3 - THERMODYNAMIC FEATURES

A state of equilibrium can be defined in any system where the intensive variables (pressure, temperature, concentration, etc.) remain constant over time. In this chapter we will describe the state of equilibrium in an electrochemical system and give examples of conditions in which equilibrium can be observed [1]. In fact, the state of equilibrium is not always necessarily observed, since it cannot always be reached on the time scale of the experiment.

When a system is in equilibrium there is no movement of species on the macroscopic scale, resulting in a zero current. However, when the current is zero this does not necessarily mean that the system is in equilibrium, since a compensation of charge fluxes of different carriers can occur. This is the case when the interfacial open-circuit potential is a mixed potential [2] or for a liquid junction, a salt bridge, in an electrochemical system at open circuit [3].

3.1 - CONCEPTS OF POTENTIAL

The term potential is used frequently in different fields of physics and chemistry. It always refers to the energy per unit quantity related to the matter in question (number, mass, charge, etc.). Here we are particularly interested in electric and chemical energies. Therefore we will speak on the one hand in terms of electric potential: by using the quantity of charge (in C) as a quantity parameter, the electric potential is expressed in volts ($V = J\,C^{-1}$). On the other hand, by using the amount of substance (in mol) as a quantity parameter, the chemical potential is expressed in $J\,mol^{-1}$.

In a material these potentials are macroscopic, and represent an average across a large volume compared to atomic sizes (higher than a few tens of nm^3).

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[1] As presented in section 2.1, an electrochemical system is defined as being isolated without any possibility of exchanging energy or matter with the surroundings. To make a different comparison to that in section 2.1, imagine an apple on a table. One can say it is in equilibrium, yet if the table is removed, then its equilibrium state is its new position on the ground. In the same way, all isolated electrochemical systems have an equilibrium state, yet this state is often very different after a current has been allowed to flow through an electric load, in other words once the system has functioned as a power source.

[2] Section 2.4.1 outlines this type of behaviour, which can be seen at an interface that is at open circuit however not in equilibrium.

[3] As described in qualitative terms in section 2.1.1, when there is a salt bridge or a liquid junction through a porous membrane, it takes an extremely long time to reach a state of equilibrium where a perfect mix of solutions is achieved. Generally a quasi-steady state is observed at open circuit (i.e., at zero current) where the molar fluxes are low but not zero (see appendix A.1.1).

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3_3,

3.1.1 - ELECTRIC POTENTIAL

In equilibrium, the electric charges found in a medium or in vacuum generate an electric field which itself derives from a scalar called the electric potential. From a mathematical point of view, this electric potential is defined up to a constant. In physics this constant is generally defined by taking vacuum at infinite distance as the potential reference. Thereupon, the term potential is used for any value using this reference and the term voltage is used for the difference between two potentials. A voltage is therefore independent of the reference used (vacuum, earth or any other).

More generally speaking, when equilibrium is disrupted (in physics this constitutes the change from electrostatics to electrokinetics), a magnetic field is associated *a priori* with the electric field. These two fields are then described using the MAXWELL equations. In electrochemistry, other than in exceptional cases[4], one can disregard the effects of magnetic field, and so in this scenario the electric field is derived from a potential, and therefore the MAXWELL equations are reduced to the POISSON law:

$$\nabla^2 V = -\frac{\rho_{ch}}{\varepsilon}$$

with:	V	the electric potential, in the general sense	[V]
	ρ_{ch}	the charge density	[C m^{-3}]
	ε	the dielectric permittivity of the medium	[A^2 s^4 kg^{-1} m^{-3}]

3.1.1.1 - ELECTRIC POTENTIAL AND ELECTRONEUTRALITY

In equilibrium all conductors are equipotential and uncharged in volume. In other words, electroneutrality applies at any macroscopic point in the volume. However, once on the atomic scale, this rule can no longer be upheld since here there are negatively charged electrons and positively charged nuclei. If there is a macroscopic perturbation in the charge distribution, then electroneutrality is restored, though only outside the interfacial zones, with a very fast transient state (lasting about a femtosecond[5] in a metal, see below).

Take the example of an electric conductor with a fixed initial volume charge distribution (denoted by $\rho_{ch} = \rho_0 \neq 0$), such that there is no electroneutrality. It is assumed that the OHM law can be written here using a constant conductivity and relative dielectric permittivity of the medium in question. By applying simple calculations one can estimate the characteristic time constant for the spontaneous process of returning to equilibrium, where the conducting volume is equipotential and electroneutrality applies throughout the volume. The charge is then spread over the surface, i.e., at the interface with the external medium.

By combining the OHM law ($\mathbf{j} = \sigma \mathbf{E} = -\sigma\, \mathbf{grad}\, V$), the POISSON law ($\nabla^2 V = -\frac{\rho_{ch}}{\varepsilon}$) and the equation for charge preservation[6] ($\frac{\partial \rho_{ch}}{\partial t} = -\operatorname{div} \mathbf{j}$), the following differential equation is obtained:

---

[4] The aluminium industry is an example where magnetic fields in an electrochemical system cannot be disregarded. During the process of industrial aluminium electrolysis the extremely high current flow builds up a strong magnetic field. This in turn triggers waves on the liquid surface which can subsequently create short circuits between the anode and cathode.

[5] That is to say 10^{-15} s.

$$\frac{\partial \rho_{ch}}{\partial t} = \sigma \ \text{div}\,(\textbf{grad}\, V) = -\frac{\sigma}{\varepsilon}\,\rho_{ch}$$

Electroneutrality, $\rho_{ch} = 0$, is therefore reached *via* an exponential law of the following type:

$$\rho_{ch} = \rho_0\, e^{-\frac{t}{\tau}}$$

with a time constant of $\tau = \dfrac{\varepsilon}{\sigma} = \dfrac{\varepsilon_0\ \varepsilon_r}{\sigma}$.

For an electrolytic aqueous solution, the order of magnitude of σ is 1 S m^{-1} [7] and ε_r is around 80. Therefore this results in a time constant of around 1 ns [8].

For a metal such as copper, the order of magnitude of σ is 10^7 S m^{-1} and $\varepsilon_r \approx 1$. The time constant is therefore around 10^{-18} s.

The current flow through an electrochemical cell is capable of sustaining a slight deviation from electroneutrality. However, it must be remembered that although this deviation is very low in numerical terms, it can nonetheless trigger a significant change in the potential profile, due to the very low value of ε[9]. Consequently, in a usual electrochemical system one can apply the electroneutrality equation to describe the concentration profiles in the electrolyte, outside the interface zones. However, it should not be inferred that it can be used to define the electric potential through the LAPLACE law ($\nabla^2 V = 0$) which is applicable only when electroneutrality is strictly respected (see appendix A.4.1).

3.1.1.2 - VOLTA AND GALVANI POTENTIALS

The laws of electrostatics show that a conductor that is in vacuum is equipotential in volume: it can therefore only be charged on the surface. The electrostatic potential is constant throughout the conductor volume, but then it suddenly varies at the conductor surface, before finally seeing slower changes in vacuum further away from the conductor. The potential difference between the conductor volume and vacuum at infinite distance, φ, can be divided into two terms, as depicted in figure 3.1 with $\varphi = \psi + \chi$. These terms are respectively called:

- GALVANI potential or internal potential, ψ, which is the electric potential difference between the conductor inside and vacuum at infinite distance;

---

[6] Charge preservation can be expressed by combining the mass balances in volume for different charged species, as described in section 4.1.2.

[7] Table 4.1 in section 4.2.2.3 gives conductivity values for various charge carriers in different conductors.

[8] With $\dfrac{1}{4\pi\ \varepsilon_0} = 9 \times 10^9$ *SI*.

[9] Appendix A.4.1 outlines an example of electrolysis with a diluted electrolyte containing only Ag^+ *and* NO_3^- *ions. It gives several orders of magnitude for the impact on the potential profiles caused by deviation from electroneutrality (see figure A.17 in appendix A.4.1). In particular, a deviation from electroneutrality of around* 10^{-14} *mol* L^{-1} *in aqueous solution does not cause a shift from the* LAPLACE *law (linear potential profile), while a deviation of around* 10^{-11} *mol* L^{-1} *cannot be overlooked when describing the potential profile.*

- VOLTA potential or external potential, ψ, which is the electric potential difference between the outlet of the interfacial zone and vacuum at infinite distance;
- surface electric voltage, χ, which is the voltage across the interfacial zone[10]. The surface voltage, χ, is notably linked to the surface charge[11]. However, even without surface charge, surface dipoles can lead to a significant surface electric voltage.

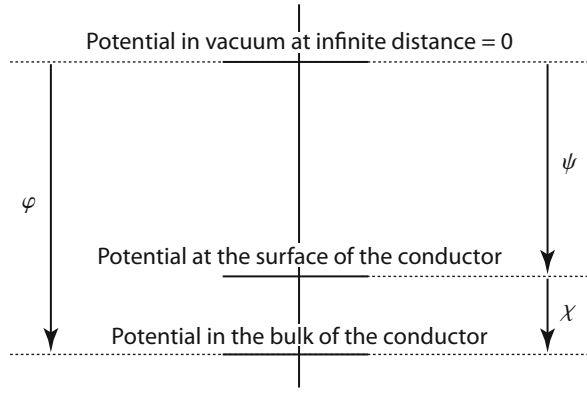


Figure 3.1 - Potential levels for a conducting volume in vacuum

3.1.2 - CHEMICAL AND ELECTROCHEMICAL POTENTIALS

3.1.2.1 - CHEMICAL POTENTIAL

In thermochemistry, the chemical potential of an uncharged species i is defined by the following equation:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{n_{j \neq i}, T, P}$$

with: G the system's GIBBS energy [J]
n_i the amount of substance of the species i [mol]
n_j the amount of substance of each other species [mol]

μ_i is the partial molar GIBBS energy. Using EULER's identity, valid for all homogeneous functions of degree 1, one can show that the GIBBS energy can be expressed by the following sum:

$$G = \sum_i n_i \, \mu_i$$

Therefore μ_i represents the contribution of species i (relative to one mole) to the system's GIBBS energy, i.e., in interaction with other species in the medium in question.

---

[10] The term surface potential is sometimes used, although the correct term is surface voltage.

[11] Appendix A.3.1 outlines the calculations for the electrostatic potential profile, as well as the values of the three voltages described here, relating to the case of a conducting surface-charged sphere that is in equilibrium, in vacuum.

This is also the work required for the reversible transport of one mole of species i to switch from infinite distance in vacuum to the bulk of the system, at T and P constant.

The activity of species i, a_i (a dimensionless number), is defined in terms of its chemical potential by the following equation:

$$\mu_i = \mu_i^\circ + \mathrm{R}T \ln a_i$$

where μ_i° is the standard chemical potential of species i at temperature T.

A standard state corresponding to $a_i = 1$ should be defined for each species. Except in the case of solutions (see below), most of the time the standard state of species i at temperature T corresponds to the pure compound in its physical state (gas, solid, liquid) at the same temperature and under the standard pressure of $P^\circ = 1$ bar. A standard state of reference is also defined for each pure compound, and this corresponds to the standard state of the pure compound in its most stable physical state at the temperature in question.

Furthermore, one can also define ideal behaviours. In order to describe a compound in a real system, the degree of deviation from the ideal situation is characterised by the activity coefficient, which is a dimensionless number as the activity itself.

⏩ *For gases*

The standard state is the ideal gas corresponding to the standard pressure P° [12]. The activity (also called the fugacity) of a compound i in a gas mixture under total pressure P is therefore defined by:

$$a_i = \gamma_i \, x_i \frac{P}{P^\circ} = \gamma_i \frac{P_i}{P^\circ}$$

with: γ_i the activity coefficient, or the fugacity coefficient of the gas i in the mixture, taking the interactions in the gas mixture into account
x_i the molar fraction of the compound i in the gas mixture
P_i the partial pressure of the gas i in the mixture [bar]

⏩ *For solutions*

In a liquid mixture, when there is a fairly balanced composition in the compounds then the pure compounds can be kept as standard states using the molar ratios to define the ideal activities. Consequently, the activities are expressed as $a_{i,x} = \gamma_{i,x} \, x_i$. However, the solutions most commonly seen in electrochemistry involve a compound, called a solvent, which is found in much greater quantity than other compounds, called solutes. Here one often distinguishes between these two types of compounds by choosing a different standard state for the solvent and the solutes:

- for the solvent, the standard state is the pure compound at standard pressure P°. For a moderately concentrated solution, $x_{\text{solvent}} \approx 1$, therefore $\gamma_{\text{solvent}} \approx 1$ and it is consequently often recognised that $a_{\text{solvent}} = \gamma_{\text{solvent}} \, x_{\text{solvent}} \approx 1$;

---

[12] At very low pressure all gases behave like an ideal gas. This remains true up to 1 bar (= P°) for most usual gases, but deviations occur at high pressure.

- for the solutes, the standard state is a hypothetical solution without any interaction between the solutes' ions and molecules (this solution is called infinitely diluted), under $P°$, extrapolated at $C° = 1$ mol L^{-1} (or $m° = 1$ mol kg^{-1}) :

$$a_i = \gamma_i \frac{C_i}{C°} \qquad \text{with} \quad \gamma_i \xrightarrow[\sum_k C_k \to 0]{} 1 \quad (\text{or} \quad a_{i,m} = \gamma_{i,m} \frac{m_i}{m°})$$

▸▸ *For solids*

The standard state corresponds to a solid alone in its own phase at standard pressure $P°$. Solids are frequently found in their standard state. However in electrochemistry there are cases where the solid phase is a solid solution, for example with metal alloys or insertion materials used in many batteries. Here therefore the activities are defined using composition parameters (for example with the atomic fraction for alloys, or the concentration for solid electrolytes, etc.).

3.1.2.2 - ELECTROCHEMICAL POTENTIAL

The state of an electrochemical system depends on an additional parameter, namely the GALVANI potential, φ. Therefore, when referring to a species in electrochemical systems, one frequently sees the term ' electrochemical potential ' used instead of ' chemical potential ', even though they represent exactly the same concept. Namely, both represent the contribution of species i, charged or not, to the GIBBS energy in the medium in question. The tilde mark is then placed over the symbol to point out that the intensive parameter φ is taken into account:

$$\widetilde{G} = \sum_i n_i \widetilde{\mu}_i$$

For a metal, the electrochemical potential of electrons corresponds to a measurable quantity[13]. However it is more difficult to envisage the experimental determination of an ion's electrochemical potential in an electrolyte. In fact, due to the media's electroneutrality, it is impossible for an ion intake to occur in an experiment without simultaneously there being a counter-ion, at the very least. Therefore, one can only access the electrolyte's electrochemical potential, this term being identical to its corresponding chemical potential. There are different consequences entailed here, which will be outlined later in this chapter: the definition of a solute's mean activity (section 3.2.1.1), and the convention for the thermodynamic data of ions in a solution (section 3.1.2.3).

The interactions between species i and other surrounding species involve electric forces which themselves are not simply the result of the influence of the local macroscopic electric potential.

However the electrochemical potential of ions can be divided into two terms, one called ' purely electric ' and the other called ' chemical potential '. This is because the latter term shares the same form as that of the equations seen above:

$$\widetilde{\mu}_i = \mu°_i + \mathrm{R}T \ln a_i + z_i \mathcal{F} \varphi = \mu_i + z_i \mathcal{F} \varphi$$

---

[13] This quantity is related to the electron work function as described in section 3.2.2.3.

One must remember that this common language can be confusing. In particular, the activity of an ion can depend *a priori* on the value of the electric potential. By way of simplifying, the so-called ' chemical potential ' is often said not to depend on the electric potential but rather depend exclusively on the medium's chemical composition (as in the DEBYE-HÜCKEL law, see section 3.2.1.3).

Once electroneutrality applies, it is no longer necessary to describe the system in terms of electrochemical potential, and the only quantities experimentally available then become the electrolytes' chemical potentials. On the other hand, if one wishes to describe media that demonstrate a deviation from electroneutrality, for instance interfacial zones in electrochemistry, then the concept of electrochemical potential becomes a very useful tool [14].

3.1.2.3 - CONVENTION FOR THERMODYNAMIC DATA TABLES

In thermodynamic data tables (standard enthalpies or GIBBS energies of formation and standard molar entropies) which relate to compounds other than ions in a solution, the common convention that is applied involves setting the values of standard enthalpy and standard GIBBS energy of formation (or chemical potential) equal to 0 J mol^{-1} for all simple pure elements in their stable physical state at the temperature in question. The data therefore refer to the formation of substances from simple elements.

The thermodynamic quantities relating to the anion and cation cannot be measured separately for ions in a solution due to the electroneutrality (experimental thermodynamic data only concern electrolytes). Therefore, an additional convention is introduced here, known as LATIMER's convention. This involves setting the proton's chemical potential equal to zero:

$$\forall\, T \qquad \mu^{\circ}_{H^+} = 0 \text{ J mol}^{-1}$$

where H^+ represents the solvated proton in the solvent in question (aqueous or not) [15].

It is possible to deduce the chemical potential values for other ions in a solution by using experimental measurements of standard GIBBS energy of reaction. This convention can be stretched to include values for enthalpy, entropy and the heat capacity of protons in a solution, all of which are set equal to zero.

---

[14] Such is the case when describing interfaces in equilibrium (see section 3.3) or when splitting a current into migration and diffusion currents (see section 4.2.1).

[15] This convention, which is similar to the one used for choosing the H^+/H_2 couple for the SHE, enables one to give a clear definition to thermodynamic data, even if these data may at times be virtual. However, one must be aware that such choices do not enable one to make easy comparisons between thermodynamic data in different solvents. Indeed, the energy of the solvated proton strongly depends on the medium in question, because the ion is very small in size and therefore very sensitive to electrostatic effects. Other reference compounds are used for making comparisons across different media, for instance in electrochemistry in linking different standard potentials scales to each other. In this instance, it is common for the standard GIBBS energy of solvation of BPh_4^- $AsPh_4^+$ (two large size ions of opposite charges) to be divided into two equal parts for each ion, regardless of the solvent. This extra-thermodynamic assumption then enables one to compare thermodynamic data in different solvents.

FUEL CELLS

Document written with the kind collaboration of E. ROSSINOT, head of the fuel cells team and A. RENARD, communications manager for Axane, Sassenage, France

A fuel cell is an electrochemical system which supplies electrical energy generated by spontaneous electrochemical reactions that take place between oxygen found in air and hydrogen. This is the case for the simplest fuel cell systems, though other fuels are also currently being studied. Insofar as only water is produced in this main reaction, it is the system of choice for a non-polluting power supply.

As in many batteries, several individual cells are connected in series or in parallel to obtain the electric characteristics (energy, power) necessary for applications. It should be noted that fuel cells are particular in the field of batteries given their use of gas reagents: they are open systems with a continuous gas flow feeding in. They are therefore more complicated to manage than a closed battery. However, the fact of decoupling the system's power and energy functions does provide an advantage. The power supplied depends on the active surface of the electrodes used, while the energy depends on the size of the hydrogen tank that is connected to the core of the cell inside the system.

In fuel cell systems where the internal working temperature is around 70 °C, the electrolyte is a polymer material which allows the conduction process to take effect via protons. A cell is then made up of this electrolyte placed between two electrodes containing a catalyst.

At the anode, hydrogen is oxidized:

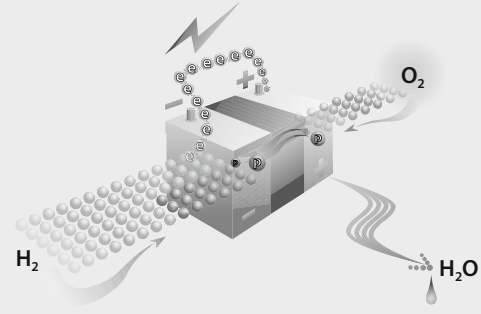
$$2\,H_2 \longrightarrow 4\,H^+ + 4\,e^-$$

At the cathode, oxygen is reduced:

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$$

The balance is:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$



An energy solution with many advantages…

- High energy efficiency, excellent current quality
- Autonomy, mobility and reliability
- No harmful emissions (in the case of hydrogen fuel)
- Modularity (elementary cells either in series or in parallel)
- Simple and noiseless when in operation
- Indoor or outdoor use (high resistance to weather conditions)

… and great opportunities.

Considering that it remains a priority to comply with environmental constraints the fuel cell can be seen as a very promising power source in the fields of transport, small portable objects and energy distribution.

- **Mobile applications**

  By way of example one can cite applications in telecommunications, propelling small electric vehicles or boats, uses in scientific or rescue missions (firefighters, rescue teams, medical emergencies, etc.) as well as in the cinema and building industry or indeed for any type of work, at any time and in any place.

Examples of nomadic applications *(picture provided by Axane)*
Axane is a wholly-owned subsidiary of the Air Liquide group. It aims to develop fuel cells systems powered by hydrogen, which are the core of the power supply offer proposed by Air Liquide Hydrogen Energy. These turnkey energy solutions are for new emerging markets (telecom antennas, one-off outdoor events, off-grid sensors, etc.)

- **Stationary or sedentary applications**

  These cover continuous power supply in isolated areas; for example telecommunication antennas or relays, lighting critical sites or even providing power supply to measuring equipment, etc.

  Moreover they are used for backup power supply (i.e., capable of taking over a main energy supply system in the event of power failure): for instance for telecommunications, health or the banking sector, etc.

Examples of sedentary applications *(picture provided by Axane)*
A system installed in difficult climatic conditions (–5°C to 33 °C and with a humidity of 26% to 100%) performed over 10 000 h of continuous operation (about one year and 10 MWh of cumulative energy supplied) without maintenance work.

Table 3.1 shows an extract from a thermodynamic data table at 25 °C.

Table 3.1 - Thermodynamic data

Compound		$\Delta_f H°$ [kJ mol^{-1}]	$\Delta_f G° = \mu°$ [kJ mol^{-1}]	$S°$ [J K^{-1} mol^{-1}]	$C_P°$ [J K^{-1} mol^{-1}]
F_2	gas	0	0	202.7	31.3
F^-	gas	– 270.7			
F^-	aq. sol.	– 332.6	– 278.8	– 13.8	– 106.7
H^+	gas	1536.2	1523	109	20.8
H^+	aq. sol.	0	0	0	0
H^+	non-aq. sol.	0	0	0	0
H_2	gas	0	0	130.6	28.8
H_2O	liquid	– 285.2	– 237.2	69.9	75.3

Note that for any given ion, different values can be found depending on its physical state, i.e., whether it is in a solution or in gaseous plasma. In the latter case, a particular convention is needed to produce thermodynamic data which is similar to the LATIMER convention. Therefore, the gaseous H^+ data given above are obtained by setting the electrochemical potential of electrons in the plasma at zero at any temperature.

3.2 - THERMODYNAMIC EQUILIBRIUM IN A MONOPHASIC SYSTEM

As previously stated, any conducting phase in equilibrium is equipotential in its volume and electroneutrality applies at each point [16].

Through an analogy with thermochemistry, the thermodynamic equilibrium is expressed in these conducting systems by the following:

- in the absence of any possible chemical reaction,

$$\forall\, i \qquad \widetilde{\mu}_i = \text{Cst} \qquad \text{in the volume}$$

- in the presence of one or several possible chemical reactions (index r), the thermodynamic equilibrium is expressed by the following equation:

$$\forall\, r \qquad \Delta_r \widetilde{G} = \sum_i \nu_{i,r}\, \widetilde{\mu}_i = 0 \qquad \text{in the volume}$$

  whereby $\nu_{i,r}$ is the algebraic stoichiometric number of species i in the reaction r in question [17].

Because a chemical reaction always preserves the charge (identical overall charge on both sides of the balanced equation), then the electrochemical GIBBS energy of reaction, $\Delta_r \widetilde{G}$, and the chemical GIBBS energy of reaction, $\Delta_r G$, are identical (see the example below).

---

[16] Describing the interfacial thermodynamic equilibrium is covered in section 3.3.

[17] Some authors prefer the concept of affinity to that of GIBBS energy of reaction. In fact, using affinity helps avoid possible confusion between variations in GIBBS energy, ΔG (J) and GIBBS energy of reaction, $\Delta_r G$ (J mol^{-1}).

The previous equation is then expressed in the following form:

$$\Delta_r \widetilde{G} = \Delta_r G = \Delta_r G^\circ + \mathsf{R}T \ln \prod_i a_i^{\nu_{i,r}} = 0$$

or: $$K_{eq}(T) = \prod_i a_i^{\nu_{i,r}}$$ mass action law

with $$0 = \Delta_r G^\circ(T) + \mathsf{R}T \ln K_{eq}(T)$$

Chemical reactions may be redox reactions as shown below.

For example, in an aqueous solution containing fully dissociated potassium iodide, KI, and dissolved diiodine, I_2, the redox equilibrium of the couples I_2/I_3^- and I_3^-/I^- is rapidly observed in the homogeneous phase:

$$I^- + I_2 \rightleftharpoons I_3^-$$

In equilibrium, one can write:

$$\begin{aligned} 0 = \Delta_r \widetilde{G} &= \widetilde{\mu}_{I_3^-} - \widetilde{\mu}_{I^-} - \widetilde{\mu}_{I_2} \\ &= \mu_{I_3^-} - \cancel{\mathcal{F}\varphi} - \mu_{I^-} + \cancel{\mathcal{F}\varphi} - \mu_{I_2} = \Delta_r G \end{aligned}$$

3.2.1 - ELECTROLYTIC SOLUTION

3.2.1.1 - MEAN ACTIVITY AND MEAN ACTIVITY COEFFICIENT

Remember that in experimental conditions it is impossible to measure the electrochemical potential of an ion in an electrolytic solution. An ion's amount cannot be modified without a simultaneous change in the amount of at least one other ions. Here therefore one defines mean values, which can be determined based on experiments [18].

For example, one mole of a fully dissociated solute of the type $A_{p_+}B_{p_-}$, with the respective algebraic ion charge numbers z_+ and z_-, corresponds to p_+ mole(s) of A^{z+} and p_- mole(s) of B^{z-}.

We then have the equation: $$z_+ p_+ + z_- p_- = 0$$

The only experimentally accessible quantity is the solute's electrochemical potential, which is identical to its chemical potential:

$$\begin{aligned} \widetilde{\mu}_{A_{p_+}B_{p_-}} &= p_+ \widetilde{\mu}_{A^{z+}} + p_- \widetilde{\mu}_{B^{z-}} \\ &= p_+ \mu_{A^{z+}} + \cancel{p_+ z_+ \varphi} + p_- \mu_{B^{z-}} + \cancel{p_- z_- \varphi} \\ &= \mu_{A_{p_+}B_{p_-}} \end{aligned}$$

[18] *Appendix A.3.2 gives a few examples to show how common equations written using individual ion activities can wrongly suggest that these quantities are measurable. Indeed, the most rigorous equations always include quantities that involve mean activities. Two typical examples of these include potentiometric measurements either using selective electrodes or as in cells with a liquid junction (or salt bridge).*

The mean electrochemical potential of the solute is defined by the following equation, with $p = p_+ + p_-$ representing the number of ions in the compound $A_{p_+}B_{p_-}$:

$$\widetilde{\mu}_\pm = \mu_\pm = \frac{1}{p_+ + p_-}\mu_{A_{p_+}B_{p_-}} = \frac{1}{p}\mu_{A_{p_+}B_{p_-}}$$

then,
$$\widetilde{\mu}_\pm = \mu_\pm = \frac{p_+ \mu^\circ_{A^{z+}} + p_- \mu^\circ_{B^{z-}}}{p} + \frac{RT}{p}\ln a_+^{p_+} + \frac{RT}{p}\ln a_-^{p_-}$$
$$= \mu^\circ_\pm + \frac{RT}{p}\ln a_+^{p_+}\ln a_-^{p_-}$$

The definition for the solute's mean activity derives from the previous equation:

$$\widetilde{\mu}_\pm = \mu_\pm = \mu^\circ_\pm + RT\ln a_\pm$$

hence: $a_\pm = \sqrt[p]{a_-^{p_-}\, a_+^{p_+}}$ ***or*** $a_{A_{p_+}B_{p_-}} = a_\pm^{\,p} = a_+^{p_+} a_-^{p_-}$

The mean concentrations and activity coefficients can be defined based on the concentrations of each ion, which are measurable in an experiment:

$$C_\pm = \sqrt[p]{C_-^{p_-}\, C_+^{p_+}} \quad \text{and} \quad \gamma_\pm = \sqrt[p]{\gamma_-^{p_-}\, \gamma_+^{p_+}}$$

with the usual equation linking activity, concentration and activity coefficient as being:

$$a_\pm = \gamma_\pm C_\pm$$

For example, for a 1–1 electrolyte such as KCl, the mean quantities correspond to geometric means:

$$p_+ = p_- = 1 \qquad \text{hence} \quad \begin{cases} a_\pm = \sqrt{a_+ a_-} \\ \gamma_\pm = \sqrt{\gamma_+ \gamma_-} \\ C_\pm = \sqrt{C_+ C_-} \end{cases}$$

These equations can also be applied to electrolyte mixtures. In these cases, even if anions and cations can have different concentrations, yet their mean values are always expressed in a similar way (see KCl in the following example in section 3.2.1.2).

3.2.1.2 - IONIC STRENGTH

LEWIS, RANDALL and BRÖNSTED showed through experiments in diluted solutions, that each mean activity coefficient depends on all the different kinds of ions in the electrolyte, through the ionic strength, I_s [19]:

$$\log \gamma_\pm = A\, z_+\, z_- \sqrt{I_s}$$

with
$$I_s = \frac{1}{2}\sum_i C_i\, {z_i}^2$$

[19] In many documents, the symbol typically used to indicate ionic strength is I. We prefer I_s to avoid confusion between this quantity and the current I.

Now let us turn to the case of aqueous solutions at 25 °C: $A \approx 0.5$ $L^{1/2}$ $mol^{-1/2}$, with the ionic strength I_s and the concentrations C_i expressed in mol L^{-1}. This relationship, which has been verified *via* experiment, is quite accurate for media with an ionic strength such as $I_s \leq 10^{-3}$ mol L^{-1} (or exceptionally up to 10^{-2} mol L^{-1}). Remember that the charge numbers are algebraic, therefore the product $z_+ z_-$ is always negative. Consequently, when this equation applies, the mean activity coefficient is a number below 1.

We can estimate the mean activities and activity coefficients for an aqueous solution containing a mixture of zinc chloride, $ZnCl_2$, with a concentration of 0.001 mol $L^{-1}$and potassium nitrate, KNO_3, with a concentration of 0.003 mol L^{-1}.

The ionic strength of the solution is equal to:

$$I_s = \frac{1}{2}\left[\, 0.001\,(1\times 2^2 + 2\times 1^2) + 0.003\,(1\times 1^2 + 1\times 1^2)\,\right] = 0.006 \text{ mol L}^{-1}$$

The mean activities and activity coefficients can be calculated for the electrolytes $ZnCl_2$ and KNO_3, but also for KCl and $Zn(NO_3)_2$ [20].

For example for KCl, $\log \gamma_\pm = -A\sqrt{0.006}$ hence $\gamma_\pm = 0.91$

$a_\pm = \gamma_\pm C_\pm$ and $C_\pm = \sqrt{0.003 \times 0.002} = 0.0024$ mol L^{-1} $a_\pm = 0.0022$

For example for $ZnCl_2$, $\log \gamma_\pm = -2A\sqrt{0.006}$ hence $\gamma_\pm = 0.84$

$a_\pm = \gamma_\pm C_\pm$ and $C_\pm = \sqrt[3]{0.001\,(2\times 0.001)^2} = 0.0016$ mol L^{-1} $a_\pm = 0.0013$

The ions' charges play a very important role in the electric interactions and therefore in the values of the activity coefficients. Table 3.2 illustrates this property by giving values for ionic strength and mean activity coefficients (calculated from the previous equations) for different types of electrolytes in a concentration equal to 10^{-3} mol L^{-1}.

Table 3.2 - Examples of ionic strength and mean activity coefficient values

Type of electrolyte : z_+–z_-	Examples	I_s (10^{-3} mol L^{-1})	$\gamma_\pm$
1–1	NaCl	1	0.96
1–2 or 2–1	Na_2SO_4 or $ZnCl_2$	3	0.88
1–3 or 3–1	Na_3PO_4 or $CeCl_3$	6	0.76
2–2	$CuSO_4$	4	0.74
2–3 or 3–2	$Ca_3(PO_4)_2$ or $Ce_2(SO_4)_3$	15	0.42

[20] The concepts of mean activity or mean activity coefficient of a given electrolyte in a solution containing more than two types of ions are relevant and moreover correspond to quantities which are accessible via experiment. For example in the case of an aqueous solution obtained by dissolving silver nitrate, potassium chloride and sodium perchlorate, the solubility of silver chloride is directly related to the mean activity of AgCl in this medium. Another example, which is very important in the aluminium industry, is that of molten salt used in industrial electrolysis. At about 1000°C, the salt contains Na^+, F^-, AlF_5^{2-}, AlF_6^{3-} and AlF_4^- ions. The gas atmosphere found above such an electrolyte is mainly composed of $NaAlF_4$. The corresponding pressure measurement enables one to determine the mean activity of sodium tetrafluoro-aluminate.

The ionic strength of a given solution is unique. Therefore, when respecting the validity limits of the previous equation, one can state that electrolytes of the same type (i.e., with the same value for the product $z_+ z_-$), all have the same mean activity coefficient for a given ionic strength, regardless of their concentration.

When a supporting electrolyte is used in electrolytic solutions, its advantages go beyond the direct impact upon the properties of mass transport[21]. In fact, the supporting electrolyte fixes the ionic strength of the solution. In other words, a solution with a supporting electrolyte is a solution with a buffered ionic strength.

3.2.1.3 - DEBYE-HÜCKEL'S MODEL

The theoretical model put forward by DEBYE and HÜCKEL helps one to understand the experimental law outlined above. In order to determine any deviation from the ideal situation, the approach consists firstly in calculating the interactions exerted by all other ions on a central ion[22]. These interactions then appear as a corrective term in the electrostatic potential around the central ion, and are subsequently expressed as an activity coefficient for the ion.

Let us specify the different hypotheses laid out by the DEBYE-HÜCKEL model and the subsequent approximations which help one develop a means of expressing the activity coefficient of various ions in an electrolyte. Nearly all the assumptions, expressed below, are based on the fact that this theory is developed for dilute solutions:

- all solutes are strong electrolytes, and therefore fully dissociated. In particular, it is assumed that there are no neutral molecules, except for the solvent, and that there are no ion pairs;
- the electric permittivity of the medium is constant and equal to that of the pure solvent, regardless of its position in relation to the central ion;
- the interactions between the different ions in the solution are exclusively electrostatic (COULOMB's law);
- the system's layout is spherically symmetric around each ion, which is considered as a point in relation to the distances in question;
- the COULOMB energy is, in absolute value, much lower than the thermal energy.

The assumptions above lead to a law called the limiting DEBYE-HÜCKEL law:

$$\log \gamma_k = -A\, {z_k}^2 \sqrt{I_s}$$

For aqueous solutions at 25 °C, the theoretical expression of A leads to the same value, $A \approx 0.5\ \mathrm{L}^{1/2}\,\mathrm{mol}^{-1/2}$, if the ionic strength I_s and the concentrations C_i are expressed in mol L^{-1}. This law is applied generally when the ionic strength is lower than 10^{-3} mol L^{-1}.

---

[21] See section 2.2.4.4.

[22] Appendix A.3.3 lays out the full reasoning and calculations behind DEBYE-HÜCKEL's limiting law, covering all the various steps, based on the assumptions listed here.

When the ionic strength value is higher than 10^{-3} mol L^{-1}, then one can use the following equation, which is known as the extended DEBYE-HÜCKEL law [23]:

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

This equation results from a calculation similar to the previous one, although the charges are not considered as point charges. At room temperature, when the ionic strength is higher than 10^{-3} mol L^{-1} one needs to use the extended law (which corresponds to an adjustment of about 10% on the logarithm, for an ionic strength of 10^{-3} mol L^{-1}). This extended law is generally applied to cases showing ionic strengths of up to 10^{-2} mol L^{-1} (and exceptionally 10^{-1} mol L^{-1}).

It is easy to switch from the theoretical expression of an ion's activity coefficient to the theoretical expression of an electrolyte's mean activity coefficient, which is the only expression that can be compared to experimental data. For example, the limiting law gives the following:

$$\log \gamma_\pm = \frac{1}{p}\left(p_- \log \gamma_- + p_+ \log \gamma_+\right) = -A\sqrt{I_s}\,\frac{p_-\, z_-^2 + p_+\, z_+^2}{p_+ + p_-}$$

and because $p_-\, z_- + p_+\, z_+ = 0$, with z_+ and z_- algebraic, then:

$$\log \gamma_\pm = -A\sqrt{I_s}\,\frac{-p_+\, z_+\, z_- - p_-\, z_-\, z_+}{p_+ + p_-}$$

hence:

$$\log \gamma_\pm = A\, z_-\, z_+ \sqrt{I_s}$$

Scientific literature shows how the experimental curves that represent the variation in the mean activity coefficients as a function of the molality (i.e., the amount of substance in mol per kilogram of solvent [24]), often have a minimum. Moreover, the value of the mean activity coefficient may exceed 1 (see figure 3.2). Therefore, when dealing with concentrated electrolytes, one can see how the experimental results rapidly seem to deviate from the variation laws as presented above (they all show a monotonic variation in the mean activity coefficient as a function of the molality or the concentration).

In reality, these experimental results are not wholly inconsistent with the DEBYE-HÜCKEL model, whereby the mean activity coefficient decreases as the molality increases. This comes down to taking into account the fact that a usual solute/solvent description is no longer satisfactory for concentrated electrolytes. Indeed, when dealing with concentrated electrolytes, the number of solvent molecules involved in the solvation sphere, close to the ions, cannot be ignored when compared to the total number of solvent molecules. Once one takes this phenomenon into account, then three types of adjustment emerge, each of which are laid out in detail below.

---

[23] The extended DEBYE-HÜCKEL law is described in more detail in appendix A.3.3.

[24] In an experiment, it is much easier to obtain an accurate value for the molality of a concentrated solution (that is, the amount of solute introduced in 1 kg of solvent) than it is to know its concentration, and this due to the volume variations caused by the mixing. Frequently as a result, experimental thermodynamic data relating to concentrated solutions are presented using the molality scale. Then, in order to return to a concentration scale, one firstly needs to know the data relating to the solutions' density changes, as a function of their composition.

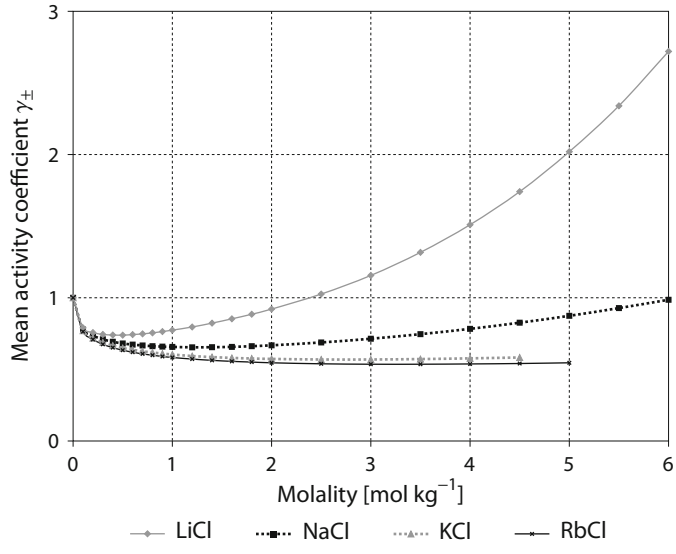


Figure 3.2 - Evolution of the mean activity coefficient as a function of the molality for some solutes in aqueous solutions

When dealing with concentrated solutions, it is necessary to:

- replace the apparent molality (the amount of ions per unit mass of solvent) by the actual molality of solvated ions, i.e., the ratio of the amount of solvated ions to the mass of free solvent molecules. The actual molality is not datum that can be directly obtained from experiments, because one must firstly assume a value for the hydration number, which is *a priori* different for each solute. The actual molality is higher than the apparent molality.

$$m_{\text{actual}} = \frac{m_{\text{apparent}}}{1 - \frac{18}{1000}\, n_{\text{hydratation}}\, m_{\text{apparent}}}$$

- calculate the actual activity coefficient corresponding to the actual molality, assuming that the energies (chemical potentials) are equal in both the real system and the non-hydrated apparent system:

$$A^+_{\text{hydrated}} + Cl^-_{\text{hydrated}} \equiv A^+ + Cl^- + n_{\text{hydratation}}\, H_2O$$

$$2\,R\,T \ln a_{\pm_{\text{actual}}} = 2\,R\,T \ln a_{\pm_{\text{apparent}}} + n_{\text{hydratation}} R\,T \ln a_{\text{water}}$$

or

$$\left(a_{\pm_{\text{actual}}}\right)^2 = \left(a_{\pm_{\text{apparent}}}\right)^2 \left(a_{\text{water}}\right)^{n_{\text{hydratation}}}$$

hence

$$\gamma_{\pm_{\text{actual}}} = \gamma_{\pm_{\text{apparent}}} \frac{m_{\pm_{\text{apparent}}}}{m_{\pm_{\text{actual}}}} (a_{\text{water}})^{n_{\text{hydratation}}/2}$$

- and finally take into account that the water activity cannot be considered as equal to 1:

$$a_{\text{water}} \approx x_{\text{free water}} = \frac{n_{\text{free water}}}{n_{\text{free water}} + n_+ + n_-} = \frac{1 - \frac{18}{1000}\, n_{\text{hydratation}}\, m_{\text{apparent}}}{1 - \frac{18}{1000}\,(n_{\text{hydratation}} - 2)\, m_{\text{apparent}}}$$

These last two adjustments give the following equation for the mean actual activity coefficient of the electrolyte:

$$\gamma_{\pm_{actual}} = \gamma_{\pm_{apparent}} \frac{\left(1 - \frac{18}{1000} n_{hydratation}\, m_{apparent}\right)^{\left(1+n_{hydratation}/2\right)}}{\left(1 - \frac{18}{1000}(n_{hydratation} - 2) m_{apparent}\right)^{\left(n_{hydratation}/2\right)}}$$

Figure 3.3 shows how the ions hydration phenomenon works on experimental data relating to aqueous electrolytes containing lithium chloride in variable amounts, and assuming that the hydration number is equal to 7.

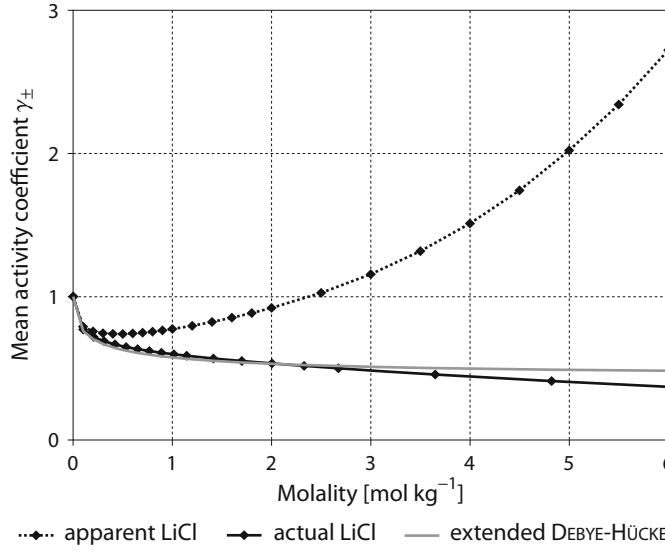


Figure 3.3 - Variations of the apparent and actual mean activity coefficients as a function of the apparent molality for aqueous solutions of LiCl

Also shown here is the curve calculated from the extended DEBYE-HÜCKEL law, having taken into account the experimental density variations in the concentrated solutions (i.e., the relationship between molality and concentration). This figure shows how, if one applies the correct terms to define concentration in highly concentrated media, then the experimental mean activity coefficients are not too far off those prescribed by the extended DEBYE-HÜCKEL law. There is no minimum on the curve with actual values, and the mean activity coefficient never exceeds 1.

3.2.2 - METALLIC ELECTRODE

3.2.2.1 - ELECTROCHEMICAL POTENTIAL

Electron activity is considered to be constant in the bulk of a metal. This is a realistic assumption, given that there is a large quantity of charge carriers present, i.e., of mobile electrons.

Therefore, by setting the activity of the electrons as equal to 1, their standard state is defined as their actual state in the metal:

$$\mu_e = \mu^\circ_e$$

thus:

$$\tilde{\mu}_e = \mu^\circ_e - \mathcal{F}\varphi$$

3.2.2.2 - FERMI'S ENERGY

The FERMI-DIRAC statistics dictate that the electrochemical potential of electrons corresponds to the electronic level with an occupation probability of 1/2.

This constitutes the highest energy level occupied by electrons at zero temperature (0 K), and is known as the FERMI energy (or HOMO energy[25]). Therefore, since it is generally possible to disregard temperature influence, the following equation emerges:

$$\tilde{\mu}_e(T) \approx \tilde{\mu}_e(0\,\mathrm{K}) = \mathcal{N}E_F$$

whereby $\tilde{\mu}_e$ is expressed in J mol^{-1}, $\mathcal{N}$ is the AVOGADRO constant, E_F is expressed in J, or more commonly in eV[26]. If one takes as the reference the energy of the electrons in vacuum at infinite distance, then these two values become negative[27].

3.2.2.3 - ELECTRON WORK FUNCTION

The FERMI level depends very heavily on the surface charge of the metal. In data tables, these values are given for the non-charged metal: namely the work function of an electron. It is possible to obtain this quantity *via* experiments, since it is a measure of the amount of work needed to remove an electron from the non-charged metal in vacuum and take it away at infinite distance.

One therefore ends up with:

$$\frac{\tilde{\mu}_e}{\mathcal{N}} = -W_{extr} - |e|\psi$$

with ψ as the VOLTA potential or external potential,

or:

$$W_{extr} = -\frac{\mu^\circ_e}{\mathcal{N}} + |e|\chi$$

with χ as the surface electric voltage, representing the difference between the GALVANI potential and the VOLTA potential ($\varphi = \psi + \chi$).

W_{extr} is a positive quantity, expressed in J or more commonly in eV.

In addition, one must remember that:

- E_F, W_{extr}, ψ, $\tilde{\mu}_e$ are experimentally accessible quantities,
- φ, μ°_e, χ are not experimentally accessible quantities.

---

[25] HOMO is the acronym for Highest Occupied Molecular Orbital.

[26] 1 eV = 1.6×10^{-19} J.

[27] The typical reference used in solid state physics is the energy level of the fundamental state, i.e.*, a quantum state with the lowest energy. So, the FERMI energy values of different metals are usually positive in data tables.*

As for the metals most often used in electrochemistry (namely silver, copper or zinc) the electron work function values are 4 to 5 eV. For single-crystals this value is influenced by the particular type of crystalline face. This is hardly surprising given that the metal's surface properties affect the electric surface voltage χ. The differences that can be observed between different types of crystalline faces vary by about 0.1 eV.

3.3 - THERMODYNAMIC EQUILIBRIUM AT AN INTERFACE

In equilibrium, an interface never provides a seat for the macroscopic displacement of species. In particular, it does not have a current flowing through[28]. These macroscopic properties can relate to a very different set of microscopic situations. In the case of reactive interfaces (where one or more reactions can occur), here the equilibrium state is a dynamic phenomenon whereby, on a microscopic scale, there are more or less species reacting at the surface. In this instance therefore, the equilibrium corresponds to a situation whereby at any given moment, there is an equal number of species reacting in one direction as in the other. Let us take the example of the transfer reaction of a species from one phase to another[29]. Here the equilibrium is reached whenever there are exactly as many species crossing the interface in one direction as in the opposite direction, at any given moment. On the other hand, when an interface is non-reactive, there is a total absence of microscopic movement across the interface at all times, and in particular in thermodynamic equilibrium. In this instance the thermodynamic equilibrium is not written in the same manner, as will be explained in detail in the next section.

3.3.1 - THERMODYNAMIC EQUILIBRIUM AT A NON-REACTIVE INTERFACE

In the case of a non-reactive interface, it is not possible to reach thermodynamic equilibrium *via* mass exchange. Species accumulate on both sides of the interface, subsequently creating a surface composition that minimizes the energy level. However this phenomenon is necessarily transient. The same arguments apply to the thermodynamics of surfaces, which are for example used to define oil/water emulsions, soap bubbles, etc. Here, a surface energy term is brought into play, which is based on the surface tension and surface excess concentrations.

When an electrochemical interface is non-reactive it is called an ideally polarisable interface or blocking electrode. This situation is generally only found in a limited potential range. Moreover, while the thermodynamic equilibrium is being established, charged species can be transiently seen to accumulate on both sides of the interface, while the overall interface remains neutral. There is therefore a transient current reflecting the variation in the surface charge excesses on both sides, depending on the voltage across

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[28] Remember that the opposite is not true: an interface with no current flowing through it is not necessarily in equilibrium (see introduction to chapter 3).

[29] Let us recall (see section 2.2.1.2) that we have chosen to look at interfacial exchange phenomena as reactive processes, and therefore not use the terms that differentiate between permeable and impermeable interfaces: all interfaces here are considered as impermeable, with or without reactive processes.

the interface. The interfacial zone behaves like a capacitor and is called the electrochemical double layer.

This phenomenon is identical to the one found in n/p, p/n or SCHOTTKY's diodes, where it is called the space charge phenomenon. The GOUY-CHAPMAN-STERN model is the name given to the detailed description of the double layer structure, when dealing with a simple, ideally polarisable interface[30]. This theory is based on principles that are relatively close to principles behind the DEBYE-HÜCKEL model. It will be not described in detail here. It essentially boils down to writing that the electrochemical potential of each species is constant in the phase where it is present, which in turn creates a link between the potential and concentration profiles of charged species in the interfacial zone. This is a satisfactory way of accounting for the experimental values of double layer capacitances in a typical setup. Based on this theory, the electrochemical double layer consists of two zones, hence its name. The first one, located next to the electrode, is called the compact or HELMHOLTZ layer. Its thickness L_H is about a few Å, which constitutes the negligible distance at which solvated ions can approach the surface. The potential profile is linear inside this layer. The second one is called the diffuse layer[31], and the order of magnitude of its thickness is the DEBYE length L_D [32]. Inside this second layer, the potential varies more slowly.

Without actually studying the whole mathematical equation of the potential profile in the double layer, one can remember that when the potential difference between the terminals of the diffuse double layer is moderate, then the variations inside the latter are close to an exponential function[33]:

$$\varphi - \varphi_{\text{solution}} = \text{Cst}\ e^{-\frac{x-L_H}{L_D}}$$

Figure 3.4 shows the shape of the potential variations, as a function of the distance from the interface on the double layer thickness scale.

For concentrated solutions (for instance those involving a supporting electrolyte with a concentration higher than 0.1 mol L^{-1}), the DEBYE length is less than one nanometer and one can consider the double layer as being reduced to the compact layer. For very dilute solutions (for instance with an ionic strength of about 10^{-5} mol L^{-1}), the DEBYE length is about 0.1 µm and the diffuse layer represents most of the volume in the double layer. It should be remembered that the electrochemical double layer is typically about a few nanometers in thickness.

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[30] It is more complicated to describe the interfacial zone if specific adsorption phenomena are involved. The description often follows a model using several capacitors in series or in parallel.

[31] This terminology is rather awkward because it may cause confusion with the diffusion layer. However it is commonly used to designate this part of the double layer.

[32] The DEBYE length is defined in mathematical terms in appendix A.3.3 which describes the DEBYE-HÜCKEL theory. Some orders of magnitude are given later in the text.

[33] Typically, potential profiles of the exponential type are found in the diffuse layer, when the overall interfacial voltage has values of about 50 mV for a 1–1 electrolyte. This applies to numerous experimental situations.

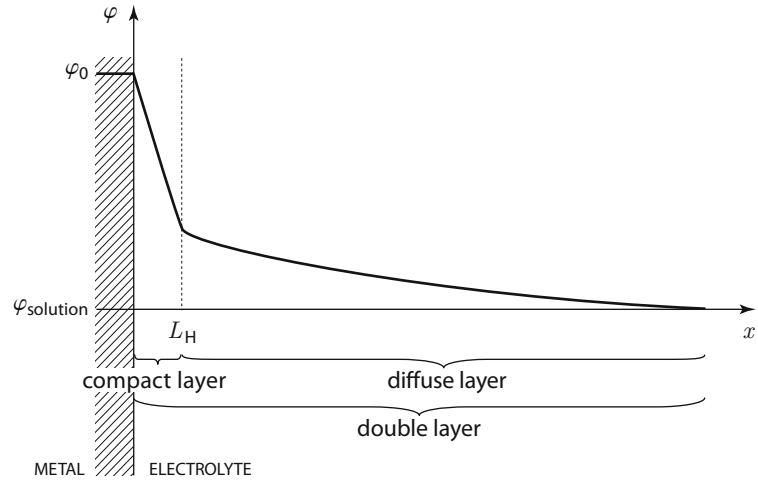


Figure 3.4 - Potential profile in the electrochemical double layer

This book will make little reference to phenomena relating to this double layer. Yet a number of applications in electrochemistry, such as electrophoresis, electroosmosis, supercapacitors, etc. are rooted in these same phenomena.

In the following section we will focus on reactive interfaces. Here again, thermodynamic equilibrium corresponds to particular potential profiles in the interfacial zone. Although double layer phenomena do indeed also come into play for these reactive interfaces, here our analysis will be carried out on a much broader scale than merely the double layer alone. Therefore the potential profile appears simply as flat in both extreme phases, showing discontinuity when crossing the interface. This discontinuity, this potential difference between the two phases, is what thermodynamics connects up to the system's composition, as explained below.

3.3.2 - THERMODYNAMIC EQUILIBRIUM AT A REACTIVE INTERFACE

By analogy with the case of chemical reactions in volumes, the state of thermodynamic electrochemical equilibrium corresponds to a zero value for the electrochemical GIBBS energy of reaction:

$$\forall\, r \qquad \Delta_r \widetilde{G} = \sum_i \nu_{i,r} \widetilde{\mu}_i = 0$$

When dealing with the particular case of reactive phenomena at an interface, the species in question (reactants or products) are not all in the same phase. This has a significant impact in electrochemistry because the species involved in the reaction are not subjected to the same electric potential. Therefore, although the charge balance in the chemical reaction is zero, as soon as charged species are involved then the chemical GIBBS energy of reaction is not zero:

$$\Delta_r \widetilde{G} = 0 \qquad \text{but} \qquad \Delta_r G \neq 0$$

It is a very quick process to write the thermodynamic equilibrium of a reactive interface if you are using electrochemical potentials. The equation that emerges shows the difference in GALVANI potentials at the interface in equilibrium. Different examples are studied below.

- Let us first study the simplest interfacial reaction, i.e., the exchange of one species between two phases. One has to distinguish whether the exchanged particle is charged or not. First let us look at the exchange of molecules M, as shown in figure 3.5.

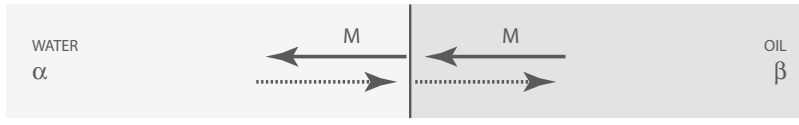


Figure 3.5 - Exchange equilibrium of a molecule at an interface water | oil

For instance, this example relates to the equilibrium found between two solutions containing alcohol in water and alcohol in oil.

The surface reaction is the following: $\underset{\alpha}{M} \rightleftharpoons \underset{\beta}{M}$

The thermodynamic equilibrium results in the following equation:

$$\Delta_r \widetilde{G} = \widetilde{\mu}_{M_\beta} - \widetilde{\mu}_{M_\alpha} = 0$$

or $$\widetilde{\mu}_{M_\beta} = \widetilde{\mu}_{M_\alpha}$$

and since it is a molecule (neutral species): $$\mu_{M_\beta} = \mu_{M_\alpha}$$

- Secondly, let us now consider the exchange of one particular charged species, assuming that it is the only reactive phenomenon at the interface. This is the case, for example, of an AgCl solid crystal in equilibrium with an aqueous solution containing Ag^+ ions, as shown in figure 3.6.

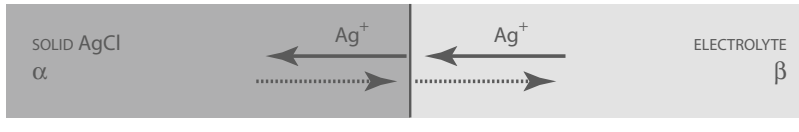


Figure 3.6 - Exchange equilibrium of Ag^+ ions between a crystal of AgCl and an aqueous solution

The surface reaction is the following: $\underset{\alpha}{Ag^+} \rightleftharpoons \underset{\beta}{Ag^+}$

The thermodynamic equilibrium results in the following equation:

$$\Delta_r \widetilde{G} = \widetilde{\mu}_{Ag^+_\beta} - \widetilde{\mu}_{Ag^+_\alpha} = 0$$

or, since Ag^+ is a cation: $$\mu_{Ag^+_\beta} + \mathcal{F}\varphi_\beta = \mu_{Ag^+_\alpha} + \mathcal{F}\varphi_\alpha$$

The difference in GALVANI potentials between the two phases is therefore:

$$\varphi_\beta - \varphi_\alpha = \frac{1}{\mathcal{F}}\left(\mu_{Ag^+_\alpha} - \mu_{Ag^+_\beta}\right)$$

- Now let us take the example of the phase transfer reaction between an aqueous solution containing potassium chloride and a solution containing crown ether L (a complexing agent of K^+ ions) in an organic solvent, as shown in figure 3.7 [34].

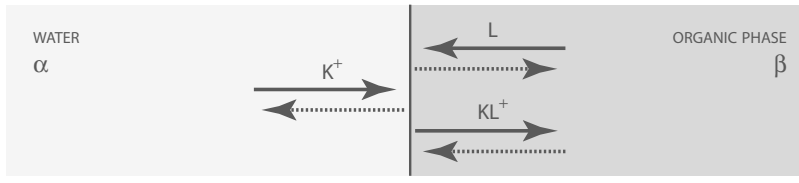


Figure 3.7 - Complexation equilibrium at a water | organic phase interface

The surface reaction is the following:

$$\underset{\alpha}{K^+} + \underset{\beta}{L} \rightleftharpoons \underset{\beta}{KL^+}$$

The thermodynamic equilibrium results in the following equation:

$$\tilde{\mu}_{L_\beta} + \tilde{\mu}_{K^+_\alpha} = \tilde{\mu}_{KL^+_\beta}$$

or:

$$\mu_{L_\beta} + \mu_{K^+_\alpha} + \mathcal{F}\varphi_\alpha = \mu_{KL^+_\beta} + \mathcal{F}\varphi_\beta$$

The difference in internal potentials (or GALVANI) between the two phases is therefore:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu_{KL^+_\beta} - \mu_{K^+_\alpha} - \mu_{L_\beta})$$

- Finally, let us consider the example of the redox equilibrium between ferric and ferrous ions at a platinum electrode, as shown in figure 3.8.

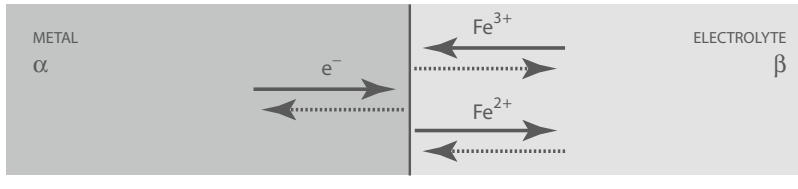


Figure 3.8 - Redox equilibrium at a metal | electrolyte interface

The surface reaction is the following:

$$\underset{\beta}{Fe^{2+}} \rightleftharpoons \underset{\alpha}{e^-} + \underset{\beta}{Fe^{3+}}$$

The thermodynamic equilibrium results in the following equation:

$$\tilde{\mu}_{e_\alpha} + \tilde{\mu}_{Fe^{3+}_\beta} = \tilde{\mu}_{Fe^{2+}_\beta}$$

or:

$$\mu_{e_\alpha} - \mathcal{F}\varphi_\alpha + \mu_{Fe^{3+}_\beta} + 3\mathcal{F}\varphi_\beta = \mu_{Fe^{2+}_\beta} + 2\mathcal{F}\varphi_\beta$$

The difference in internal potentials (or GALVANI) between the two phases is expressed in the following equation:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu_{Fe^{3+}_\beta} + \mu_{e_\alpha} - \mu_{Fe^{2+}_\beta})$$

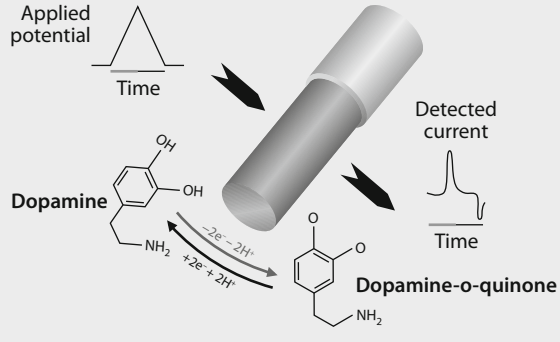
[34] *This kind of interface is found in some specific electrodes with a liquid (or polymer) membrane containing complexes. Valinomycin is a complexing compound which is selective to K^+ ions. It is used in membranes of selective electrodes based on PVC.*

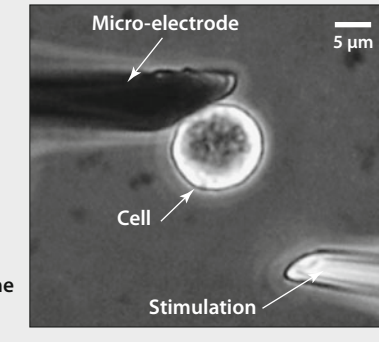
ELECTROCHEMISTRY AND NEUROBIOLOGY

Document written with the kind collaboration of S. ARBAULT, of the Department of Chemistry, at the Ecole Normale Supérieure in Paris, France

Electrochemistry made its first contribution to biology and medicine with the works of L. CLARK in the early 1950's. He came up with the first electrochemical sensor based on an amperometric method in order to measure out dissolved oxygen in water, especially in biological fluids. It was only after the early 1970's that on the back of this type of device, other electrochemical biosensors were developed (specifically for detecting glucose, or chemical neurotransmitters). In the case of neurobiology, these developments reflected the need to understand how mechanisms worked for the chemical transmission of neuronal information, a field of study which has been in evidence since the late 1960's.

Moreover, the 1970's marked the development of new electrochemical tools, including microelectrodes. These tools quickly found a new field of applications: *in vivo* measurements. Indeed, if you take the case of carbon fibers measuring from 5 to 30 µm in diameter, you can see how microelectrodes share the same dimensions as living cells. They therefore have a slightly invasive effect when inserted into cellular tissue. Fundamental studies have also demonstrated how during analysis the time constants offered by microelectrodes are significantly lower than those offered by conventional millimetre electrodes. When a very high voltammetry scanning rate is applied (several hundreds of volts per second) it is possible to study transient phenomena in the range of milliseconds. Several research groups have developed this type of analysis using carbon microelectrodes to understand the mechanisms behind how dopamine, a major neurotransmitter in the central nervous system, is released. The studies which were pioneered on slices of rodent brain were then able to be carried out *in vivo* on the brains of anaesthetized animals.





The principle of detecting dopamine at the surface of a carbon fiber microelectrode and the view under a microscope of a detection experiment carried out on a single cell

*On the left, dopamine detection: reprinted from Trends Anal. Chem., **22**, PHILLIPS P.E.M. and WIGHTMAN R.M., Critical guidelines for validation of the selectivity of in-vivo chemical microsensors, 509-514, © 2003, with permission from Elsevier ; On the right, microelectrode: AMATORE C., ARBAULT S., BONIFAS I., BOURET Y., ERARD M. and GUILLE M.: Dynamics of full fusion during vesicula exocytotic events: release of adrenaline by chromaffin cells. ChemPhysChem. 2003. **4**. 147-154. © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)*

During the 1980-1990's science highlighted and demonstrated the essential neurobiological mechanisms behind dopamine systems. The research developed by R.M. WIGHTMAM and his team contributed greatly to this domain, in particular in showing the process of reuptake by neurons of dopamine that is released in excess quantities by the synapse. This phenomenon has been quantified, and studied kinetically and pharmacologically. It also helped to understand the cocaine-induced delay effects on the release of dopamine in the zones of brain related to learning activities, memory and sensations of pleasure.

Thank to recent technical developments, particularly in the field of miniaturizing measurement tools and data transfer *via* wireless communication, tests can now even be carried out on animals which are awake and mobile. Today it is possible to make a link between measurements in brain activity and an animal behaviour when it is stimulated by the presence of a fellow creature of the opposite sex or when it enters a process of drug addiction.

However, these *in vivo* studies are based on the principle of detection experiments carried out in the brain's extracellular fluid. They therefore do not allow for the mechanism of the chemical transmission of nervous stimuli to be analysed. In the early 1990's, several teams were able to study this phenomenon on a living cell by placing the surface of an electrochemical sensor, such as a carbon microelectrode, a few micrometers away from a cell membrane. Currently, when the results of this detection process are analysed in quantitative terms, fluxes of about a thousand molecules per millisecond are shown. Therefore, the various kinetic steps involved in the release process, which is called exocytosis, can be then differentiated and analysed in terms of the biological and physicochemical parameters of the cell and its environment.

Due to its advantages and synergy with other research techniques in membrane processes, this technique has been incorporated in neurobiology laboratories and has been used to study exocytosis of several types of neurotransmitters as well as the release processes of many other molecules of biological interest. These molecules can be neuromodulators (nitrogen monoxide, ascorbic acid, etc.), metabolites of cellular energy (oxygen, ATP, glucose, etc.), or even highly reactive molecules derived from immune defence processes (hydrogen peroxide, peroxynitrite, etc.).

Finally, over and above its significant contribution to the discovery and understanding of fundamental neurobiological mechanisms, this domain of electrochemistry has possibly achieved its greatest success in its use in clinical practice and operating theatres. Today electrochemical sensors are routinely used to investigate cerebral pathology in patients following a stroke or those with other suspected brain abnormalities.

These equations only make links between quantities in equilibrium. For charged species, they link the difference in GALVANI potentials to the chemical compositions of the two phases in equilibrium. Most of the time, these equations are insufficient because they don't make the connection between the system's initial conditions and the equilibrium state that is finally reached. Taken from this point of view, it becomes all the more important to make the distinction between charged species and neutral species, as shown in the following paragraphs.

3.3.3 - THERMODYNAMIC EQUILIBRIUM AT A REACTIVE INTERFACE INVOLVING A SINGLE REACTION BETWEEN NEUTRAL SPECIES

Here we will present the simplest case of molecule exchange between two immiscible phases (see previous figure 3.5). Thermodynamic equilibrium is established from any initial state by means of exchanging molecules through the junction, until the chemical potentials are equal, i.e., by transient molecule fluxes. Take the example of a membrane which only allows molecules M to be exchanged, and which separates two solutions, α and β, with the following initial condition [35]:

$$\mu_{0_\alpha} > \mu_{0_\beta}$$

When the two parts of the system are placed in contact, then the molecules M move from the solution with the highest chemical potential (α) towards the solution with the lowest chemical potential (β), as shown in figure 3.9.

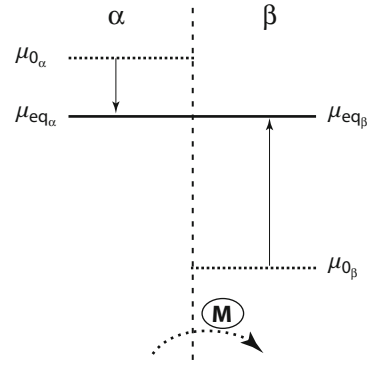


Figure 3.9 – Junction with single exchange of molecule M

In this case, the thermodynamic equilibrium is reached once the molecule being exchanged has equal chemical potential on both sides of the membrane. This generally requires a large number of molecules to be displaced, as well as a large change in the chemical potentials of the species M in both phases between the initial state and the equilibrium state. It may therefore take a long time to reach this equilibrium state. In

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[35] Be careful with the different symbols used: μ_{0_α} (initial value) and μ°_α (standard value) should not be confused.

equilibrium, the following equation indicates the activities ratio between the two phases for the molecule being exchanged [35]:

$$\ln\left(\frac{a_{\mathrm{eq}_\alpha}}{a_{\mathrm{eq}_\beta}}\right) = \frac{\mu^\circ{}_\alpha - \mu^\circ{}_\beta}{\mathrm{R}T}$$

In the particular case where both solutions in contact are in the same solvent [36], then the standard chemical potentials are identical in both phases. Here, the thermodynamic equilibrium is then achieved once the solutions are identical on both sides of the membrane, since in equilibrium the activities of the molecule being exchanged must be equal in both phases.

In more general cases the activities ratio in the two media in equilibrium is called the partition coefficient. This can hold very different values (varying especially from 1) depending on the solvents used, as shown in examples in table 3.3.

Table 3.3 - Examples of partition coefficients

Molecule	Solvent	$a_{\mathrm{solvent}}/a_{\mathrm{water}}$
diiode	CCl_4	10^2
salicylic acid	$CHCl_3$	2
decanoïc acid	$CHCl_3$	2×10^4
oxine	$CHCl_3$	5×10^2

3.3.4 - THERMODYNAMIC EQUILIBRIUM AT A REACTIVE INTERFACE INVOLVING A SINGLE REACTION BETWEEN CHARGED SPECIES

Firstly we will study the basic case of only one charged species being exchanged at the interface between two phases. Then we will go on to examine the most typical case found in electrochemistry of a redox reaction at a metal | electrolyte interface.

3.3.4.1 - JUNCTION WITH THE EXCHANGE OF A SINGLE CHARGED SPECIES

The thermodynamic equilibrium is reached by exchanging charges through the junction, up until the point where the electrochemical potentials of the ion being exchanged are equal on both sides of the junction. This process generates a transient current. For example, imagine a membrane which only allows M^+ cations to be exchanged. As shown in figure 3.10, the membrane separates two solutions, α and β, where M^+ starts out initially with different electrochemical potentials, with the following condition:

$$\tilde{\mu}_{0_\alpha} > \tilde{\mu}_{0_\beta}$$

[36] *Here one can imagine a system with a membrane of minimal thickness, which would prevent the two solutions from being rapidly mixed via convection.*

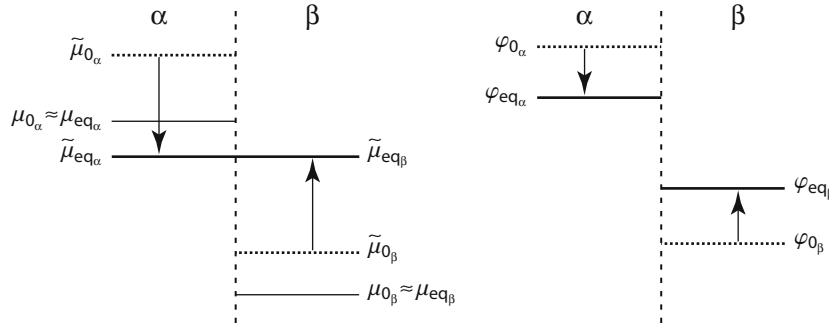

Figure 3.10 - Junction showing the single exchange of a M^+ cation from phase α to phase β
Changes in chemical and electrochemical potentials (diagram on the left) and in GALVANI potentials (diagram on the right) between initial and equilibrium states

When the system is set in contact, M^+ cations can be seen to move from the solution with the highest electrochemical potential (α) towards the solution with the lowest electrochemical potential (β). Given that conducting media can only be charged at the surface, then the charge movement through the junction results in a shift in the surface charge excess of both phases, therefore resulting in a significant variation in electric potentials (internal and external). In thermodynamic equilibrium one can see a difference *a priori* between the GALVANI potentials in each of the two phases. This is called the junction voltage.

It is reasonable to assume [37] ***that during the mass exchange process between two media, where at the outset there is a difference in the electrochemical potential of the species being exchanged, the process of reaching equilibrium leads to:***

- ***a significant concentration variation between the initial state and the equilibrium state for a molecule exchange (neutral species);***
- ***a negligible concentration variation for the exchange of a single charged species, yet a significant variation in the junction voltage.***

Above all, one must keep in mind the following significant consequence for thermodynamic laws at such interfaces: for exchanges involving a single charged species, the concentrations, and therefore the chemical potentials, remain unchanged between the system's initial and equilibrium states. Therefore, the junction voltage in equilibrium is expressed as a function of the chemical potentials in the two phases, through the following equation:

$$\varphi_\alpha - \varphi_\beta = \frac{\mu_{i\beta} - \mu_{i\alpha}}{z_i \mathcal{F}}$$

with the chemical potentials corresponding to the initial compositions of the phases α and β. This junction voltage is generally non-zero. Moreover, from a practical point of view, it is generally reached quite rapidly because to establish this thermodynamic equilibrium very few charges are required to move.

---

[37] Appendix A.3.4 focuses on examples that give the calculations in the case of fictive systems, though also highlighting this difference in behaviour between molecules and charged species.

Two particular examples of such single-exchange junctions are given below:

- the metallic junction: here only electrons are exchanged between two different metals at room temperature. An equilibrium state is rapidly reached (about 10^{-18} s) when two different metals are set in contact [38]. In equilibrium state, the FERMI levels are identical, as are the electrons' electrochemical potentials. This results in the following electric junction voltage:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathscr{F}}(\mu_{e_\alpha} - \mu_{e_\beta}) = \text{Cst}$$

  It is not possible to obtain such a junction voltage *via* experiment. The voltage measurement taken with a voltmeter always corresponds to a measurement between two identical metals (the internal terminal connections of the voltmeter). Therefore, for a system with a metallic junction, the voltage measurement always includes at least two electronic junctions, and only the algebraic sum of the two junction voltages is measurable. On a chain of electronic conductors at the same temperature, the voltage measured is therefore always zero. Nevertheless, if the junctions involved in the chain are not at the same temperature, then a non-zero voltage can be measured (generally about 10 µV for a temperature difference of 1 °C): this is the operating principle of a thermocouple.
- the single-exchange ionic junction: an example of this type can be found in the contact made between an electrolyte solution and a barely soluble ionic conducting solid, with a common ion. Equally, another example could even be two electrolyte solutions with different concentrations separated by a membrane that only lets one of the ions through.

  Equilibrium is rapidly reached and the ionic junction voltage is given by:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{z_i \mathscr{F}}(\mu_{i_\beta} - \mu_{i_\alpha}) = \underbrace{\frac{1}{z_i \mathscr{F}}(\mu^\circ{}_{i_\beta} - \mu^\circ{}_{i_\alpha})}_{\text{Cst}} + \frac{RT}{z_i \mathscr{F}} \ln \frac{a_{i_\beta}}{a_{i_\alpha}}$$

  The order of magnitude of this type of junction voltage can be relatively high (mV to V). However, one should keep in mind that it cannot be measured directly, just as in the case of electronic junctions.

Now imagine a junction where there is a selective membrane separating two solutions in the same solvent with different concentrations. Given that the standard chemical potentials are equal, then the constant is zero in the equation for the junction voltage, and the voltage is therefore directly linked to the activities ratio of the ion being exchanged between the two solutions.

An example of a single-exchange ionic junction can be found in the contact between a silver chloride ionic solid which is poorly soluble in water (phase α, including two sub-lattices of Ag^+ and Cl^- ions) and an aqueous solution of silver chloride (phase β, containing solvated Ag^+ and Cl^- ions). In fact, even if there are two types of ions common to both phases, only Ag^+ ions are mobile in the solid phase. At thermodynamic equilibrium, the following equation can be written (relating to the Ag^+ exchange reaction):

[38] The same phenomenon can be seen involving two metals of the same chemical nature but with different structures, such as two silver single-crystal faces: Ag (100) and Ag (110).

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu^\circ_{Ag^+_\beta} - \mu^\circ_{Ag^+_\alpha}) + \frac{RT}{\mathcal{F}} \ln \frac{a_{Ag^+_\beta}}{a_{Ag^+_\alpha}}$$

Following the definition of standard states in solid AgCl, $a_{Ag^+_\alpha} = a_{Cl^-_\alpha} = a_{AgCl_\alpha} = 1$. The voltage is therefore:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu^\circ_{Ag^+_\beta} - \mu^\circ_{Ag^+_\alpha}) + \frac{RT}{\mathcal{F}} \ln a_{Ag^+_\beta}$$

The junction voltage can also be presented in an equation as a function of the activity of Cl^- ions in the solution. For these purposes, one uses the solubility equilibrium of AgCl:

$$AgCl_\alpha \rightleftharpoons Ag^+_\beta + Cl^-_\beta$$

$$\ln(a_{Ag^+_\beta} a_{Cl^-_\beta}) = \ln K_{eq} = \frac{\mu^\circ_{AgCl_\alpha} - \mu^\circ_{Ag^+_\beta} - \mu^\circ_{Cl^-_\beta}}{RT} = \frac{\mu^\circ_{Ag^+_\alpha} + \mu^\circ_{Cl^-_\alpha} - \mu^\circ_{Ag^+_\beta} - \mu^\circ_{Cl^-_\beta}}{RT}$$

Combining the previous two equations gives the following:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu^\circ_{Cl^-_\alpha} - \mu^\circ_{Cl^-_\beta}) - \frac{RT}{\mathcal{F}} \ln(a_{Ag^+_\beta} a_{Cl^-_\beta}) + \frac{RT}{\mathcal{F}} \ln a_{Ag^+_\beta}$$

and therefore in thermodynamic equilibrium, the following is obtained:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu^\circ_{Cl^-_\alpha} - \mu^\circ_{Cl^-_\beta}) - \frac{RT}{\mathcal{F}} \ln a_{Cl^-_\beta}$$

This last equation is identical to the one that would be obtained if Cl^- ions were exchanged instead of Ag^+ ions [39]. Thermodynamic measurements cannot distinguish these different mechanisms, therefore they do not enable one to determine the nature of the species being exchanged.

The junction voltage of this type of interface (single exchange) is non-zero in equilibrium. Assuming that the activity coefficients of the anions and cations are equal in same phase [40] and taking into account the electroneutrality of the media α and β, then this junction voltage can be written in the following simple equation:

$$\varphi_\alpha - \varphi_\beta = \frac{1}{2\mathcal{F}}(\mu^\circ_{Ag^+_\beta} - \mu^\circ_{Cl^-_\beta} - \mu^\circ_{Ag^+_\alpha} + \mu^\circ_{Cl^-_\alpha})$$

3.3.4.2 - REACTIVE ELECTROCHEMICAL INTERFACE WITH A SINGLE REACTION

The same reasoning can be applied to the case of an electrochemical interface, i.e., for a metallic phase in contact with an electrolyte containing electroactive species that are able to perform an electrochemical reaction at the interface. Furthermore, just as in the case of single-exchange junctions described above, here we will assume that the process of reaching equilibrium at a reactive electrochemical interface, whatever its initial state, only leads to negligible concentration variations [41]. In other words a very small quantity of species is transformed, yet a significant variation can be seen in the interfacial voltage.

---

[39] Section 3.4.2.2 outlines other examples of thermodynamic equilibrium equations for this system. Moreover, keep in mind that the GALVANI voltage between the two sides of an interface cannot be obtained in an experiment. The activity of a single ion appears in the equation, and is also a non-measurable quantity (see appendix A.3.2).

[40] Assuming that the cation and anion activity coefficients are equal, which is in the case particular in the context of the DEBYE-HÜCKEL theory, simplifies the calculation yet without making the reasoning any less general.

[41] Appendix A.3.4 highlights this property using the example of calculations on fictive systems.

Let us remember the following main consequence at these interfaces according to thermodynamic laws: the concentrations and therefore the chemical potentials are not modified by the process of reaching equilibrium.

Therefore, for example, if an inert electrode is immersed in an aqueous solution containing Fe^{2+} and Fe^{3+} ions, the potential difference between the metal and the solution spontaneously adopts the value given by thermodynamics. Moreover, in practical terms, equilibrium is generally reached quite rapidly, since very few charges are required to move.

In the case of any redox couple, the equilibrium interfacial voltage is given by the following equation, which is close to the usual expression of the NERNST law:

$$\varphi_{metal} - \varphi_{electrolyte} = \frac{1}{\mathscr{F}}\left(\mu_{e_{metal}} + \frac{1}{\nu_e}\sum_i \nu_i \mu_i \right) = Cst + \frac{RT}{\nu_e \mathscr{F}} ln \prod_i a_i^{\nu_i}$$

where ν_i is the algebraic stoichiometric number of species i in the redox half-reaction and the activities are those of the compounds in the initial state. Given that the coefficient ν_e is algebraic in this equation, the sign for the interfacial voltage is not dependent on the direction chosen to write the reaction. The chemical potential of electrons, which is not zero, is included in the constant. As in the case of the previous junctions, it is not possible to directly measure this voltage during an experiment nor is it possible to have tables giving values for the constant for each different type of interface[42]. Seen from this point of view, the equation does not demonstrate the NERNST law (see section 3.4.1.2), which indicates a measurable quantity for a complete electrochemical chain, and not just for a single interface.

3.3.5 - MULTI-REACTIVE JUNCTION OR INTERFACE

When several reactive phenomena co-exist at the same interface, it is necessary to express the equilibrium state by writing that the electrochemical GIBBS energies of reaction are zero for each phenomenon. In particular, keep in mind that when writing the equation for a combination of different equilibria in the form of a single overall equilibrium, this does not provide all the information necessary to give a thorough description of the interface equilibrium, as explained below in the example of multiple junctions.

As for a junction where several species can be exchanged, the ionic junction voltage in equilibrium relates to the differences between the chemical potentials of each charged species, based on the following equations:

$$\begin{aligned} \forall\, i \qquad \varphi_\alpha - \varphi_\beta &= \frac{1}{z_i \mathscr{F}} (\mu_{i_\beta} - \mu_{i_\alpha}) \\ &= \frac{1}{z_i \mathscr{F}} (\mu^\circ{}_{i_\beta} - \mu^\circ{}_{i_\alpha}) + \frac{RT}{z_i \mathscr{F}} \ln \frac{a_{i_\beta}}{a_{i_\alpha}} \\ &= \mathrm{Cst}_i + \frac{RT}{z_i \mathscr{F}} \ln \frac{a_{i_\beta}}{a_{i_\alpha}} \end{aligned}$$

[42] For example, remember that the electrochemical potential of electrons in a metal is a measurable quantity and that their chemical potential is not measurable (see section 3.2.2).

Therefore, relationships are formed between the chemical potentials of two types of exchanged species, X^{z_i} and Y^{z_j},

$$z_i\,\mu_{j\beta} - z_j\,\mu_{i\beta} = z_i\,\mu_{j\alpha} - z_j\,\mu_{i\alpha}$$

and corresponding to the following chemical equilibrium:

$$z_i\,Y^{z_j}{}_\alpha + (-z_j)\,X^{z_i}{}_\alpha \rightleftharpoons z_i\,Y^{z_j}{}_\beta + (-z_j)\,X^{z_i}{}_\beta$$

Depending on the value of the equilibrium constant, the equilibrium state is more or less different from the initial state, and is reached after a transfer of variable amounts of species. Two extreme examples can be given:

- two solutions containing electrolytes with different concentrations in the same solvent, separated by a non-selective membrane;

  Let us imagine the contact between two aqueous solutions containing sodium chloride, each with a different concentration (C_α and C_β). The activity coefficients for the anions and cations in the same medium are set as equal. This is a valid approximation if applying the DEBYE-HÜCKEL theory, as it is a way of simplifying the calculations without distorting the reasoning in any way. The ion activities in each of the two phases are denoted respectively by a_α and a_β.

  In thermodynamic equilibrium,

  $$\varphi_\alpha - \varphi_\beta = 0 + \frac{RT}{\mathcal{F}}\ln\frac{a_\beta}{a_\alpha} \qquad \text{for } Na^+$$

  $$\varphi_\alpha - \varphi_\beta = 0 - \frac{RT}{\mathcal{F}}\ln\frac{a_\beta}{a_\alpha} \qquad \text{for } Cl^-$$

  Therefore, when this system is in equilibrium it results in the following equation:

  $$\varphi_\alpha = \varphi_\beta \quad \text{and} \quad a_\alpha = a_\beta$$

  The equilibrium is only reached once the GALVANI potential and the chemical potentials of each type of species are both identical in the two phases. The junction voltage is therefore zero in equilibrium, which indeed can take a long time to reach.

- two solutions containing the same electrolyte in two different solvents.

  For example, consider the interface between two types of polymer electrolytes which are both different in nature, yet contain the same type of ions (e.g. the cation Li^+ and the anion bis-(trifluoromethanesulfonyl)-imide written $TFSI^-$). As above, the activity coefficients of the anions and cations in the same medium are set as equal. The ion activities will be denoted by a_α and a_β in each of the two phases.

  In thermodynamic equilibrium,

  $$\varphi_\alpha - \varphi_\beta = \frac{1}{\mathcal{F}}(\mu^\circ_{Li^+_\beta} - \mu^\circ_{Li^+_\alpha}) + \frac{RT}{\mathcal{F}}\ln\frac{a_\beta}{a_\alpha} = \frac{1}{\mathcal{F}}(\mu^\circ_{TFSI^-_\alpha} - \mu^\circ_{TFSI^-_\beta}) - \frac{RT}{\mathcal{F}}\ln\frac{a_\beta}{a_\alpha}$$

  so,

  $$2RT\ln\frac{a_\beta}{a_\alpha} = \mu^\circ_{Li^+_\beta} + \mu^\circ_{TFSI^-_\beta} - \mu^\circ_{Li^+_\alpha} - \mu^\circ_{TFSI^-_\alpha} = Cst$$

  This equation is nothing more than the law of mass action applied to the following equilibrium:

  $$Li^+{}_\alpha + TFSI^-{}_\alpha \rightleftharpoons Li^+{}_\beta + TFSI^-{}_\beta$$

  and there is a non-zero junction voltage at equilibrium:

  $$\varphi_\alpha - \varphi_\beta = \frac{1}{2\mathcal{F}}(\mu^\circ_{Li^+_\beta} - \mu^\circ_{TFSI^-_\beta} - \mu^\circ_{Li^+_\alpha} + \mu^\circ_{TFSI^-_\alpha})$$

In this case, when the multiple junction reaches equilibrium, the latter's junction voltage is not zero.

3.4 - ELECTROCHEMICAL SYSTEMS IN EQUILIBRIUM

The equilibrium state of electrochemical cells at open circuit is described below. This section will therefore be focusing on the equilibrium state of these systems when no current is allowed to be supplied to an external circuit. When dealing with an electrochemical cell that enables electric energy exchange with the environment (for instance when cell terminals are connected by a resistor) the system shifts towards a new equilibrium state, which will not be described here.

Remember that in an electrochemical chain in thermodynamic equilibrium, the conducting volumes are equipotential and the overall equilibrium voltage is the sum of all the potential differences at the interfaces [43]. In order to be rigorous when writing the thermodynamic equations for electrochemical cells in equilibrium, it is particularly vital in this section to remember to include the terminal electronic junctions which are inevitable during experimental measurements using a voltmeter. In fact, one must keep in mind that a voltmeter's internal connections are always made of the same material. The measurement corresponds to the VOLTA potential difference, which is equal to the GALVANI voltage for two identical materials. For example, in a DANIELL cell the voltage measured corresponds to the following:

$$Cu' \,|\, Zn \,|\, ZnSO_4 \text{ aqueous solution } ||\, CuSO_4 \text{ aqueous solution } |\, Cu$$

Numerous applications have been developed in the field of chemical analysis using potentiometric measurements as indicators, including the production of potentiometric sensors and titration devices. In this chapter, we will focus on the defining principles of these potentiometric methods at zero current when these systems are in thermodynamic equilibrium, which is not necessarily true for all potentiometric measurements. In particular, the following description is confined to electrochemical cells with no ionic junction. In practice, these results will also be applied to many experimental cases in which ionic junction voltages can be neglected [44].

3.4.1 - ELECTROCHEMICAL CELLS WITH NO IONIC JUNCTION

This section studies systems without any ionic junction. Depending on the particular redox couples in question, this category may correspond to an experimental system or to a system which cannot be built, yet whose thermodynamic characteristics can still be defined nonetheless.

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[43] The distribution of potentials in an electrochemical system in equilibrium is shown in section 2.1.1.

[44] Appendix A.3.2 addresses these questions in more thorough detail: even if the ionic junction voltage is negligible in numerical terms, it may nonetheless be important to consider it from a fundamental point of view.

3.4.1.1 - THERMODYNAMIC REACTION QUANTITIES

For simple electrochemical cells, the electromotive force, emf, can be easily linked to the thermodynamic reaction quantities by using the same equations as those previously demonstrated for GALVANI voltages at an interface in equilibrium.

For example for the following electrochemical cell:

Cu' | Pt, H_2 | aqueous solution containing H_2SO_4 and $CuSO_4$ | Cu

the equilibrium at both electrochemical interfaces results in:

$$\varphi_{Cu} - \varphi_{solution} = \frac{1}{2\mathcal{F}}\left(2\mu_{e_{Cu}} + \mu_{Cu^{2+}} - \mu_{Cu}\right)$$

$$\varphi_{Pt} - \varphi_{solution} = \frac{1}{\mathcal{F}}\left(\mu_{e_{Pt}} + \mu_{H^+} - \frac{1}{2}\mu_{H_2}\right)$$

The equilibrium at the Cu' | Pt electronic junction equalises the electrochemical potentials of the electrons in both metals ($\widetilde{\mu}_{e_{Pt}} = \widetilde{\mu}_{e_{Cu'}}$) and therefore the previous equation can be written as a function of the parameters of Cu':

$$\varphi_{Cu'} - \varphi_{solution} = \frac{1}{\mathcal{F}}\left(\mu_{e_{Cu'}} + \mu_{H^+} - \frac{1}{2}\mu_{H_2}\right)$$

Here, when a rigorous demonstration is required, one can see quite how important it is to write the complete chain with the terminal electronic junctions. Indeed, since the electrons' chemical potential terms concern connexions that are made of the same metal, these terms, which cannot be obtained *via* experiment, end up cancelling each other out ($\mu^\circ_{e_{Cu}} - \mu^\circ_{e_{Cu'}}$). Consequently, all that remains in the voltage expression is the chemical potentials of chemical compounds.

By writing the emf with Cu as the working electrode and Cu' as the counter-electrode, $U = \varphi_{Cu} - \varphi_{Cu'}$, the following equation is obtained:

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

with the GIBBS energy of reaction written for the following overall reaction:

$$Cu^{2+} + H_2 \rightleftharpoons Cu + 2H^+$$

Note that the writing convention above is used to clearly define the sign of the quantities in question.

To take a more general case, let us imagine an electrochemical cell, which may possibly be fictive, where the sum of the ionic junction voltages is zero. This would give the following equations:

$$\Delta_r \boldsymbol{G} = \nu_e \mathcal{F} \boldsymbol{U}$$

$$\Delta_r \boldsymbol{S} = -\nu_e \mathcal{F}\left(\frac{\partial \boldsymbol{U}}{\partial \boldsymbol{T}}\right)_P$$

$$\Delta_r \boldsymbol{H} = \nu_e \mathcal{F}\left[\boldsymbol{U} - \boldsymbol{T}\left(\frac{\partial \boldsymbol{U}}{\partial \boldsymbol{T}}\right)_P\right]$$

whereby ν_e, is the algebraic stoichiometric number of electrons in the redox couple's half-reaction at the working electrode, and U is the difference in internal potentials between the working electrode and the counter-electrode, $U = \varphi_{WE} - \varphi_{CE}$.

Note that the previous equations imply that the reaction is written in the direction of the redox half-reaction at the working electrode. Yet this choice is nothing more than a convention to help ensure there are no ambiguities over the signs. This choice in direction does not by any means represent a real reaction. Keep in mind that these relationships are valid in thermodynamic equilibrium, therefore when no current flows. Therefore in particular the terms cathode and anode have no meaning in this case.

When the different species involved in the overall reaction are taken in their standard state, then a standard emf, $U°$, can also be defined:

$$U° = \frac{\Delta_r G°}{\nu_e \mathcal{F}}$$

A typical order of magnitude for standard GIBBS energy of reaction is 100 kJ mol^{-1}. At room temperature, this equates to a standard voltage of about one volt.

Note that for redox couples involving H^+ or OH^- in their redox half-reaction, it is vital to specify whether the standard state is set for H^+ or OH^-. In other words, this means that the relevant pH has to be specified to define $U°$:

$pH = 0$	standard conditions for H^+	$(a_{H^+} = 1)$
$pH = 14$	standard conditions for OH^-	$(a_{OH^-} = 1)$

Remember that in thermodynamic data tables (standard GIBBS energies and enthalpies of formation) the following conventions are used:

- the standard GIBBS energy of formation (or chemical potential) of all simple elements is zero, at any temperature;
- the standard GIBBS energy of formation (or chemical potential) of protons in a solution is zero:

$$\forall\, T \qquad \mu°_{H^+} = 0 \text{ J mol}^{-1}$$

For example, the standard emf of the following cell, at $pH = 0$, can be given using thermodynamic data (assuming the ionic junction voltage is zero [44]):

Pt | Cu | aqueous solution containing Cu^{2+} | | aqueous solution containing Mn^{2+}, MnO_4^- and H^+ | Pt'

The thermodynamic data give these values at 25 °C, following the convention $\mu°_{H^+} = 0$ J mol^{-1}:

$$\mu°_{H_2O} = -237.2 \text{ kJ mol}^{-1} \qquad \mu°_{MnO_4^-} = -447.3 \text{ kJ mol}^{-1}$$

$$\mu°_{Mn^{2+}} = -228.1 \text{ kJ mol}^{-1} \qquad \mu°_{Cu^{2+}} = +65.5 \text{ kJ mol}^{-1}$$

The two redox half-reactions are:

$$\begin{array}{rcl} 5\,e^- + MnO_4^- + 8\,H^+ & \rightleftharpoons & Mn^{2+} + 4\,H_2O \\ (\qquad\qquad Cu & \rightleftharpoons & Cu^{2+} + 2\,e^- \qquad\qquad)\times 5/2 \\ \hline \frac{5}{2}\,Cu + MnO_4^- + 8\,H^+ & \rightleftharpoons & Mn^{2+} + 4\,H_2O + \frac{5}{2}\,Cu^{2+} \end{array}$$

For this equilibrium, by choosing the Pt' electrode as the working electrode, you get the following equation:

$$\Delta_r G° = -5\mathcal{F}U°$$

Consequently, when taking into account that copper is a simple element ($\mu°_{Cu} = 0$ J mol^{-1}), the emf at 25 °C is:

$$U° = -\frac{1}{5\mathcal{F}}\left(\mu°_{Mn^{2+}} + 4\,\mu°_{H_2O} + \frac{5}{2}\mu°_{Cu^{2+}} - \mu°_{MnO_4^-}\right) = +1.17 \text{ V}$$

CORROSION OF REINFORCED CONCRETE

Document written with the kind cooperation of E. CHAUVEAU, R&D engineer for the company Ugitech, based in Ugine, France

The HASSAN II mosque in Casablanca was built in the 1990's. The architect, inspired by a verse from the Koran that says '*God's throne was on water*', designed a luxurious building with two thirds of its total surface above the waters of the Atlantic Ocean. The foundations, which were exposed to the effects of sea water and wind, required 26 000 m^3 of concrete and 59 000 m^3 of rip-rap. By 1998, signs of the building degradation began to show mainly related to corrosion of the structures submitted to wave movements and contact with sea water.

Degradation shown on a pillar due to the marine environment *(© Christine RAYNAUD - BTPM)*

The mechanisms which led to this highly rapid deterioration process are briefly laid out below. Concrete is made up of a mixture of cement, sand and aggregates (stones and gravel). The process which allows concrete to set is caused by the hydration of calcium orthosilicate, based on the following reaction:

$$4\ H_2O + 2\ Ca_2SiO_4 \rightleftharpoons Ca_3Si_2O_7{,}3\ H_2O + Ca(OH)_2$$

This reaction explains the basic character of concrete. Because concrete has poor mechanical tensile properties, the idea of introducing a mesh of carbon steel bars (called rebars) emerged in 1870. The concrete is separated from each bar by an interface layer of cement, whose porosity can vary mainly depending on the precise composition of the concrete as well as on the water content of the structure. Care is usually taken to leave a minimum thickness of 30 mm of concrete between each steel bar close to the surface and the external surface of the structure. In fact, when concrete is exposed to humid conditions, water penetrates by means of capillarity, and there is a risk that the hydrated area may eventually spread as far as the steel bars. When this occurs, a second mechanism usually comes into play which helps prolong the durability of the structures: due to the chemical properties particular to concrete, the pH in the damp zones is close to 12, meaning the steel bars become coated with a passivating and protecting layer of FeOOH.

The two major causes of the more or less accelerated corrosion of the bars are:

- if there are high atmospheric levels of carbon dioxide, the gas diffuses through the porous hydrated zone, thus causing the pH to drop locally. From a pH value of below about 9, the metal protection stops because FeOOH becomes hydrated to form non-protecting $Fe(OH)_3$;

- if the surrounding medium is charged with chloride ions (saline water), these ions can also diffuse through to the metal-concrete interface and depassivate the metal on account of forming chlorinated compounds.

These two phenomena can occur simultaneously, but the risk of carbonation is low in the case of submerged concrete. When the bars are depassivated, corrosion caused by dioxygen can occur, triggering reaction products. The swelling caused by these products as they gradually increase in volume, eventually lead to cracks forming, and even causing the concrete to break. Thereafter, the corrosion process may then spread along the reinforced elements, creeping through the interface layer between the metal and concrete, and damaging the building.

The measures most commonly taken to prevent corrosion include opting for compact concrete formulas with low levels of porosity, protecting the steel surfaces through galvanisation, and by introducing soluble anodes (zinc or magnesium). Owing to their lower redox potentials, these sacrificial anodes are more vulnerable to oxidation, thus protecting the steel from corroding. Other techniques are used such as concrete surface metal plating, epoxy resin coatings on steel bars or even choosing stainless steel for the bars. In some situations, the steel bars mesh can be treated using cathodic protection, namely by setting them at a reducing potential.

In the case of the mosque in Casablanca, the deterioration was so rapid that a prompt decision had to be taken regarding repair work to maintain the building. Since 2005, a temporary dyke has been built so as to provide a dry working environment in which to operate (using 200 000 m^3 of a mixture of various materials, 2800 concrete tetrapods each with a volume of 6.3 m^3), and entailing the demolition of 8000 m^3 of concrete, the injection of 1200 m^3 of grout and mortar, and above all the development of 10 000 m^3 of high-performance concrete reinforced with 1300 tons of ferrito and austenitic Duplex stainless steel bars (Ugitech). The estimated cost of this work is 50 million Euros, that is about 5% of the original construction costs.

Reconstruction, using high-performance stainless steel reinforced concrete, of the 100 external combs supporting the peripheral slabs. The columns are called 'combs' because they have a wave-breaking effect. In the background you can see the sea and temporary dyke that was built to keep the construction site dry, as well as the tetrapods maintaining the dyke. *(© Christine RAYNAUD - BTPM).*

3.4.1.2 - NERNST'S LAW

Remember that the potential reference chosen in electrochemistry is the virtual system called the standard hydrogen electrode (SHE):

$$H^+/H_2 \text{ with }, \forall T \begin{cases} a_{H^+} = a_{H_2} = 1 \\ \gamma_{H^+} = \gamma_{H_2} = 1 \end{cases}$$

The virtual nature of this system essentially arises from the fact that molar acidic solutions are non-ideal. Indeed, if one can obtain an acidic solution with a mean activity equal to 1, the mean activity coefficient will be different from 1 nonetheless.

By definition, the potential of a redox couple *vs* SHE is the emf of the fictive electrochemical cell, whereby the working electrode is in the half-cell involving the redox couple in question. The counter-electrode is the standard hydrogen electrode at the same temperature. The terminals are made of the same metals and the sum of the possible ionic junction voltages are considered to be equal to zero. In this case we therefore have: $E_{/SHE} = \varphi_{metal} - \varphi_{metal\,SHE}$

For example, the potential of the Ag^+/Ag couple *vs* SHE is equal to the emf of the electrochemical cell:

$$Ag', H_2 \,|\, H^+ (std) \,||\, Ag^+ \,|\, Ag$$

When writing the equilibrium: $Ag^+ + \frac{1}{2} H_2 \rightleftharpoons Ag + H^+$

we obtain: $$E = -\frac{\Delta_r G}{\mathcal{F}} = \frac{1}{\mathcal{F}}\left(\mu_{Ag^+} + \frac{1}{2}\mu^\circ_{H_2} - \mu^\circ_{H^+} - \mu_{Ag} \right) = \frac{\mu_{Ag^+}}{\mathcal{F}}$$

and: $$E = E^\circ + \frac{RT}{\mathcal{F}} \ln a_{Ag^+}$$

with: $$E^\circ = \frac{\mu^\circ_{Ag^+}}{\mathcal{F}}$$

Therefore, the potential of a redox couple only depends on its own thermodynamic data. More generally, by applying the conventions previously outlined, we end up with the following NERNST law equation:

$$E_{/Ref} = E^\circ_{/Ref} + \frac{RT}{\nu_e \mathcal{F}} \ln \prod_i a_i^{\nu_i}$$

where i represents each species involved in the redox half-reaction, except for the electrons, ν_i is the stoichiometric number of the species i, a_i is its activity in equilibrium and ν_e is the electron's stoichiometric number.

Thermodynamic data enable one to predict the direction in which a system will spontaneously evolve, based on the thermodynamic criteria. When keeping within the bounds of these criteria, it is possible to take such an approach based on a potential scale[45] (applying a similar line of reasoning to that used for acido-basic reactions analysed on a pK_a scale). Presenting the data in this way, using what we call the γ rule, is particularly

[45] Just as in the qualitative description of current-potential curves in section 2.3, it is the apparent standard potential, when relevant, that is positioned and used for this type of reasoning.

useful for redox reactions in a solution[46]. However, one can rapidly see the limits of its application when dealing with electrochemical systems because the kinetics of different reactions can upset these predictions. In this case it is therefore better to apply reasonings based on current-potential curves (see sections 2.3 and 2.4), which enables one to visualize the results obtained from a potential scale. However at the same time it also gives a broader view, which immediately incites one to take into account the thermodynamic and kinetic aspects.

Let us take one of the examples previously outlined involving spontaneous evolution, using current-potential curves (see figure 2.33 in section 2.4.1). This example relates to the corrosion of a copper piece by dioxygen, when immersed in an acidic solution which is not deaerated. Three redox couples are involved in the system: Cu^{2+}/Cu, H^+, H_2O/H_2 and $O_2/H_2O,OH^-$. They are positioned on the scale of thermodynamic apparent potentials, as shown in figure 3.11. We will assume that the pH of the system is equal to 1: the apparent standard potential of the $H^+,H_2O/H_2$ couple is equal to $-0.06\ V_{/SHE}$ and that of the $O_2/H_2O,OH^-$ couple is $+1.17\ V_{/SHE}$. As far as copper is concerned, the apparent standard potential is equal to the standard potential of the Cu^{2+}/Cu couple, i.e., $+0.34\ V_{/SHE}$. The species present in the system are circled in the diagram (by convention, oxidants are positioned on the left and reductants on the right).

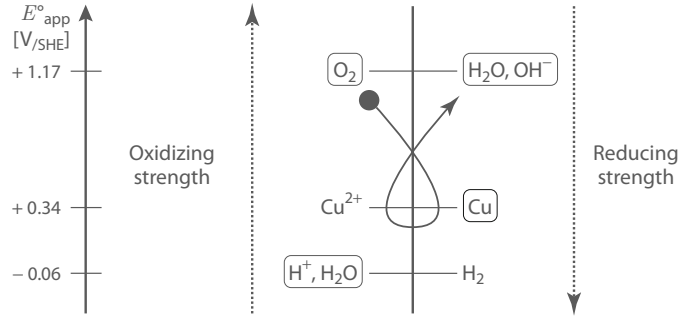

Figure 3.11 - Using a scale of apparent thermodynamic potential

In this type of diagram, one can immediately visualize whether a spontaneous reaction can occur or not: a reaction is possible if an oxidant (O_2) is present and if its couple has an apparent standard potential higher than that of the couple corresponding to the reductant (Cu) which must also be present.

Here therefore we can obtain the result for spontaneous evolution in the system at open circuit. This equates to the balance of both the oxidation and reduction half-reactions which corresponds to the corrosion phenomenon:

$$4\,H^+ + 4\,e^- + O_2 \longrightarrow 2\,H_2O$$
$$(\quad Cu \longrightarrow Cu^{2+} + 2\,e^- \quad) \times 2$$
$$O_2 + 4\,H^+ + 2\,Cu \longrightarrow 2\,H_2O + 2\,Cu^{2+}$$

It must be remembered that this reasoning is based on purely thermodynamic criteria.

[46] The γrule enables one, at a glance, to identify which reactions could spontaneously occur between redox species belonging to different couples. Its name is so called because a minuscule gamma letter is written on the redox potential axis which starts from the Ox_1 species of the couple with the highest potential, and moves towards the Red_2 species of a couple with a lower potential, thus identifying both reactants. Then the two reaction products are found by finishing the γwriting via Ox_2 and ending with Red_1 in the upper right-hand part. The reaction $Ox_1 + Red_2 \rightarrow Red_1 + Ox_2$ obviously requires Ox_1 and Red_2 to actually be present in the system.

3.4.1.3 - CONSIDERING MULTIPLE CHEMICAL EQUILIBRIA

When several chemical equilibria are involved, the equilibrium concentrations depend on all of them, and the redox equilibria can be displaced by other possible reactions (for example, precipitation, complexation or acido-basic reactions). For example, when poorly soluble redox species are involved, they can cause a highly significant change in the corresponding couple's standard potential, as shown in table 3.4. When stable complexes in one (or two) species of a redox couple are involved, then they can also cause a highly significant change in the corresponding standard potential, as shown in table 3.5.

Examples of standard potentials

Table 3.4 - Influence of precipitation

Couple	$E°$ [$V_{/SHE}$]
Ag^+/Ag	+ 0.80
$AgCl/Ag$	+ 0.22
Hg_2^{2+}/Hg	+ 0.79
Hg_2SO_4/Hg	+ 0.61
Hg_2I_2/Hg	− 0.04
Pb^{2+}/Pb	−0.13
$PbSO_4/Pb$	−0.36

Table 3.5 - Influence of complexation

Couple	$E°$ [$V_{/SHE}$]
Fe^{3+}/Fe^{2+}	+ 0.77
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	+ 0.36
$Fe(o\text{-}phen)_3^{3+}/Fe(o\text{-}phen)_3^{2+}$	+ 1.14
Ag^+/Ag	+ 0.80
$Ag(NH_3)_2^+/Ag$	+ 0.37
$Au(CN)_2^-/Au$	−0.60
$Au(SCN)_2^-/Au$	+ 0.70

One can rapidly establish the relationship between the standard potentials of different couples with equilibrium constants simply by writing the corresponding balanced reactions. The NERNST law can also be applied here provided that all the species involved in the solution are considered, however low their concentrations.

For example, the standard potential value of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple can be calculated based on that of the Fe^{3+}/Fe^{2+} couple and on the complexation constants of $Fe(CN)_6^{3-}$ ($pK_{d_1} = 42$) and $Fe(CN)_6^{4-}$ ions ($pK_{d_2} = 35$).

▸ ***First method*** - When cyanide ions are involved, the major species are the complexes, yet with very low quantities of Fe^{3+} and Fe^{2+} ions in equilibrium. The NERNST law can equally be written for these two couples, giving the same electrode potential:

$$E = E°_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} + \frac{RT}{\mathcal{F}} \ln \frac{a_{Fe(CN)_6^{3-}}}{a_{Fe(CN)_6^{4-}}} \quad \text{and} \quad E = E°_{Fe^{3+}/Fe^{2+}} + \frac{RT}{\mathcal{F}} \ln \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

which leads to:

$$E°_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = E°_{Fe^{3+}/Fe^{2+}} + \frac{RT}{\mathcal{F}} \ln \frac{a_{Fe^{3+}}\, a_{Fe(CN)_6^{4-}}}{a_{Fe^{2+}}\, a_{Fe(CN)_6^{3-}}}$$

$$= E°_{Fe^{3+}/Fe^{2+}} + \frac{RT}{\mathcal{F}} \ln \frac{K_{d_1}(a_{CN^-})^6}{K_{d_2}(a_{CN^-})^6}$$

therefore, at 25 °C: $E°_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = E°_{Fe^{3+}/Fe^{2+}} - 0.059\ pK_{d_1} + 0.059\ pK_{d_2} = +0.36\ V_{/SHE}$

- ***Second method*** - more elegant and faster (especially if there is a significant number of simultaneous equilibria):

$$\begin{array}{ll} Fe^{2+} \rightleftharpoons Fe^{3+} + e^- & \Delta_r G^\circ = \mathscr{F} E^\circ_{Fe^{3+}/Fe^{2+}} \\ Fe^{3+} + 6\,CN^- \rightleftharpoons Fe(CN)_6^{3-} & \Delta_r G^\circ = R\,T \ln K_{d_1} \\ Fe(CN)_6^{4-} \rightleftharpoons Fe^{2+} + 6\,CN^- & \Delta_r G^\circ = -R\,T \ln K_{d_2} \\ \hline Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^- & \Delta_r G^\circ = \mathscr{F} E^\circ_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} \end{array}$$

therefore: $E^\circ_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.059\ pK_{d_1} + 0.059\ pK_{d_2} = +0.36\ V_{/SHE}$

3.4.1.4 - PARTICULAR CASES INVOLVING ACIDO-BASIC EQUILIBRIA

It is very common for acido-basic equilibria, and therefore for the pH of electrolytes, to have an influence on potential values. In thermodynamic equilibrium, this influence can be depicted *via* various diagrams, usually called POURBAIX diagrams or E/pH diagrams.

These diagrams can be particularly useful in predicting the thermodynamic behaviour of systems involving several redox couples, each depending on pH in a different way. Obviously this study is focused on redox chemistry in a solution. However, this issue also has an important role in electrochemistry, for example in corrosion or when predicting reactions (main and parasitic) using apparent standard potentials (see section 2.4). Of course these diagrams only give information on a thermodynamic point of view. A system can only be fully described if its kinetic parameters are also included (see section 2.3). Here we will not go into detail about the plotting and use of such diagrams, as this can be found in many other books. Only one example is outlined briefly below.

In the Cl(+I)/Cl(–I) system, you can find the chlorine species with the oxidation number (+I) in the form of HClO or ClO^-, depending on the medium's pH. Therefore, depending on the predominance areas for the acidic and basic forms of Cl(+I), which themselves are governed by the pH, the following two couples emerge:

- HClO/Cl^- couple: $Cl^- + H_2O \rightleftharpoons HClO + H^+ + 2\,e^-$

  Applying the NERNST law to this couple gives the following equation:

$$E = E^\circ_{HClO/Cl^-} + \frac{R\,T}{2\,\mathscr{F}} \ln \frac{[HClO][H^+]}{[Cl^-]}$$

  which at room temperature, and when following the graph conventions of the POURBAIX diagrams (here $[HClO] = [Cl^-]$), therefore gives:

$$E = E^\circ_{HClO/Cl^-} - 0.03\ pH = (1.5 - 0.03\ pH)\ V_{/SHE}$$

- ClO^-/Cl^- couple: $Cl^- + H_2O \rightleftharpoons ClO^- + 2\,H^+ + 2\,e^-$

  Applying the NERNST law to this new couple gives the following equation:

$$E = E^\circ_{ClO^-/Cl^-} + \frac{R\,T}{2\,\mathscr{F}} \ln \frac{[ClO^-][H^+]^2}{[Cl^-]}$$

  when following the graph conventions of the POURBAIX diagrams (here $[ClO^-] = [Cl^-]$) and with the continuity of E at $pH = pK_a$, one obtains:

$$E = E^\circ_{HClO/Cl^-} + 0.03\ pK_a - 0.06\ pH$$

Figure 3.12 shows the shape of the POURBAIX diagram as applied to the Cl(+I)/Cl(–I) system. In the same pH range, the two straight lines symbolizing the water redox couples are also indicated using grey lines.

One example of when the POURBAIX diagram is applied involves studying the stability domains of aqueous solutions. To illustrate, the diagram below clearly shows that JAVEL water (equimolar mixture of Cl^- and ClO^- ions with a pH close to 10) is not a thermodynamically stable solution since its redox potential is higher than that of the $O_2/H_2O,OH^-$ couple. However, given the slow kinetics of water oxidation by ClO^- hypochlorite ions, the JAVEL water remains relatively stable on a usual time scale.

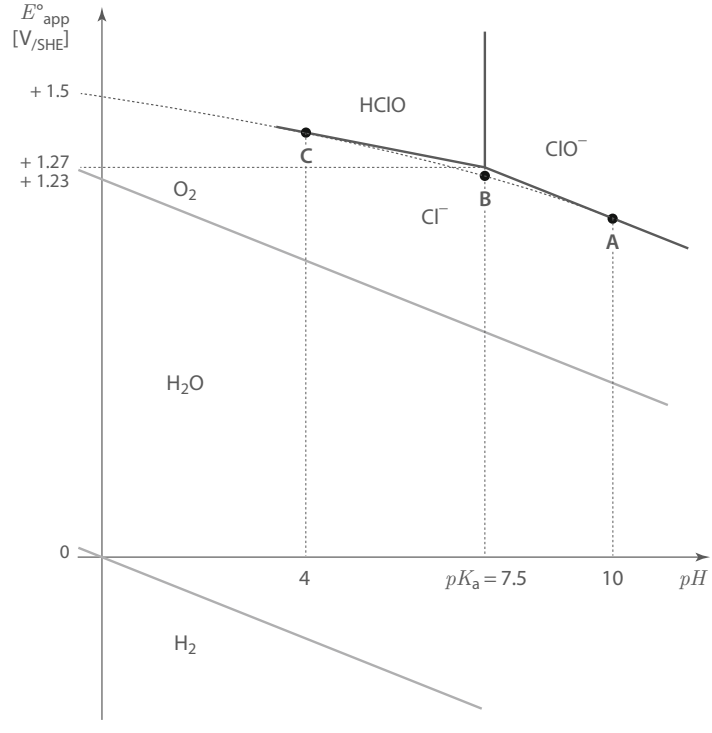

Figure 3.12 - The POURBAIX diagram of chlorine in aqueous solution, restricted to the Cl(+I)/Cl(–I) system

The POURBAIX diagrams are also used in electrochemistry to determine the curve depicting the change in open-circuit potential of an inert electrode (for example a platinum electrode) immersed in a dearated solution of JAVEL water when sulphuric acid is gradually added to this solution.

To give an idea of values, let us take a JAVEL water solution with an initial concentration of 0.5 mol L^{-1} in ClO^- and Cl^- ions, at $pH = 10$. One can assume that it does not react with water, since the kinetics involved is extremely slow.

- This solution is symbolized on the POURBAIX diagram in figure 3.12 by point A ($pH = 10$; $E = 1.12$ $V_{/SHE}$). ClO^- and Cl^- ions are the predominant chlorine species in the solution. From the pK_a value, the concentration in HClO (minority) can be calculated: 1.6×10^{-3} mol L^{-1}.

  When the pH is lowered by adding sulfuric acid, then the following reaction is first seen:

  $$ClO^- + H^+ \rightleftharpoons HClO$$

  When the ClO^- concentration gradually decreases, then the corresponding point moves along a curve slightly below the straight line of the POURBAIX diagram, since this straight line represents the potential whenever Cl^- and ClO^- are equimolar (which is no longer the case).

- At point B, i.e., when the pH is equal to pK_a of the acido-basic HClO/ClO^- couple ($pH = 7.5$), these two species share equal concentration. The potential is $E = 1.26\ V_{/SHE}$. HClO, ClO^- and Cl^- are the major chlorine species in the solution (with a Cl^- concentration of 0.5 mol L^{-1} and HClO and ClO^- concentrations of 0.25 mol L^{-1}).
- While the pH is still decreasing (between B and C), again due to the previous main reaction, ClO^- becomes the minor species compared to HClO. For example at point C at $pH = 4$ ($E = 1.38\ V_{/SHE}$), HClO and Cl^- are the major species of the chlorine element in the solution (concentration of 0.5 mol L^{-1}). The concentration of minor species can therefore be calculated: ClO^- has a concentration of 2×10^{-4} mol L^{-1}.

If the pH decreases even further then other chlorinated species will appear, such as Cl_2 gas, a phenomenon which is not addressed here.

3.4.2 - EXPERIMENTAL ASPECTS

Remember that for electrochemical measurements, voltmeters with field effect transistors which have particularly high input impedance are used[47]. When taking a voltage measurement, one can identify two vital but still insufficient experimental criteria of equilibrium:

- no evolution over time in the measured voltage,
- the voltage measured is independent of the system's hydrodynamic conditions (mechanical stirring).

3.4.2.1 - IONIC JUNCTIONS

In general, the voltages of ionic junctions in equilibrium are not zero and must be taken into account in the overall voltage value. However, in many typical experimental cases (e.g., the junction between two solutions through a salt bridge), the junctions involved are multiple ionic junctions for which the sum of junction voltages plays an insignificant role in quasi-steady state conditions[48]. For such cases, the voltage measured at the system's terminals is very close to the algebraic sum of the equilibrium voltages of the electrochemical interfaces[49].

3.4.2.2 - REFERENCE ELECTRODES

In experimental conditions any redox couple can be used to create a reference electrode, as long as its composition is perfectly monitored and no redox half-reaction

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[47] The input impedance is typically higher than $10^{12}\ \Omega$ for instruments used in electrochemistry.

[48] In the case of solutions separated by a membrane or a porous material, the equilibrium state corresponds to a perfect mixture of the two solutions. However, it takes a very long time to reach this state, if the porosity and/or the geometric configuration of the interfacial zone are well chosen (see section 4.4.2). In such a case, the key phenomenon to consider therefore is the fact that the quasi-steady state is rapidly reached. This latter state has different solutions compositions and non-zero junction voltages. From an experimental point of view, the aim is to minimize this quasi-steady-state ionic junction voltages. Different examples are outlined in appendix A.1.1.

[49] Appendix A.3.2 addresses these points in more thorough detail: even if the ionic junction voltage is negligible in numerical terms, it may nonetheless be important to consider it from a fundamental point of view.

kinetics intervenes[50]. Indeed, the corresponding electrochemical interface should reach thermodynamic equilibrium rapidly on the measurement's time scale which is typically much less than one second.

Two other interesting criteria may come into play:

- the sum of the voltages of the ionic junctions with the other half-cell is negligible;
- the reference half-cell's potential remains unchanged if accidental current has flown through this electrode[51].

Here we will briefly summarise three typical examples which have already been laid out in section 1.5.1.2.

▸▸ *Hydrogen electrode (HE)*

The hydrogen electrode is made by bubbling dihydrogen into a solution with a known pH, on a platinum electrode (or platinised platinum[52]), corresponding to the following half-cell:

$$\text{Platinised Pt, } H_2 \text{ (1 bar)} \mid H^+ \text{ of concentration } C \mid$$

Therefore, the half-cell involves the following H^+/H_2 couple:

$$H_2 \rightleftharpoons 2\,H^+ + 2\,e^-$$

In equilibrium, the NERNST law can be used to express the half-cell's potential with the following equation:

$$E_{/\text{SHE}} = \frac{RT}{\mathcal{F}} \ln \frac{a_{H^+}}{\sqrt{a_{H_2}}}$$

Remember that even if a molar concentration of a strong mono-acid is chosen (the HE is called a NHE in this instance), then this reference electrode is not a SHE because the real compounds are not in their standard state. Figure 3.13 shows this difference on the mean activity coefficient of hydrogen chloride acidic solutions. In practice, if one wishes to use a hydrogen electrode whose potential is as close as possible to that of the SHE, then one would use an acidic solution whose concentration is slightly higher than 1 mol L^{-1}. For example, if you take the case of HCl, a concentration equal to 1.2 mol L^{-1} is chosen because of a mean activity equal to $1.2 \times 0.84 \approx 1$ (0.84 is the mean activity coefficient found in figure 3.13). These values all depend on the system's temperature.

Platinised platinum is used to make the reaction very fast. In practice, the gaseous dihydrogen, the dihydrogen dissolved in the solution and the hydrogen adsorbed at the electrode surface must also reach a state in which they are in equilibrium. In experimental conditions this is not an easy situation to manage, and therefore it is tricky to use such an electrode as reference.

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[50] Here one often refers to a fast or reversible couple, which is defined in precise detail in sections 4.3.2.5 and 6.

[51] This can be achieved, for example, with a SCE. If a current flows through the electrode, then chloride ions are either consumed or produced at the electrode, but the solid potassium chloride keeps the chloride concentration constant in the saturated solution.

[52] Note [66] of section 1.5.1.2 gives a rapid definition of the characteristics and interest of using platinised platinum in electrochemistry.

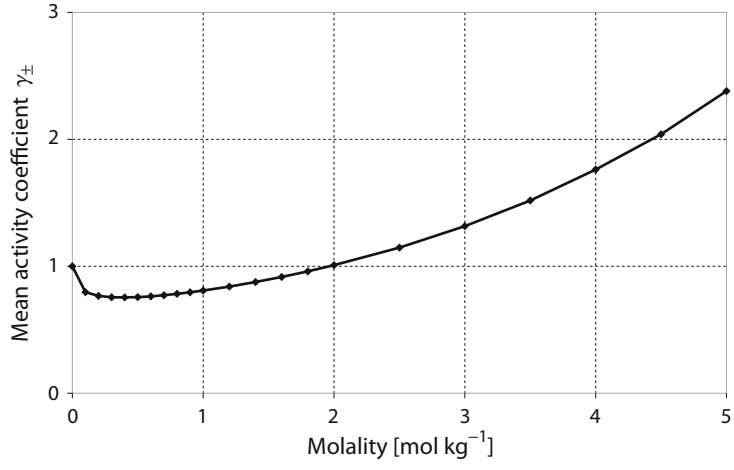


Figure 3.13 - Mean activity coefficient at 25 °C of hydrogen chloride acid in aqueous solutions at different concentrations

▸▸ *Silver chloride electrode*

The silver chloride electrode is made up of a silver wire coated with silver chloride, immersed in an aqueous solution of potassium chloride. Usually a solution is used with a high concentration of chloride ions (from 1 to 3 mol L^{-1}), yet with levels below saturation in KCl. This is done to prevent silver chlorocomplexes ($AgCl_2^-$ and $AgCl_3^{2-}$) from forming, as this would consume AgCl and chloride ions, and in turn fix a different potential value from the value originally expected.

The half-cell's electrochemical chain is therefore the following:

$$\text{Ag} \mid \text{AgCl} \mid \text{KCl aqueous solution of concentration } C \mid$$

AgCl is a pure separate phase (with an activity equal to 1). It is an ionic solid where only Ag^+ ions are mobile.

The following equation gives the overall equilibrium developing in this half-cell, involving the AgCl/Ag couple:

$$\text{Ag} + \text{Cl}^- \rightleftharpoons \text{AgCl} + \text{e}^-$$

At equilibrium, the NERNST law can be used to express the half-cell's potential with the following equation:

$$E = E^\circ_{\text{AgCl/Ag}} - \frac{RT}{\mathcal{F}} \ln a_{\text{Cl}^-}$$

◤ It may be interesting to focus in greater detail on the structure of the half-cell, which involves several interfaces all in equilibrium. The potential expression as indicated above should be applicable to all cases.

- ▸ The first way of examining the half-cell's equilibria is to develop it as follows:

$$\text{Ag} \mid \text{AgCl} \mid \text{KCl aqueous solution of concentration } C \mid$$

  - ▸▸ with an Ag | AgCl interface which is reactive (see section 3.3.4) :

$$\text{Ag} \rightleftharpoons \text{Ag}^+_{\text{AgCl}} + \text{e}^-$$

where Ag^+_{AgCl} is an Ag^+ ion mobile in the AgCl solid phase.

The following equation is obtained at equilibrium:

$$\varphi_{Ag} - \varphi_{AgCl} = \frac{1}{\mathscr{F}}(\mu_{e_{Ag}} + \mu_{Ag^+_{AgCl}} - \mu_{Ag})$$
$$= \frac{1}{\mathscr{F}}(\mu_{e_{Ag}} + \mu^\circ_{Ag^+_{AgCl}} - \mu^\circ_{Ag}) + \frac{RT}{\mathscr{F}} \ln a_{Ag^+_{AgCl}}$$
$$= Cst + \frac{RT}{\mathscr{F}} \ln a_{Ag^+_{AgCl}}$$

- with an AgCl | KCl interface solution which is reactive due to Ag^+ ion exchange since Ag^+ ions can be found (in small quantity) in the solution, as a result of the AgCl solubility equilibrium. In equilibrium (see single-exchange ionic junction in section 3.3.4 with the example of AgCl considered as an ionic solid in which only Ag^+ ions are mobile), the following equation is obtained:

$$\varphi_{sol} - \varphi_{AgCl} = \frac{RT}{\mathscr{F}} \ln\left(\frac{a_{Ag^+_{AgCl}}}{a_{Ag^+_{sol}}}\right) + \frac{\mu^\circ_{Ag^+_{AgCl}} - \mu^\circ_{Ag^+_{sol}}}{\mathscr{F}}$$

The solubility equilibrium of AgCl leads to the following equation which links the activities of Ag^+ and Cl^- in the solution: $AgCl \rightleftharpoons Ag^+_{sol} + Cl^-_{sol}$

$$\ln(a_{Ag^+_{sol}} a_{Cl^-_{sol}}) = \ln K_{eq} = \frac{\mu^\circ_{AgCl} - \mu^\circ_{Ag^+_{sol}} - \mu^\circ_{Cl^-_{sol}}}{RT}$$

Finally, one obtains the following:

$$\varphi_{Ag} - \varphi_{sol} = \frac{1}{\mathscr{F}}(\mu_{e_{Ag}} + \mu^\circ_{AgCl} - \mu^\circ_{Ag} - \mu^\circ_{Cl^-_{sol}}) - \frac{RT}{\mathscr{F}} \ln a_{Cl^-_{sol}}$$
$$= Cst - \frac{RT}{\mathscr{F}} \ln a_{Cl^-_{sol}}$$

- One could also consider the second interface as a reactive interface by writing the chemical equilibrium as follows: $AgCl \rightleftharpoons Ag^+_{AgCl} + Cl^-_{sol}$

The equilibrium of the interface in question corresponds to the following relationship between the different electrochemical potentials:

$$\tilde{\mu}_{Cl^-_{sol}} + \tilde{\mu}_{Ag^+_{AgCl}} = \tilde{\mu}_{AgCl}$$

Therefore the internal potential difference between the two phases is expressed by the following equation:

$$\varphi_{AgCl} - \varphi_{sol} = \frac{1}{\mathscr{F}}(\mu_{AgCl} - \mu_{Ag^+_{AgCl}} - \mu_{Cl^-_{sol}}) = \frac{1}{\mathscr{F}}(\mu^\circ_{AgCl} - \mu^\circ_{Ag^+_{AgCl}} - \mu^\circ_{Cl^-_{sol}}) - \frac{RT}{\mathscr{F}} \ln(a_{Ag^+_{AgCl}} a_{Cl^-_{sol}})$$

Finally, we obtain the following again:

$$\varphi_{Ag} - \varphi_{sol} = \frac{1}{\mathscr{F}}(\mu_{e_{Ag}} + \mu^\circ_{AgCl} - \mu^\circ_{Ag} - \mu^\circ_{Cl^-_{sol}}) - \frac{RT}{\mathscr{F}} \ln a_{Cl^-_{sol}} = Cst - \frac{RT}{\mathscr{F}} \ln a_{Cl^-_{sol}}$$

which transforms as below once a reference electrode is introduced [53]:

$$E_{/Ref} = E^\circ_{AgCl/Ag} - \frac{RT}{\mathscr{F}} \ln a_{Cl^-_{sol}}$$

[53] *It is essential to remember the specific meaning of this equation. The GALVANI voltage $\varphi_{Ag} - \varphi_{sol}$ at the electrochemical interface terminals is presented in terms of a rigorous equation. However, it is inaccessible in experimental conditions. Once the electrode potential E is written in relation to a reference electrode, then the latter loses all rigour, since the ionic junction voltages in the electrochemical chain end up being disregarded. Consequently, as explained in appendix A.3.2, one cannot say that the chloride ion activity is a measured quantity, contrary to what this expression might suggest.*

If we base our approach on purely thermodynamic point of view, then it would be possible to build this reference electrode by placing a silver wire into a solution saturated in silver chloride, with no direct contact between the silver wire and the silver chloride precipitate. The reactive interface here would be therefore Ag | solution and the electrode's potential subsequently depends on the concentration of Ag^+ ions within the solution. However, since this concentration is extremely low (because silver chloride is barely soluble) and the equilibrium potential is a logarithmic function, the system is very sensitive to even the slightest perturbation (for example a concentration change ranging from 10^{-18} to 10^{-17} mol L^{-1} leads to a change in potential of 60 mV). Natural convection occurring in the solution or a very small current flow are both phenomena which could have a significant impact on the electrode's open-circuit potential. Finally, other electroactive species contained in very small quantities (e.g., dissolved dioxygen or another redox couple) could compete with the Ag^+/Ag equilibrium to determine the electrode potential (mixed potential).

▸▸ *Calomel electrode (Hg_2Cl_2)*

The calomel electrode is created by combining mercury mixed with calomel (Hg_2Cl_2, a solid mercury (I) salt barely soluble in water) with an aqueous solution of potassium chloride. Unlike in the previous chemical system, there is no risk of chlorocomplex forming, therefore a saturated solution of potassium chloride is most widely used (i.e., with a concentration close to 5 mol L^{-1} at room temperature).

Therefore the following electrochemical half-cell chain is formed:

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{KCl aqueous solution of concentration } C \mid$$

The equilibria involved in this half-cell can be described by taking into account the Hg_2Cl_2/Hg couple in the following way:

$$2\,\text{Hg} + 2\,\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2 + 2\,\text{e}^-$$

At equilibrium, the NERNST law can be used to express the half-cell's potential with the following equation:

$$E = E^\circ_{\text{Hg}_2\text{Cl}_2/\text{Hg}} - \frac{RT}{\mathcal{F}} \ln a_{\text{Cl}^-}$$

Calomel is crushed together with mercury for practical reasons, but also to ensure the redox system's rapidity. The resulting mixture is then put in contact, on the one hand, with mercury (in which a platinum wire is immersed) and also separately on the other hand with an aqueous solution containing potassium chloride[54]. If this electrode is set to be used in a solution containing silver salts, then an intermediate salt bridge must be introduced to prevent silver chloride precipitation. The bridge should contain a solution devoid of chloride ions, and generally with a high ionic concentration so as to minimize the two junction voltages induced by this added extension.

[54] A diagram of this reference electrode is given in figure 1.14 in section 1.5.1.2.

The HE is a proton sensor, and the two other electrodes are chloride ion sensors (in other words, with a potential depending on the activity of one type of ion). Whenever it is possible to fix the indicator ion concentration in the solution, these electrodes may be used as reference electrodes with no ionic junction. However, they are generally used in conjunction with a membrane (or a porous material) which separates them from the solution being studied. In this instance it is advisable to use concentrated solutions as reference solutions in order to minimize the ionic junction voltages. To give an example, a saturated solution could be used for the SCE. Similarly, it is assumed that by choosing potassium chloride (where the anion and cation have very close transport numbers) as a reference electrolyte containing chloride ions, it acts as a means of minimizing the junction voltages between the solutions. In this sense, minimizing junction voltages is particularly difficult when a hydrogen reference electrode is involved, because of the high value of the proton transport number in aqueous solution. This is another reason for avoiding the use of such an electrode when it cannot be used without an ionic junction [55].

[55] Appendix A.1.1 highlights the points addressed in this paragraph by giving a selection of different situations where the ionic junction voltages are numerically estimated.

QUESTIONS ON CHAPTER 3

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

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 - 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

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} .....
- containing $Cu(NO_3)_2$ with a concentration of 0.1 mol L^{-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

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

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

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

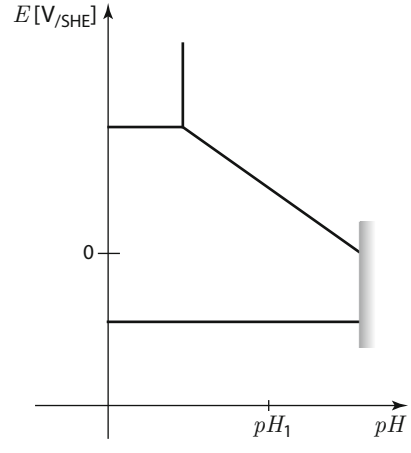
9 - Fill in the missing numbers (with the appropriate sign) in the equations below, which characterize the thermodynamic equilibrium of the following electrochemical chain: Cu' | Pt, H_2 | aqueous solution containing H_2SO_4 and $CuSO_4$ | Cu

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: $Cu^{2+} + H_2 \rightleftharpoons Cu + 2\,H^+$

$$\Delta_r G = \ldots . \mathcal{F} U = \ldots . \mu_{Cu} \ldots . \mu_{H^+} \ldots . \mu_{Cu^{2+}} \ldots . \mu_{H_2}$$

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?

  .....

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

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