2/Si couple in an acidic medium

$$\mathbf{Si + 2\,H_2O \rightleftharpoons SiO_2 + 4\,H^+ + 4\,e^-}$$

1.3.2 8 - An electrolyte is:

- an ionically conducting medium ✓ **true** false
- a vessel used for performing electrolysis true ✓ **false**
- a compound that dissolves in a solvent giving rise to ions ✓ **true** false
- a man performing electrolysis true ✓ **false**
- an electrocuted person true ✓ **false**

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

1.3.2 9 - Molten salts are media with mainly electronic conduction — true ✓ **false**

1.3.2 10 - Semiconductors are media with an electronic conduction type — ✓ **true** false

1.3.2 11 - An electrolyte can exist in a ..... state:
- solid — ✓ **true** false
- liquid — ✓ **true** false
- gas — true ✓ **false**

1.3.3 12 - The usual order of magnitude for the thickness of a metal | aqueous electrolytic solution interfacial zone is a few micrometres — true ✓ **false**

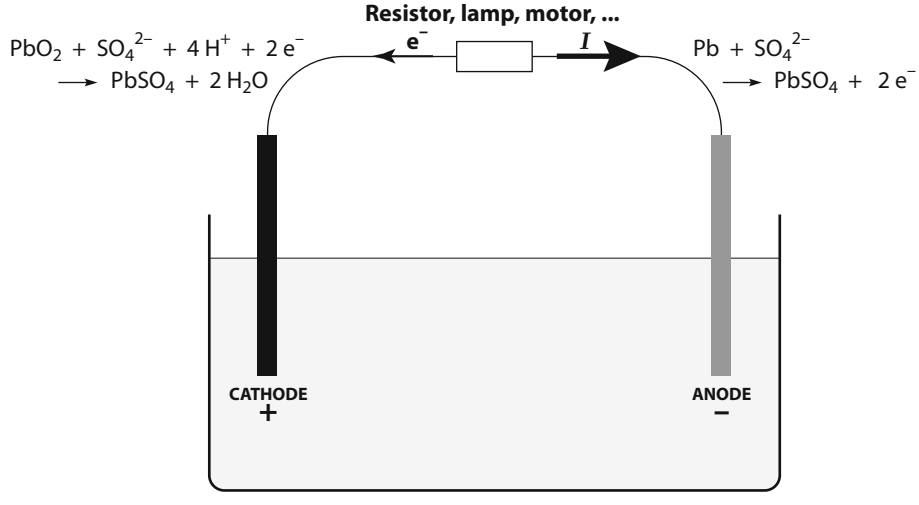
1.3.3 **1.4.4** **1.5.1** 13 - In electrochemistry, the cathode:
- is always the negative electrode of the system — true ✓ **false**
- always has a negative potential *vs* SHE — true ✓ **false**
- is always a reduction site — ✓ **true** false

1.4.1 14 - An electrolysis process is carried out between an electrode with a surface of 1 m^2 where the current density is equal to 1 mA cm^{-2} and an electrode whose active surface is a 10 cm × 10 cm square. The absolute value of the current density at this second electrode is

10^{-3} A m^{-2} 1 A m^{-2} **10^3 A m^{-2}**

1.4.3 15 - Considering the electrode reactions given below, complete the following diagram, by specifying:
- the positions of the anode and the cathode
- the direction of the current (or of the current density)
- the type of the external circuit component

(indicate your answers by replacing the question marks on the diagram)



1.4.1 **1.6.2** 16 - In a 3-electrode setup, these electrodes are called:

- **working electrode**
- **counter-electrode** or **auxiliary electrode**
- **reference electrode**

What is the name of the electronic device generally used in the lab in this case? **potentiostat**

1.5.1 17 - In electrochemistry, an electrode playing a specific role is the SHE.

- What is this specific role? **a system setting the origin of the potentials**
- What do the initials stand for? **Standard Hydrogen Electrode**
- What is the redox couple involved? **H^+/H_2**
- A potential difference exists between SHE and NHE ✓ **true** false

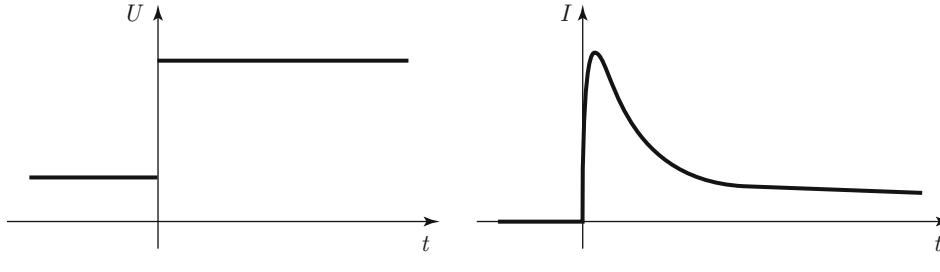
1.5.1 18 - Cite two types of reference electrodes of experimental use, and specify the redox couple involved.

- **SCE : Hg_2Cl_2/Hg**
- **silver chloride electrode: AgCl/Ag**

1.5.1 19 - A silver wire coated with silver chloride is dipped into an aqueous solution containing copper nitrate. This electrode can be used as reference electrode for measuring potentials that can be spotted in the potential scale true ✓ **false**

1.5.2 20 - When a system, not equilibrium at open circuit, is crossed by a current, then one must exclusively use the term ✓ **polarisation** overpotential

1.6.5 21 - Complete the diagram by showing the appropriate shape of the curves that would indicate the variations of the voltage and the current as a function of time, in a simple chronoamperometry experiment.



2 - SIMPLIFIED DESCRIPTION OF ELECTROCHEMICAL SYSTEMS

2.2.1 1 - The three mass transport processes are:
- **diffusion**
- **migration**
- **convection**

2.2.1 2 - One studies an interface between cobalt (metal) and an Na^+Cl^- solution in acetonitrile (an organic solvent) where the following reaction occurs:

$$Co + 4\,Cl^- \longrightarrow CoCl_4^{2-} + 2\,e^-$$

- The interface is reactive ✓ **true** false
- By convention the current sign is positive ✓ **true** false

2.2.2 3 - FARADAY's law expresses, for a redox reaction, the amount of substance transformed as a function of the amount of electric charge which crosses the interface in question. The coefficient of proportionality at the numerator involves:
- the temperature true ✓ **false**
- the FARADAY constant true ✓ **false**
- the number of electrons true ✓ **false**
- the stoichiometric number of the species in question ✓ **true** false

2.2.2 4 - In an industrial aluminium production plant, the main cathodic reaction involves the Al(III)/Al couple with a faradic yield of 90%. The amount of aluminium produced per hour in an electrolysis cell working with a current of 300 000 A is:

10^3 mol **3.4×10^3 mol** 3.6×10^3 mol 10^4 mol 3.4×10^6 mol

2.2.3 5 - The overall polarisation of an electrochemical chain can be split into different terms. In a system with no ionic junction, what do you call the term which adds itself to the two interfacial polarisations so as to gain the final overall polarisation value in the electrochemical chain? **the ohmic drop**

2.2.4 6 - The concentration of a solution containing a species with a concentration of 0.1 mol L^{-1} is also equal to

100 mol m^{-3} 10^{-4} mol m^{-3} 100 mol cm^{-3} **10^{-4} mol cm^{-3}**

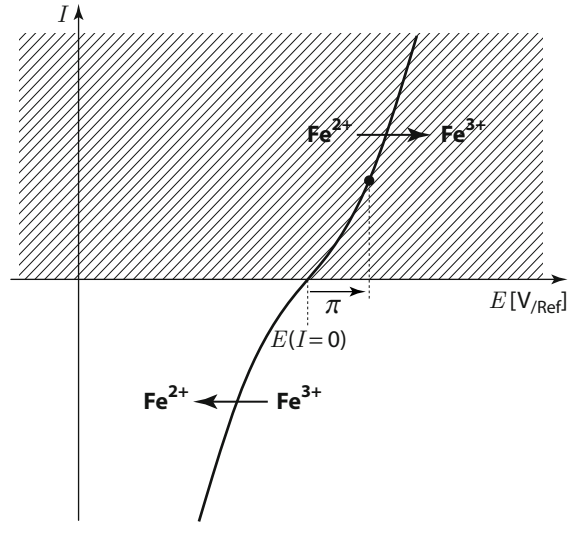
2.2.4 7 - Assuming that the molar conductivity of Cu^{2+} ions in aqueous solution is a constant equal to 10 mS m^2 mol^{-1}, then the conductivity value of these same ions in a solution with a concentration of 0.1 mol L^{-1} is:

1 S cm^{-1} **10^{-2} S cm^{-1}** **1 S m^{-1}** 10 S m^{-1}

2.2.4 8 - Adding a supporting electrolyte to an electrochemical system causes, for the electroactive ions, the decrease in:
- their transport numbers ✓ **true** false
- their ionic conductivities true ✓ **false**

2.3.1 9 - In the following diagram:

- hatch the half-plane corresponding to an anodic operating mode
- indicate the half-reactions occurring in each half-plane with the usual writing conventions, taking the example of the Fe^{3+}/Fe^{2+} couple



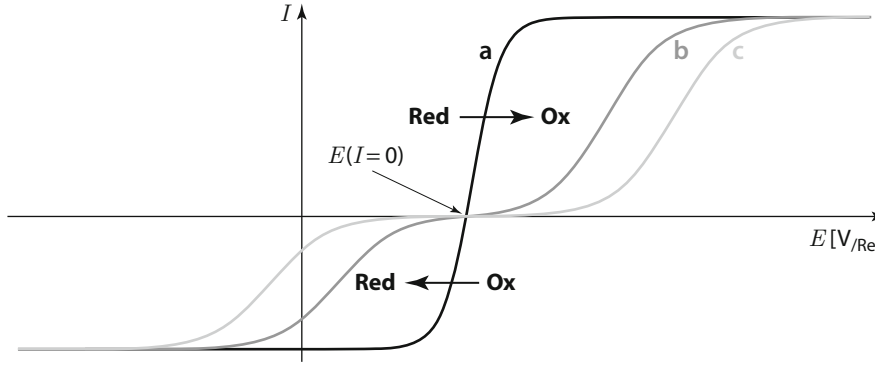
- what does the black arrow represent for the working point which is identified by a black dot?

  The anodic polarisation (or, in the example here, overpotential) of the electrode considered

2.3.1 10 - Except in very specific cases, one can predict the signs for each of the two interfacial polarisations in a given system. Therefore, in most cases, one can say that:

- the polarisation of the positive electrode is positive — true ✓ **false**
- the polarisation of the anode is positive — ✓ **true** false

2.3.3 11 - On the following diagram, draw the shape of the steady-state current-potential curves of three systems with the same open-circuit potential and the same diffusion limiting currents: a fast system (**a**), a slow system (**b**) and a very slow system (**c**).

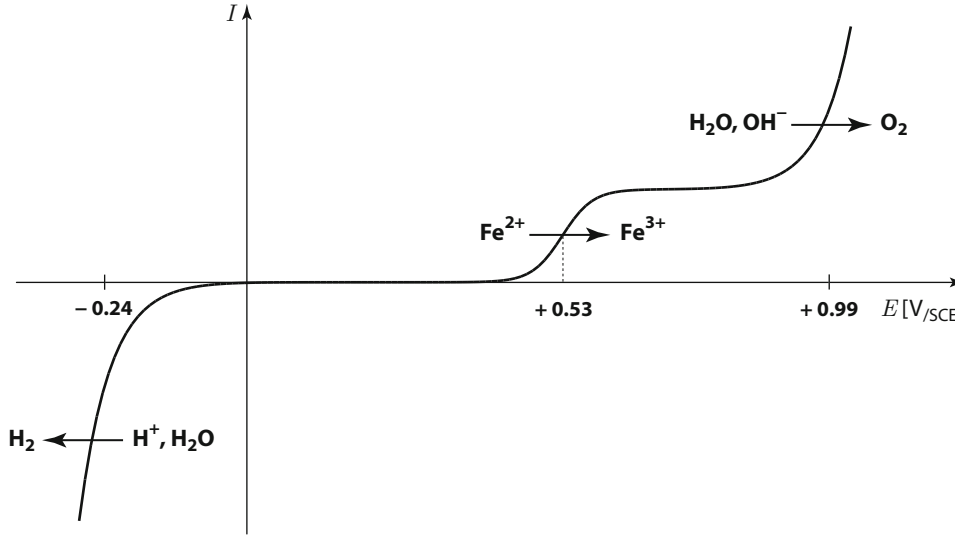


2.3 12 - On the following diagram, plot the steady-state current-potential curve of a system containing an inert working electrode dipped in a deaerated acidic aqueous solution (pH = 0), with no Fe^{3+} ions and an amount of Fe^{2+} ions befitting the existence of a limiting current. The reference electrode is a saturated calomel electrode. It will be assumed that the electrochemical window is determined by the fast half-reactions of water.

Indicate in the diagram the relevant numerical values of the potentials as well as the half-reactions involved.

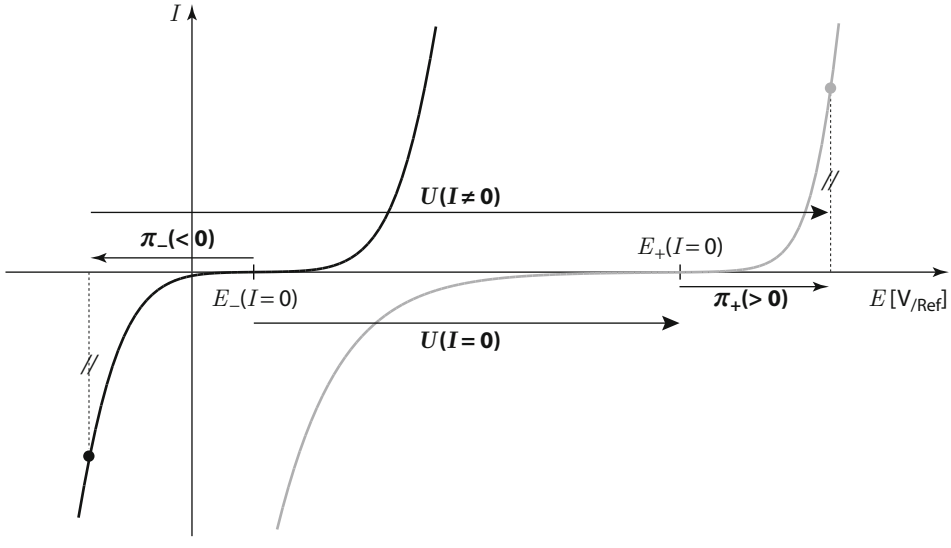
E (SCE) = + 0.24 $V_{/SHE}$ $\quad E°_{Fe^{3+}/Fe^{2+}}$ = + 0.77 $V_{/SHE}$

$E°_{H^+/H_2}$ = 0 $V_{/SHE}$ (at pH = 0) $\quad E°_{O_2/H_2O}$ = + 1.23 $V_{/SHE}$ (at pH = 0)



2.4.2 13 - Using arrows, complete the following diagram (which represents the steady-state current-potential curves of the two electrodes in a given electrochemical cell) to indicate the following:

- the system's open-circuit voltage, $U(I=0)$
- the polarisation π_- of the negative electrode at the working point indicated by a black dot
- the polarisation π_+ of the positive electrode at the corresponding working point of this electrode (indicate this second dot in the diagram)
- the corresponding working voltage, $U(I\neq 0)$



- the operating mode represented in the diagram corresponds to electrolysis ✓ **true** false

3 - THERMODYNAMIC FEATURES

3.1 1 - In an electrochemical system:
- at thermodynamic equilibrium, the current is always zero — ✓ **true** false
- if the current is zero, then the system is always in thermodynamic equilibrium — true ✓ **false**

3.1.2 2 - For the following species in their standard state:
- $\mu^\circ_{Cu} = 0$ J mol^{-1} — ✓ **true** false
- $\mu^\circ_{H^+} = 0$ J mol^{-1} — ✓ **true** false
- $\mu^\circ_{Cu^{2+}} = 0$ J mol^{-1} — true ✓ **false**
- $\mu^\circ_{H_2} = 0$ J mol^{-1} — ✓ **true** false

3.2.1 3 - Strictly speaking, if you have an aqueous solution containing ions, it is possible, for each ion individually, to measure:
- its concentration — ✓ **true** false
- its activity — true ✓ **false**

3.2.1 4 - What is the ionic strength (including the appropriate unit) of the following aqueous solutions?
- containing NaCl with a concentration of 0.1 mol L^{-1} — **0.1 mol L^{-1}**
- containing $Cu(NO_3)_2$ with a concentration of 0.1 mol L^{-1} — **0.3 mol L^{-1}**

3.2.1 5 - Based on the simplified DEBYE-HÜCKEL model, if you take the mean activity coefficient of a solute in a solution containing only NaCl, and compare it to the mean activity coefficient in a solution with the same ionic strength containing only $Cu(NO_3)_2$ then the former coefficient is

larger equal smaller

3.2.2 6 - For a metal, it is possible to measure:
- the electrochemical potential of free electrons — ✓ **true** false
- the chemical potential of free electrons — true ✓ **false**
- the GALVANI potential — true ✓ **false**
- the VOLTA potential — ✓ **true** false

3.3.3 **3.3.4** 7 - On both sides of a single-exchange junction (i.e., with interfacial reaction involving only one species) between two media in which the species studied share the same standard chemical potential, identical concentrations of exchangeable species are always seen in thermodynamic equilibrium, when the latter is:
- an ion — true ✓ **false**
- a neutral species — ✓ **true** false

3.3.4 **3.4.1** 8 - The thermodynamic equilibrium of an interface involving the Cu^{2+}/Cu couple can be illustrated in the following equation: $\varphi_{metal} - \varphi_{electrolyte} = Cst + \frac{RT}{2\mathcal{F}} \ln \frac{a_{Cu^{2+}}}{a_{Cu}}$

whereby the constant is the standard potential of the couple in question, relative to SHE — true ✓ **false**

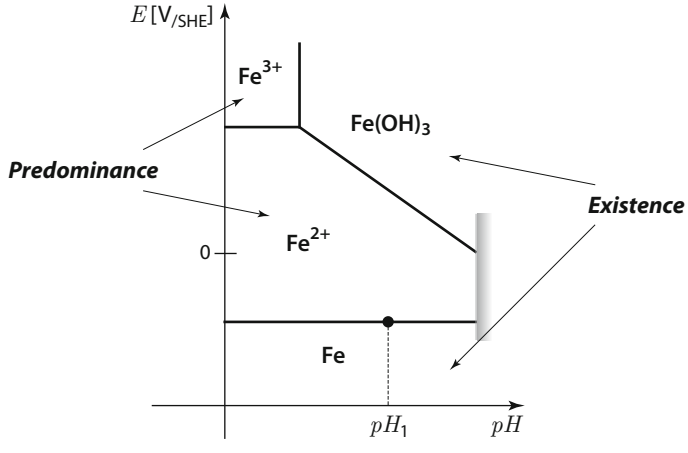
3.4.1 9 - Fill in the missing numbers (with the appropriate sign) in the equations below, which characterize the thermodynamic equilibrium of the following electrochemical chain: Cu' | Pt, H_2 | aqueous solution containing H_2SO_4 and $CuSO_4$ | Cu

Cu is chosen as the working electrode and Cu' as the counter-electrode ($U = \varphi_{Cu} - \varphi_{Cu'}$). The sign for the GIBBS energy of reaction corresponds to the overall reaction, written as: $Cu^{2+} + H_2 \rightleftharpoons Cu + 2\,H^+$

$$\Delta_r G = \mathbf{-2}\,\mathcal{F}U = \mathbf{+1}\,\mu_{Cu}\ \mathbf{+2}\,\mu_{H^+}\ \mathbf{-1}\,\mu_{Cu^{2+}}\ \mathbf{-1}\,\mu_{H_2}$$

3.4.1 10 - Complete the simplified POURBAIX diagram for iron below. It has been plotted for an overall iron element concentration equal to C_0, ($[Fe^{3+}] + [Fe^{2+}] = C_0$) in aqueous solution. You must indicate the following:

- the areas of either thermodynamic stability or predominance for the following species: Fe, $Fe(OH)_3$, Fe^{2+}, Fe^{3+}
- the point symbolizing the potential (*vs* SHE) of a piece of iron immersed in a solution of $pH = pH_1$, containing Fe^{2+} ions with the concentration C_0



In addition:

- where would you locate the point symbolizing the potential (*vs* SHE) of a piece of iron that is immersed in a solution of $pH = pH_1$ containing Fe^{2+} ions with a concentration of $C_0/100$, in relation to the previous point?

on the right | in the same place | above | **below**

- what reaction occurs in the previous system if a 0 $V_{/SHE}$ potential is imposed at this metal interface?

$$\mathbf{Fe \longrightarrow Fe^{2+} + 2\,e^-}$$

- a piece of iron is stable in a solution containing Fe^{3+} ions with the concentration C_0 — true ✓ **false**

3.4.2 11 - If a reference electrode Ag, AgCl | KCl 1 mol L^{-1} | has been stored with its tip immersed in distilled water, then calibration would show that its potential after storage

has increased | has not changed | has diminished

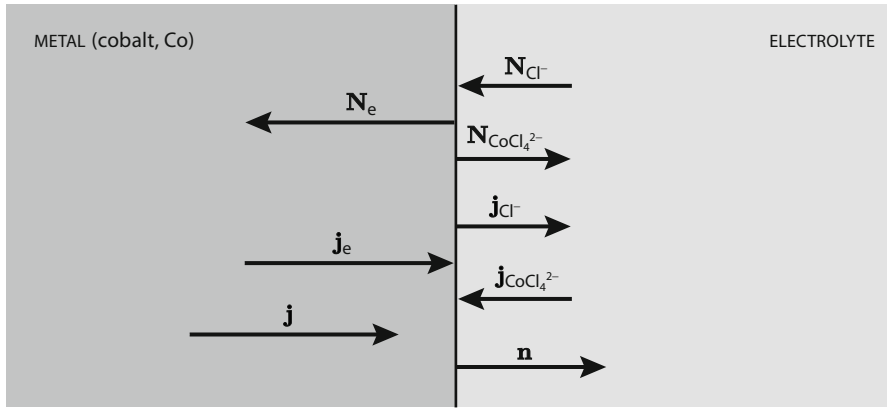
4 - CURRENT FLOW: A NON-EQUILIBRIUM PROCESS

4.1.1 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



4.1.3 2 - When a species is adsorbed at the interface, the interfacial flux and the production rate at steady state are both zero ✓ **true** false

4.2.2 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

4.2.2 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?

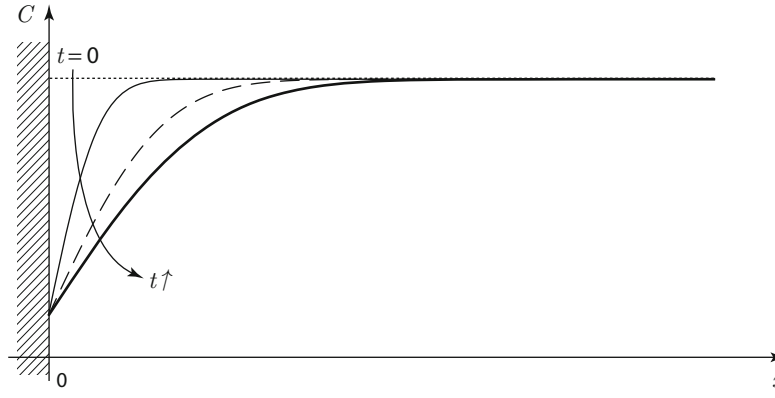
$1\ S\ m^{-1} = 10^{-2}\ S\ cm^{-1}$

4.2.2 5 - What is the order of magnitude and the unit of the diffusion coefficient of an ion in an aqueous solution at room temperature?

$10^{-9}\ m^2\ s^{-1} = 10^{-5}\ cm^2\ s^{-1}$

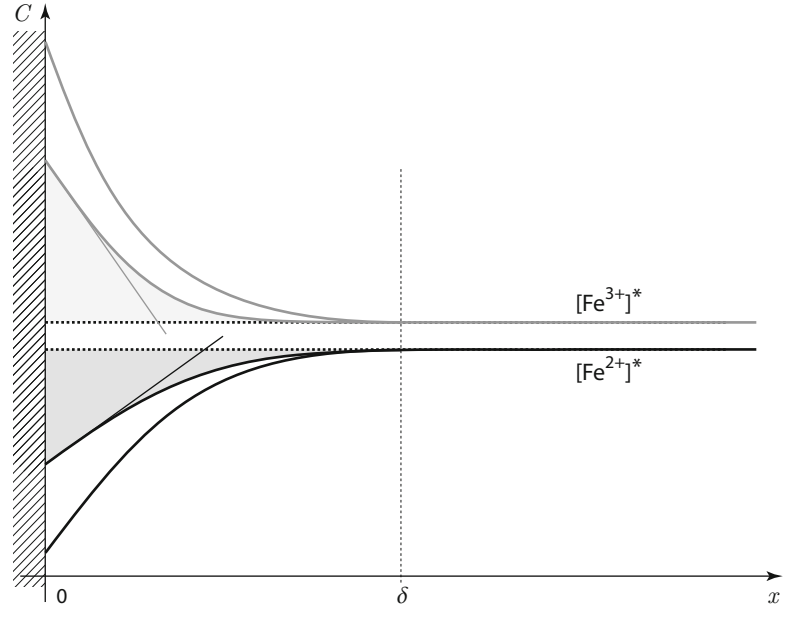
4.3.1 6 - The diagram below shows the changes over time in the concentration profile for an electroactive species of a fast redox couple in an experiment:

- at steady sate true ✓ **false**
- of voltammetry true ✓ **false**
- of chronoamperometry ✓ **true** false
- of chronopotentiometry true ✓ **false**



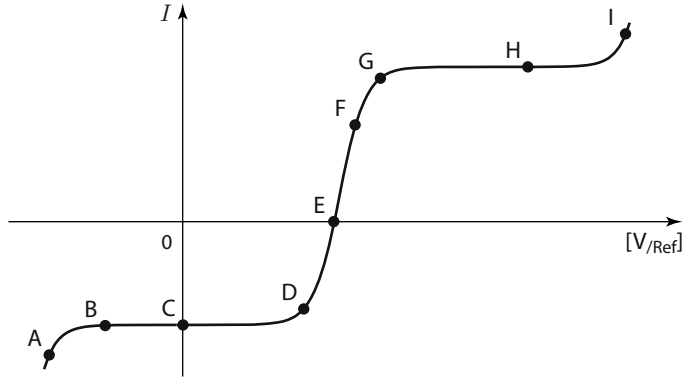
4.3.1 7 - The following diagram shows the concentration profiles for a solution containing Fe^{3+} (grey) and Fe^{2+} (black) ions. The dotted lines represent the initial instant, and the solid lines represent instant t. These profiles result from current circulation through an interface between a platinum 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? **diffusion layer thickness**
- 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.



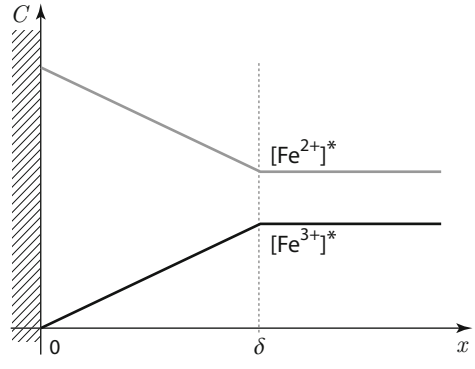
4.3.1 8 - Close to a metal | electrolyte electrochemical interface, one defines the double layer and the diffusion layer. The diffusion layer is usually much thinner than the double layer. true ✓ **false**

4.3.3 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



4.3.3 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

BIBLIOGRAPHY

IN FRENCH

- *Atlas d'équilibres électrochimiques*. M. POURBAIX. Gauthier-Villars (Paris) 1963

  One of the key reference books in the field of electrochemical thermodynamics, covering a wide number of inorganic systems in aqueous solution: standard chemical potentials, redox potentials and *E/pH* diagrams. It also includes data on the kinetic parameters involved for reducing protons in aqueous medium. Particularly useful for understanding corrosion in aqueous medium.

- *Electrochimie. Principes, méthodes et applications*. A.J. BARD, L.R. FAULKNER. Traduction : Masson (Paris) 1983

  Refer to the comments shown for the English edition.

- *Usuel de chimie générale et minérale*. M. BERNARD, F. BUSNOT. Dunod, Bordas (Paris) 1984

  A collection of numerical data covering a relatively large number of quantities used in physical chemistry and thermodynamics, mainly for inorganic species: for example acidity constants (pK_a), including those found in non-aqueous solvents, solubility constants and complexation constants. Regarding electrochemistry, you can find the redox potentials for numerous couples, the molar conductivities for the main ions in aqueous solution, the activity coefficients for electrolytes, as well as a small number of kinetic features (exchange current density, and transfer coefficient, etc.).

- *L'oxydoréduction*. J. SARRAZIN, M. VERDAGUER. Ellipses (Paris) 1991

  By describing a set of simple experiments in accessible terms, this work brings together the fundamental concepts linked to redox reactions, mainly in an aqueous phase, focusing on various parameters (*pH*, complexation and precipitation phenomena, etc.). Centring on the fields of thermodynamics and kinetics, it lays out the key concepts of electrochemistry. This book is geared towards students at beginner level, but also to more experienced scientists, such as teachers and lecturers.

- *Electrochimie analytique et réactions en solution* (tomes 1 et 2). B. TREMILLON. Masson (Paris) 1993

  A didactical work written for researchers, as well as engineers working in chemistry and physical chemistry, that spans a wide spectrum of research fields. Numerous exercises and theoretical problems to solve.

  Volume 1: Case analyses involving organic, aqueous solutions, with dissolved salts.

  Volume 2: Theoretical aspects of electrochemistry, applications, and methods used in electrochemical analysis. It includes additional information on insertion materials, solid electrolytes, semiconducting electrodes, photoelectrochemistry and the thermoelectric effect.

- *Electrochimie des solides*. C. DÉPORTES, M. DUCLOT, P. FABRY, J. FOULETIER, A. HAMMOU, M. KLEITZ, E. SIEBERT, J.L. SOUQUET. Presses Universitaires de Grenoble (Grenoble) 1994

  Aimed at master's degree or PhD students as well as researchers and specialist engineers, this work focuses on electrochemical systems using electrolytes in solid phases (ionic crystals, ceramics, different types of glass and polymers). The fundamental concepts of electrochemistry are laid out (the thermodynamics of point defects and amorphous phases, transport mechanisms, mixed conduction, and gas electrode reactions) alongside the specific research methods used. Several applications are also described.

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

- *Cinétique électrochimique*. C. MONTELLA, J.P. DIARD, B. LE GORREC. Hermann (Paris) 1996

  Lays out the fundamental concepts of electrochemistry, but with a particular focus on the theoretical aspects involved in the kinetics of electrode reactions. Covers various methods, yet with strong emphasis placed on impedance spectroscopy as well as voltamperometric methods. The main systems examined include redox reactions, electrosorption, insertion and the VOLMER-HEYROVSKY mechanism. For master's degree level, engineering students and researchers. In 2000 and 2005 the same authors and publishing house produced two books compiling exercises on electrochemical kinetics (steady state and insertion method).

- *Chimie physique expérimentale*. B. FOSSET, C. LEFROU, A. MASSON, C. MINGOTAUD. Hermann (Paris) 2000 (2nd édition en 2006)

  Targeted mainly at students preparing for competitive teaching french exams it combines both descriptions and commentaries for 110 physical chemistry experiments, with at least 40 of these linked to the field of electrochemistry. Moreover, the first part provides descriptions for different techniques, in particular related to electrochemistry.

- *Electrochimie physique et analytique*. H.H. GIRAULT. Presses polytechniques et universitaires romandes (Lausanne) 2001 (2nd édition en 2008)

  Electrochemistry as a subject is approached using the fundamental concepts of physical chemistry and physics, and the theoretical aspects are dealt with from a strictly mathematical point of view. Focusing on aqueous media, this book describes the particular phenomena involved at the electrolyte and interfaces. Various research methods are listed (amperometry, impedancemetry, and voltamperometry). Specifically targeted at students in higher education, and even stretching to researchers.

- *L'indispensable en électrochimie*. V. BERTAGNA, M. CHEMLA. Bréal (Rosny-sous-Bois) 2001

  The fundamental concepts of electrochemistry are collected together in 24 technical tables, divided by theme, featuring most of the key formulas (100 pages), with examples given for aqueous solutions. Specifically aimed at students on foundation courses, and first-year university students (including French 'IUT' students carrying out a two-year technology BA), this book can equally be used as a data form or glossary.

- *Electrochimie. Des concepts aux applications*. F. MIOMANDRE, S. SADKI, P. AUDEBERT, R. MEALLET-RENAULT. Dunod (Paris) 2005

  An overview of the different concepts involved in electrochemistry, spanning from basic theory (thermodynamics, transport and electrode kinetics, etc.) to the main applications (batteries corrosion, electrosynthesis and sensors). In addition, it covers the research methods used in electrochemistry, as well as giving an insight into organic electrochemistry. For master's degree level and engineering schools. A dozen practical experiments are described in brief, with a few problems to solve (corrections provided on the website).

- *De l'oxydoréduction à l'électrochimie*. Y. VERCHIER, F. LEMAÎTRE. Ellipses (Paris) 2006

  For first-year university students. This book bases itself initially on redox reactions as an introduction, covering the amounts and *E/pH* diagrams, before moving on to present the basics of electrochemistry (the thermodynamics and kinetics of electrode reactions), adapting its approach to the target reader. It includes a large number of basic exercises.

- *Capteurs électrochimiques. Fonctionnement, utilisation, conception. Cours et exercices corrigés*. P. FABRY, C. GONDRAN. Ellipses (Paris) 2008

  Focused on the electrochemical applications used to design sensors for ionic, molecular or gas species. Targeted at BA level and master's degree students, as well as students at engineering school, it is also adapted to self-training. This book provides a recap of the basic concepts, before then applying them to different types of transduction (amperometric, conductimetric and potentiometric sensors). There is also a selection of problems to solve with the corrections provided.

- Articles quoted from the monthly chemical review '*Actualité Chimique*''

  nov-déc 1989 : 143-147, J.F. FAUVARQUE.

  janv-fév 1992 : 1-148, numéro spécial *L'électrochimie*

  janvier 2003 : 31-41, D. DEVILLIERS, E. MAHÉ.

  février-mars 2009 : 9-119, numéro coordonné par F. BEDIOUI.

- Articles quoted from the French engineering document source site '*Techniques de l'Ingénieur*'

IN ENGLISH

- *Instrumental methods in electrochemistry*. Southampton Electrochemistry Group. Ellis Horwood Limited (Chichester) 1985

  For master's degree and PhD level, this work describes the main methods used in the field of electrochemistry (steady-state and non-steady-state) and applies them to various concepts, including kinetic models for electronic transfer, double layer and electrocatalysis. There are particular chapters focused on electro-crystallization, optical and spectroscopic methods as well as designing an electrochemical experiment, covering the suitable instruments required.

- *Industrial electrochemistry*. D. PLETCHER, F.C. WALSH. Chapman and Hall (London) 2nd edition 1990

  For master's degree level and engineers. Basic concepts, electrochemical engineering, with an exhaustive study of industrial applications, including surface treatment, corrosion and sensors.

- *Electrochemical systems*. J.S. NEWMAN. Prentice Hall Inc. (Englewood Cliffs, New Jersey) 2nd edition 1991

  This work presents electrochemistry from a macroscopic viewpoint, and is divided into 4 parts: the thermodynamics of electrochemical cells, electrochemical kinetics, transport processes, and finally current distribution and mass transfer in electrochemical systems (including porous electrodes and semiconducting electrodes). Problems to solve are presented at the end of each chapter, without the answers.

- *Principles of electrochemistry*. J. KORYTA, J. DVORAK & L. KAVAN. John Wiley & Sons (Chichester) 2nd edition 1993

  For master's degree level in physical chemistry, biology and materials science. Divided into 6 chapters: equilibria in electrolyte solutions, transport, charge transfer, double layer, kinetics (including a concise outline of the different methods used in electrochemical analysis), membrane electrochemistry and bioelectrochemistry.

- *Fundamentals of electrochemical science*. K.B. OLDHAM & J.C. MYLAND. Academic Press Inc. (San Diego) 1994

  For master's degree and PhD level. This book offers a highly mathematical approach, and is divided into 11 chapters, comprising essential reminders on the key basics in physics and chemistry, as well as in the thermodynamics of ionic solutions. It touches on the full list of notions and methods related to modern electrochemistry. Problems to solve are presented at the end of each chapter, without the answers.

- *Electrochemistry, principles, methods and applications*. C.M.A. BRETT, A.M. OLIVEIRA BRETT. Oxford University Press (Oxford) 1994

  Divided into three parts, spanning from BA level to master's degree level. Chapters 2 to 6: thermodynamics and electrochemical kinetics. Chapters 7 to 12: experimental strategy and methods used in electrochemical analysis. Chapters 13 to 17: applications (sensors and industrial electrochemistry).

- *Principles and applications of electrochemistry*. D.R. CROW.
  Blakie Academic & Professional, Chapman & Hall (London) 1994

  Master's degree level. Focusing on the aspect of physical chemistry related to solutions, equilibria, ion transport, double layer, NERNST, kinetics, applications, industrial applications and sensors. Problems to solve are presented at the end of each chapter, with the corrections provided.

- *Electrochemical process engineering. A guide to the design of electrolytic plant*.
  F. GOODRIDGE, K. SCOTT. Plenum Press (New York) 1995

  A work targeted at chemistry and engineering students at master's degree and PhD level. Covering concepts related to electrochemical engineering, kinetics, two-phase flow electrocatalysis and reactor modeling.

- *Electrochemical methods. Fundamentals and applications*. A.J. BARD, L.R. FAULKNER.
  John Wiley & Sons (New York) 2nd edition 2001

  For master's degree and PhD level. Presenting the scientific concepts of electrochemistry, methods used in electrochemical analysis, instruments, techniques used in physics for analysing interfaces and photoelectrochemistry. Problems to solve are presented at the end of each chapter, without the answers.

- *Modern electrochemistry*. J.O'M. BOCKRIS *et al.*
  Plenum Press (New York) 2nd edition

  An introduction to modern electrochemistry: each notion is based on a unique theory aimed at opening out on to a deeper exploration of the subject. Mathematical elements are provided in the appendix. For master's degree and PhD level.

  Vol. 1 : Ionics. J.O'M. BOCKRIS, A.K.N. REDDY, 1998.
  A historical presentation followed by a description of the key notions of physical chemistry which are essential for understanding the properties of electrolytes (ion-solvent and ion-ion interactions, ion transport and ionic liquids).

  Vol. 2A : Fundamentals of electrodics. J.O'M. BOCKRIS, A.K.N. REDDY, M. CAMBOA-ALDECO, 2000
  Description of electrified interfaces, electrochemical kinetics, transient analysis methods and quantum mechanics applied to electrochemical kinetics.

  Vol. 2B : Electrodics in chemistry, engineering, biology and environmental science. J.O'M. BOCKRIS, A.K.N. REDDY, 2000
  Fundamental aspects of photoelectrochemistry, electrochemical energy conversion and storage, bioelectrochemistry and electrochemistry related to the environment.

- *Fundamentals of electrochemistry*. V.S. BAGOTSKY.
  John Wiley & Sons, Wiley-Interscience (Hoboken, New Jersey) 2nd edition 2006

  The first three parts approach the classic aspects of electrochemistry on a BA/master's degree level. The fourth part touches on cutting-edge developments in the field of modern research (electrochemistry of solids, conducting polymers, physical methods for analysis, electrocatalysis, photoelectrochemistry, bioelectrochemistry, electrokinetics, interfaces between immisicible liquids, numerical simulations and nanoelectrochemistry, etc.)

- *Electrochemistry*. C.H. HAMANN, A. HAMNETT, W. VIELSTICH.
  John Wiley & Sons, Wiley Vch Verlag GmbH (Weinheim) 2nd edition 2007

  A reasonably exhaustive study of the physical chemistry involved in electrolytes and electrochemistry (kinetics and methods of analysis), and the applications, placing particular emphasis on the methods used in physics (spectroscopy and optics) for examining electrochemical interfaces.

KEY SYMBOLS

Symbol	Meaning	Usual unit	Comment
a_i	activity of ion i	dimensionless	see section 3.1.2
$a_\pm$	mean activity of a solute	dimensionless	see section 3.2.1
A	parameter for the DEBYE-HÜCKEL law	$L^{½}$ $mol^{-½}$	≈ 0.5 $L^{½}$ $mol^{-½}$ at 25 °C see section 3.2.1
C_i (or C) or $[i]$	concentration of species i	mol L^{-1}	[1]
$C°$	reference concentration (standard state)	mol L^{-1}	= 1 mol L^{-1} see section 3.1.2
$C*$	bulk concentration (in the zone far from the interface)	mol L^{-1}	
$C_{x=0}$	interfacial concentration ($x = 0$)	mol L^{-1}	see section 4.1.3
$C°_P$	standard molar heat capacity	J K^{-1} mol^{-1}	
D_i (or D)	diffusion coefficient of species i	cm^2 s^{-1}	see section 2.2.1 [2]
D_i^0	diffusion coefficient of species i at infinite dilution	cm^2 s^{-1}	see section 4.2.1
e	electron charge	C	$= -1.6 \times 10^{-19}$ C
E	electrode potential (half-cell)	$V_{/Ref}$	relative to the chosen reference see section 1.5.1
$E°$	standard potential of redox couple	$V_{/Ref}$	
$\mathbf{E}$	electric field	V m^{-1} (modulus)	
f	$f = \frac{\mathscr{F}}{RT}$	V^{-1}	38.9 V^{-1} at 25 °C
$\mathscr{F}$	FARADAY constant	C mol^{-1}	$\approx 96\,500$ C mol^{-1}
G	GIBBS energy	J	
$\tilde{G}$	GIBBS energy in an electrochemical system	J	

[1] Unit conversion for a concentration: $C = y$ *mol* $L^{-1} = y \times 10^3$ *mol* $m^{-3} = y \times 10^{-3}$ *mol* cm^{-3}.

[2] Unit conversion for a diffusion coefficient: $D = y$ cm^2 $s^{-1} = y \times 10^{-4}$ m^2 s^{-1}.

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

H	enthalpy	J	
I	current (intensity)	A	sign convention: see section 1.4.1
I_{lim}	limiting current (diffusion)	A	see section 2.3.2
I_s	ionic strength of a medium	mol L^{-1}	see section 3.1.2
$\mathbf{j}$ (j)	current density (modulus)	A m^{-2} (modulus)	see section 1.3.1 [3]
k	BOLTZMANN constant	J K^{-1}	= 1.38×10^{-23} J K^{-1}
$k°$	standard rate constant of a redox reaction (E mechanism)	cm s^{-1}	[4] see section 4.3.2
K_{eq}	equilibrium constant	dimensionless	
ℓ, L	distance between two points, width	cm	
L_D	DEBYE length	Å	see section 3.3.1 [5]
L_H	thickness of the HELMOLTZ layer	Å	see section 3.3.1
m_i	mass transport rate constant of species i	cm s^{-1}	see section 4.3.2
m_i ($m°$)	molality of species i (standard state)	mol kg^{-1}	see section 3.1.2
M_i (or M)	molar mass of species i	g mol^{-1}	
n	number of electrons exchanged in a redox half-reaction	dimensionless	positive number see section 1.2.1
n_i	amount of substance of species i	mol	
$\mathbf{n}$	vector normal to the surface	dimensionless	
$\mathcal{N}$	AVOGADRO constant	mol^{-1}	= 6.02×10^{23} mol^{-1}
$\mathbf{N}_i$ (N_i)	molar flux density of species i (modulus)	mol m^{-2} s^{-1} (modulus)	see section 4.1.1 [6]
o.n.	oxidation number (or degree)	dimensionless	
P ($P°$)	pressure (standard state)	bar	$P°$ = 1 bar [7]
P_i	partial pressure of species i	bar	
pH	potential of Hydrogen	dimensionless	$pH = -\log a_{H^+}$

[3] Unit conversion for a current density: $j = y$ A $m^{-2} = y\times10^{-4}$ A cm^{-2}.

[4] Unit conversion for a redox rate constant: $k = y$ cm $s^{-1} = y\times10^{-2}$ m s^{-1}.

[5] Unit conversion for a distance: $\ell = y$ Å $= y\times10^{-10}$ m $= y\times10^{-1}$ nm $= y\times10^{-4}$ µm $= y\times10^{-8}$ cm.

[6] Unit conversion for a molar flux density: $N = y$ mol m^{-2} $s^{-1} = y\times10^{-4}$ mol cm^{-2} s^{-1}.

[7] Unit conversion for a pressure: $P = y$ bar $= y\times10^{5}$ Pa $= (y/1.013)$ atm.

pK_i	relative to the equilibrium constant K_i	dimensionless	$pK_i = -\log K_i$
q, Q	electric charge	C	
r_{farad}	faradic yield	dimensionless	see section 2.2.2
R	ideal gas constant	J K^{-1} mol^{-1}	= 8.314 J K^{-1} mol^{-1}
R	resistance	Ω	
S ($S°$)	molar entropy (standard state)	J K^{-1} mol^{-1}	
S	S surface (or section) area	cm^2	[8]
t	time	s	
T	temperature	°C	[9]
t_i	transport number of species i	dimensionless	see section 2.2.4
$\widetilde{t}_i$	electrochemical transport number of species i	dimensionless	see section 4.1.1
u_i	electric mobility of species i	m^2 s^{-1} V^{-1}	see section 4.2.1
$\widetilde{u}_i$	electrochemical mobility of species i	mol m s^{-1} N^{-1}	or mol s kg^{-1} mol m^2 J^{-1} s^{-1} see section 4.2.1
U	potential difference (voltage)	V	
V	electric potential (general sense)	V	
v_r	volume reaction rate per unit volume	mol m^{-3} s^{-1}	see section 4.1.2
v_{S_r}	surface reaction rate per unit area	mol m^{-2} s^{-1}	see section 4.1.3
w_i	local volume production rate of species i	mol m^{-3} s^{-1}	see section 4.1.2
w_{S_i}	local surface production rate of species i	mol m^{-2} s^{-1}	see section 4.1.3
x	spatial coordinate	m	
x_i	molar fraction of species i	dimensionless	
y	insertion rate	dimensionless	see section 2.1.2
z_i	charge number of species i	dimensionless	algebraic number see section 1.2.1

[8] Unit conversion for a surface area: $S = y\ cm^2 = y \times 10^{-4}\ m^2$.

[9] Unit conversion for a temperature: $T = y$ °C = $(y + 273)$ K.

GREEK SYMBOLS

Symbol	Meaning	Usual unit	Comment
α	symmetry factor	dimensionless	see section 4.3.2
δ	thickness (e.g., diffusion layer)	µm	
$\Delta_r H$ ($\Delta_r H°$)	enthalpy of reaction (standard enthalpy of reaction)	J mol^{-1}	
$\Delta_r G$ ($\Delta_r G°$)	GIBBS energy of reaction (standard GIBBS energy of reaction)	J mol^{-1}	
γ_i	activity coefficient of species i	dimensionless	see section 3.1.2
Γ_i	surface concentration of species i	mol m^{-2}	see section 4.1.3
ε	dielectric permittivity of a medium	J^{-1} C^2 m^{-1}	
ε_0	vacuum dielectric permittivity	J^{-1} C^2 m^{-1}	= 8.855 ×10^{-12} J^{-1} C^2 m^{-1}
η	overpotential (or overvoltage) of a cell or an electrode	V	see section 1.5.2
λ_i	molar conductivity of species i	S cm^2 mol^{-1}	see section 2.2.4 [10]
λ_i^0	molar conductivity of species i at infinite dilution	S cm^2 mol^{-1}	see table 4.2, section 4.2.2
Λ	molar conductivity of a solute	S cm^2 mol^{-1}	see section 2.2.4
μ_i ($\mu_i°$)	chemical potential of species i (standard state)	J mol^{-1}	see section 3.1.2
$\widetilde{\mu}_i$	electrochemical potential of species i	J mol^{-1}	see section 3.1.2
ν_i	stoichiometric number of species i in a reaction	dimensionless	algebraic value see section 1.2.1
ξ	dimensionless potential $\xi = \frac{n\mathscr{F}}{RT}(E - E°) = nf(E - E°)$	dimensionless	see section 4.3.2
π	polarisation of a cell or an electrode	V	see section 1.5.2
ρ	electric resistivity of a medium	Ω cm	see section 2.2.4
ρ_{ch}	charge density	C m^{-3}	

[10] Unit conversion for a molar conductivity: $\lambda = y$ S cm^2 mol^{-1} = $y \times 10^{-4}$ S m^2 mol^{-1}.

σ	electric conductivity of a medium	S cm^{-1}	see section 2.2.4[11]
σ_{ch}	surface charge density	C m^{-2}	
τ	time constant	s	
φ	GALVANI potential or internal potential	V	see section 3.1.1
χ	surface electric voltage	V	see section 3.1.1
ψ	VOLTA potential or external potential	V	see section 3.1.1
$\boldsymbol{\omega}_i$ (ω_i)	local velocity of species i (modulus)	m s^{-1} (modulus)	see section 4.1.1

[11] Unit conversion for an electric conductivity: $\sigma = y$ S cm^{-1} = $y \times 10^2$ S m^{-1}.

INDEX

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3,

D

E

F

G

H

I

J

K

L

M

N

O

P

Q

R

S

T

U

V

W

Y

Z

THE AUTHORS

Christine LEFROU
is a graduate of ENS (Ecole Normale Supérieure), the elite French institution of higher education and research, and currently a university lecturer at the PHELMA engineering school (Physics, Applied Physics, Electronics and Materials Science), part of the Grenoble Institute of Technology (INP). She teaches electrochemistry on core education courses, as well as on a wide array of continuing education courses. Her research work to date has mainly focused on applying the concept of modeling material transport to the field of electrochemistry (batteries and electroanalysis).

Pierre FABRY
is a university-trained physicist, who was formerly a professor at Grenoble University (Université Joseph Fourier). He has taught electrochemistry and the structure of materials at university level, (undergraduate and master's degrees) as well as at engineering schools, and on adult training courses. His research work has focused specifically on the subject of electrochemical solids for high-temperature energy storage systems and electrochemical sensors for biomedical and environmental applications.

Jean-Claude POIGNET
was formerly a Professor of electrochemistry at the Grenoble Institute of Technology (INP). After completing a thesis on the structure and transport properties of molten salts, he then focused his research career on studying low-temperature ionic liquids, before turning his attention towards electrochemistry of molten salts between 450 and 1000°C: electrode and electrolyte materials for thermal batteries, Li or Na solutions dissolved in molten LiCl or NaCl, the cathodic separation of lanthanides and actinides and the electrosynthesis of Na, Al, Nb and Pu.