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Chapter 8

Electrochemistry: From Redox Reactions to Electrical Measurements

8.1 Introduction: From Matter to Energy

Electrochemistry is the science that studies the interconversion between chemical energy and electrical energy. It is based on a fundamental principle: **electron transfer**. While in a classical chemical reaction this transfer occurs in a disordered and local manner (direct contact between reactants), electrochemistry manages to **control** this electronic flow by spatially separating oxidation from reduction. This separation forces electrons to follow an external path, thus transforming a chemical reaction into a measurable and usable electric current. This chapter explores the thermodynamic and kinetic principles governing these transformations. Before detailing the quantitative laws of **Nernst** and **Faraday**,⁽⁵³⁾ it is essential to understand how humanity moved from the fortuitous observation of bioelectrical phenomena to the design of high-tech generators.

Historical evolution and technological implications

The mastery of spatial separation of electrochemical reactions did not happen overnight; it is the result of a long series of experimental and conceptual advances that began at the end of the Age of Enlightenment.

The biological spark (1780) It all begins with the observations of **Luigi Galvani** in 1780.⁽⁵⁴⁾ While studying frog muscle contraction under the effect of electrical discharges, he demonstrated the intrinsic link between electrical phenomena and neuromuscular excitability. Although he interpreted this as "animal electricity," his work paved the way for a new understanding of living beings and matter.

The first continuous source (1799) In response to Galvani, **Alessandro Volta** proposed a purely physical interpretation: electricity arises from contact between two different metals. He materialized this theory in 1800⁽⁵⁵⁾ with the first **voltaic pile**, an alternating stack of zinc and copper discs separated by cardboard soaked in brine. This invention was a major technological breakthrough: for the first time, scientists had a stable direct current source, a true tool for exploration for electrolysis and the nascent chemistry.

Towards stability and storage (19th century) While Volta's pile enabled discoveries, it suffered from rapid voltage drop (polarization). In 1836,⁽⁵⁶⁾ **John Frederic Daniell** solved this problem by introducing the concept of **separate compartments**: a copper electrode in copper sulfate and a zinc electrode in zinc sulfate, connected by a porous barrier. This architecture stabilized the voltage and made possible the rise of telegraphy. A few decades later, in 1859,⁽⁵⁷⁾ **Gaston Planté** reached a new milestone with the lead-acid accumulator. This was the birth of the **rechargeable battery**: a system capable not only of producing but also of storing electrical energy, foreshadowing the electrification of the automobile.

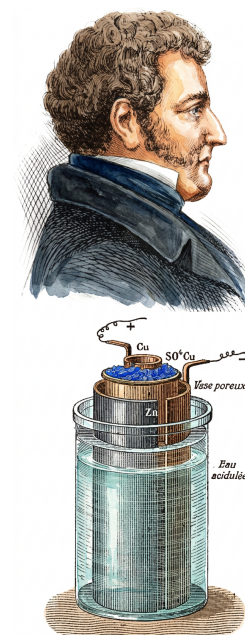
The modern era During the 20th century, the optimization of electrolytes (Leclanché dry cells) and electrode materials led to current technologies: fuel cells (direct hydrogen-to-electricity conversion) and especially Lithium-ion batteries, which now power our digital world. This historical journey perfectly illustrates how fundamental understanding of redox reactions transformed simple laboratory curiosities into technologies indispensable to our digital and mobile society.



(a) Luigi Galvani



(b) Alessandro Volta



(c) John F. Daniell

Figure 8.1 The founding fathers of electrochemistry: Galvani (observation), Volta (invention), and Daniell (refinement).

8.2 Electrochemical cells: Architecture and principles

8.2.1 Theoretical foundations and operating principles:

First imagine a very simple experiment: pour an oxidizing agent and a reducing agent into the same beaker. The reaction starts, the solution changes, sometimes a deposit appears ... but everything happens in the same place, and the released energy disperses without us being able to truly "recover" it.

To understand electrochemical cells, we must follow the next step in this story: instead of letting the reactants meet directly, we decide to separate them. We place the oxidation on one side and the reduction on the other, each on its own electrode, then connect the two electrodes with a wire. From that moment on, electrons have no choice: if they want to pass from the reducing agent to the oxidizing agent, they must take the path of the external circuit. This detour transforms a chemical reaction into a measurable electric current, hence into usable electrical energy.

This is exactly this idea — moving from an "observed" redox reaction to a "staged and controlled" redox reaction — that marks a decisive step: chemistry no longer merely describes a transformation; it learns to control it and convert its energy in a useful way, forming the basis of many energy technologies.

8.2.2 Limitations of redox reactions in homogeneous solution

In a homogeneous solution, an oxidant from the first couple (Ox_1) and a reducing agent (Red_2) from the second couple diffuse freely and can collide. The electron transfer then occurs *locally*, at direct contact between species, without any device imposing a path on the electrons or allowing regulation of the electron flow. The reaction may be spontaneous and visible (color change, metal deposition, gas evolution), but the chemical energy associated with the transformation, quantified by $\Delta_r G$, is not converted in a controlled manner into recoverable electrical work in an external circuit.

The key idea is therefore the following: when oxidation and reduction occur at the same place, the electron is exchanged "on site" within the mixture, preventing the creation of a directed and measurable electronic circulation. The resulting limitations can be analyzed from four angles: (i) electron flow, (ii) energy dissipation, (iii) measurability, (iv) chemical selectivity.

8.2.2.1 Lack of control over electron flow

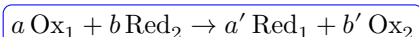
In a homogeneous redox reaction, **electrons** are transferred **locally** between molecules or ions in contact. This process is microscopic; it does not force electrons to travel through an external conductor in a single direction. Thus, even though electron exchanges do occur, they do not translate into an **exploitable electric current** in a wire, due to the lack of spatial separation of oxidation and reduction sites.

This limitation can be illustrated by a hydraulic analogy: a homogeneous mixture resembles water swirling in all directions in a basin; without a channel, it is impossible to impose a unidirectional flow capable of driving a wheel. The cell, on the contrary, corresponds to a device that **channels** the flow — electrons must pass through the external circuit.

8.2.2.2 Mechanism and energy dissipation

When an oxidizing agent (Ox_1) and a reducing agent (Red_2) are mixed in the same beaker, electron transfer occurs via **direct collisions** within the reaction medium. The possibly rapid nature of the transformation (depending on the systems and conditions) does not change the essential point: in the absence of an imposed path through an external circuit, the free energy of reaction $\Delta_r G$ is not recovered as macroscopic **electrical work**; it dissipates in an **uncontrolled** manner (most often as heat, and more generally as dissipative effects).

For a generic redox reaction:



The thermodynamic **driving force** is carried by $\Delta_r G$. In a cell, this driving force can manifest as a measurable potential difference between two separated electrodes, allowing (at maximum, under reversible conditions) conversion of $\Delta_r G$ into electrical work; in a homogeneous medium, it does not translate into an exploitable voltage between two terminals, precisely because the half-reactions are not spatially decoupled.

8.2.2.3 Lack of direct measurement capability

From an experimental point of view, a homogeneous redox reaction generally manifests through indirect indicators:

- ▷ Color changes (e.g., reduction of MnO_4^-)
- ▷ Formation of deposits or precipitates (e.g., reduction of Ag^+ to Ag)
- ▷ Gas evolution (depending on the reaction system)
- ▷ Concentration change followed by titration or spectroscopy

However, there is no proper way to measure an electromotive force (EMF) by "connecting a voltmeter to the beaker." Without separation of half-reactions on two distinct electrodes, the notion of potential difference between two terminals is experimentally ill-defined: one does not obtain a stable voltage directly associated with the two half-equations.

8.2.2.4 Selectivity and interference problems

In a system containing multiple redox couples, the homogeneous mixture favors competing reactions: several oxidants can capture electrons, and several reducing agents can donate them, at the same place and at the same time. The absence of spatial separation prevents directing the electron transfer toward a single transformation, leading to side products and a decrease in chemical and energy yield.

For example, if several oxidizing species are present simultaneously (e.g., Fe^{3+} and Cu^{2+}), the same reducing agent can react in parallel with several electron acceptors. This lack of selectivity complicates analysis, purification, and makes process optimization difficult.

Key point: Why does homogeneous redox not generate electricity?

In a homogeneous redox reaction:

- ▷ The exchanged electrons are transferred **locally**, without an imposed path through an external conductor.
- ▷ The energy associated with $\Delta_r G$ dissipates **without control** (often as heat) instead of being recovered as electrical work.
- ▷ No **directed current** is imposed in an external circuit.
- ▷ A **stable and directly measurable** EMF is not accessible without separation of the half-reactions.

8.2.3 Principle of spatial separation of half-reactions: (foundation of the cell)

The conceptual solution to overcome the limitations of homogeneous systems is the systematic spatial separation of the two constituent half-reactions of a global redox process. This idea, fully realized in electrochemical cells, is based on a rigorous hierarchical organization.

8.2.3.1 Fundamental concept: from a single beaker to a bipolar device

Rather than allowing the oxidizing and reducing agents to meet directly in the same compartment, they are isolated in two distinct **half-cells**, physically separated but connected in a controlled manner. Each half-cell constitutes an elementary electrochemical system where exclusively one of the two half-reactions takes place.

An electrochemical half-cell is a system consisting of:

- a) An **electrode**: electronic conductor (metal, graphite, etc.) serving as an interface for electron exchange.
- b) An **electrolyte**: ionic conducting solution containing the oxidized and reduced species of a specific redox couple (Ox/Red).
- c) The **electrode-electrolyte interface**: the physical location where charge transfer (half-reaction) occurs.

8.2.3.2 Architecture of a complete cell: the two-half-cell model

A galvanic (or voltaic) cell is based on the association of two distinct half-cells connected by two complementary conduction pathways:

- (i) An **external metallic circuit** where electrons flow, allowing conversion of chemical energy into electrical work.
- (ii) An **ionic bridge** (generally a salt bridge) where ions migrate, ensuring closure of the internal circuit without direct mixing of the electrolyte solutions.

Essential components and their roles

Anode (—) : Oxidation electrode

Site where the oxidation half-reaction occurs: $\text{Red} \rightarrow \text{Ox} + ne^-$. This is the electrode that produces electrons; they leave the electrode toward the external circuit. In a galvanic cell, it constitutes the **negative** terminal. Physically, one often observes at this electrode either wear (corrosion if metallic) or an increase in the concentration of oxidized species in the adjacent solution.

Cathode (+) : Reduction electrode

Site where the reduction half-reaction occurs: $\text{Ox} + ne^- \rightarrow \text{Red}$. This is the electrode that consumes electrons arriving from the external circuit from the anode. It constitutes the **positive** terminal of the cell.

One may observe either a metal deposit (if reduction leads to a metal, a phenomenon called electrodeposition or electroplating), or a decrease in the concentration of oxidized species in the surrounding solution.

External circuit: electronic pathway

Metallic connection (conducting wires) between the anode and the cathode. Electrons flow **spontaneously** from the anode (source) to the cathode (sink). This circuit allows connection of measuring devices (voltmeter) that convert electrical energy into useful work.

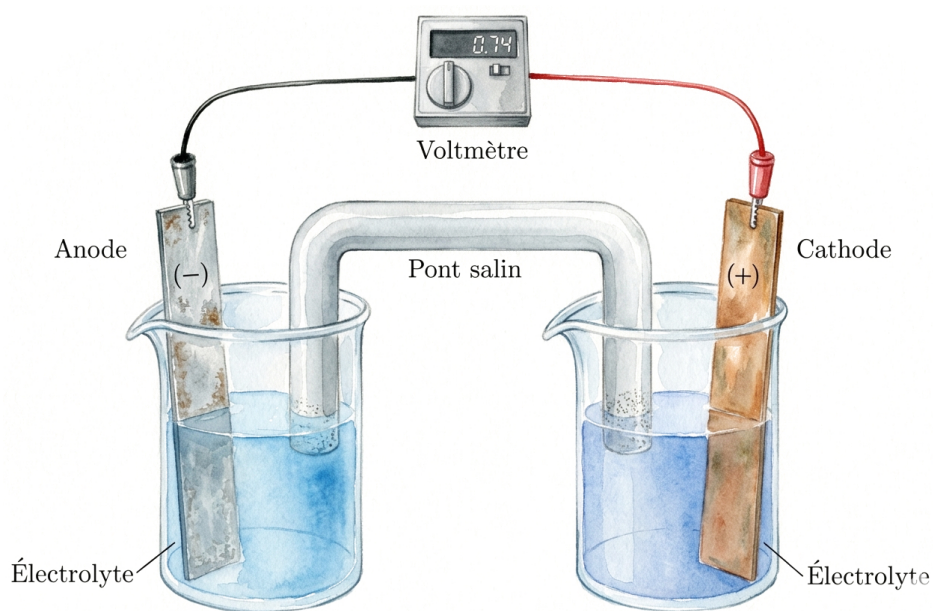


Figure 8.2 Architecture of a cell

Salt bridge: ionic pathway

Device (often an inverted U-tube containing an inert electrolyte gel such as KCl or KNO₃) connecting the solutions of the two half-cells. It ensures the ionic conduction necessary to maintain electroneutrality in each compartment:

- **Cations** migrate toward the cathodic compartment (where negative charges accumulate)
- **Anions** migrate toward the anodic compartment (where positive charges accumulate)

Without this bridge, charge accumulation would quickly stop the reaction. It also prevents direct mixing of solutions, limiting side reactions.

8.2.4 Synergistic operation and flux continuity in a galvanic cell

The sustainable operation of a galvanic cell relies on a central principle: the **indissociable coupling** between electronic transport (in the external circuit) and ionic transport (in the internal circuit). As long as the redox reaction transfers electrons at the electrode/solution interface, it simultaneously creates charge imbalances in the solutions; current can only persist if these imbalances are continuously compensated by ion migration.

Table 8.1 Observable changes in a Daniell cell during operation.

Element	Evolution	Observable consequence
Zn electrode	$\text{Zn(s)} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$	Mass decreases, visible corrosion
Cu electrode	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu(s)}$	Mass increases, metal deposit
Anodic solution	Increase $[\text{Zn}^{2+}]$	Zn^{2+} concentration increases
Cathodic solution	Decrease $[\text{Cu}^{2+}]$	Blue solution pales (if colored)
Salt bridge	Migration of K^+ , Cl^-	Charge transport, neutrality maintenance
External circuit	Electron flow e^-	Measurable current, electrical work

Two complementary conduction pathways:

- 1. External electron flow:** metallic conduction in which electrons flow from the anode to the cathode through the conducting wire (red and black in Figure 8.3), driven by the cell's electromotive force.

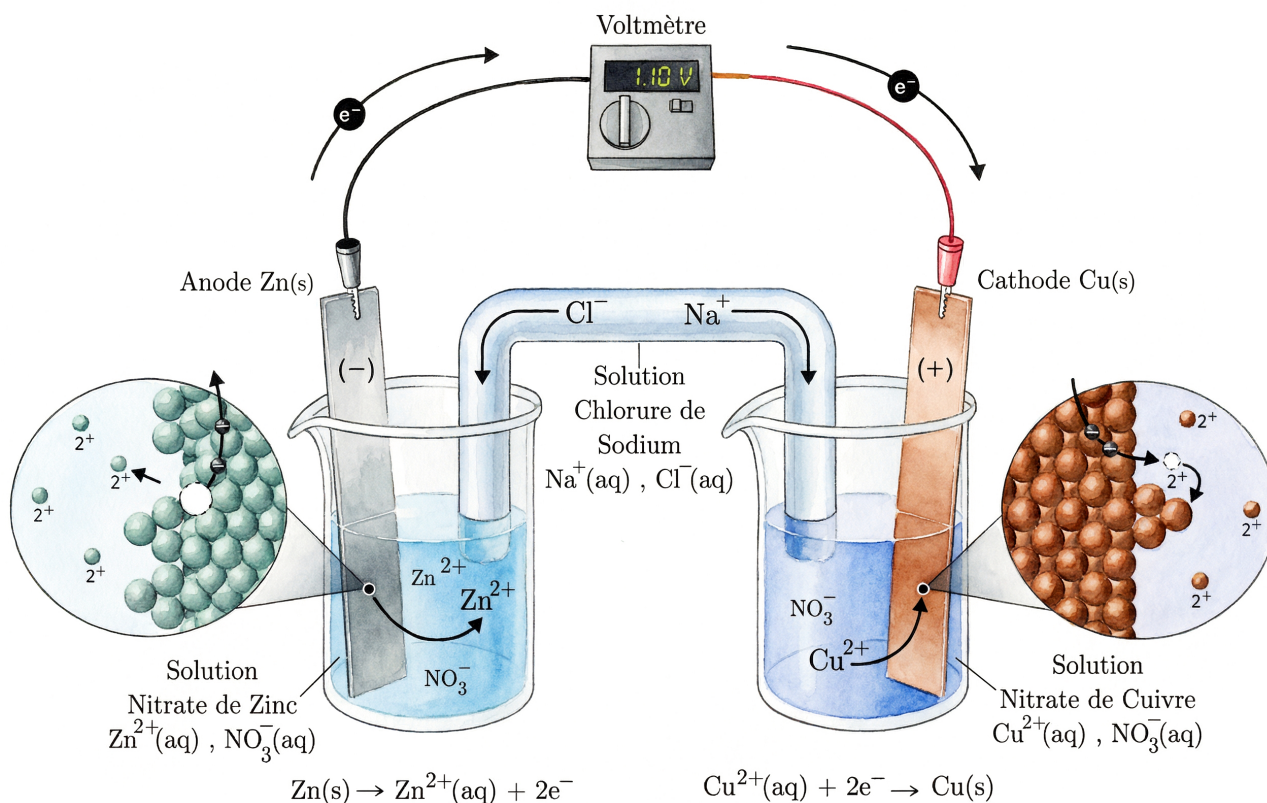


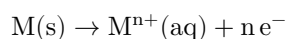
Figure 8.3 Operation of a cell

2. Internal ionic flow: electrolytic conduction within the solutions of the two half-cells and the salt bridge (or separator), primarily ensured by the migration of inert ions from the salt bridge. The bridge's **anions** migrate toward the **anodic** compartment (where cations produced by oxidation accumulate) and its **cations** migrate toward the **cathodic** compartment (where cations are consumed by reduction), thus maintaining electroneutrality in each compartment and allowing current continuity.

Caution

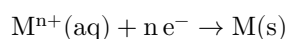
Consequences of absence of ionic conduction:

- Charge accumulation in compartments (excess positive charge on the anode side, excess negative charge on the cathode side).
 - At the anode/solution interface, oxidation produces electrons that leave the electrode toward the external circuit, while cations appear in the solution:



Thus, **the anodic compartment** tends to become globally **positive** if no supply of negative ions compensates the charge created in solution.

- At the cathode/solution interface, reduction consumes electrons from the external circuit and, very often, cations from the solution:



The disappearance of **cations** leaves a relative excess of spectator anions in **the cathodic compartment**, which tends to become globally **negative** in the absence of compensation.

- Appearance of an internal potential difference opposite to the EMF (polarization), which slows then cancels the net electron transfer.
- Rapid current drop, even if reactants are not yet exhausted.

8.2.4.1 The crucial role of the salt bridge:

If electrons only flowed in the external circuit, a fundamental problem would quickly arise inside the cell:

- At the **anode** (site of oxidation): electrons leave the electrode, leaving behind an excess of positive charges.
- At the **cathode** (site of reduction): electrons arrive in large numbers, creating an excess of negative charges.

These opposite charge accumulations would generate an internal electric field that would quickly oppose electron transfer. In practice, without a corrective device, the cell would stop functioning almost instantaneously.

It is precisely to solve this problem that a **salt bridge** (or any other device ensuring ionic conduction) is introduced. This component allows ions to migrate between the two half-cells, thus restoring charge balance and keeping the cell in operation.

The salt bridge thus fulfills several essential roles:

- a) **Maintaining electroneutrality:** by compensating for charges created by electron transfer.
- b) **Ensuring current continuity:** by dissipating charge accumulations.
- c) **Partial chemical isolation:** between solutions to avoid side reactions.
- d) **Preventing polarization:** by maintaining ionic concentration balance.

Compensation mechanism Operation relies on directional ionic migration:

- **Cations** (such as K^+) migrate toward the cathodic compartment to compensate for the electron excess.
- **Anions** (such as Cl^-) migrate toward the anodic compartment to compensate for the electron deficit.

This dual circulation creates a dynamic equilibrium where each electron flowing in the external circuit is compensated by ion movement in the bridge.

Available technologies Different devices can perform this function, each adapted to specific applications:

Table 8.2 Different types of ionic bridges and their characteristics.

Type	Typical composition	Role and mechanism
Classical salt bridge	KCl or KNO_3 gel in agar-agar (vegetable gelatin)	Provides spectator ions (K^+ , Cl^-) that migrate to neutralize accumulated charges
Porous membrane	Ceramic, sintered glass	Physical barrier allowing slow ion diffusion while preventing rapid mixing of solutions
Ion-exchange membrane	Sulfonated resin (cationic) or quaternary ammonium (anionic)	Allows selective migration of specific cations or anions
Polymer separator	Microporous polyethylene, polypropylene	Porous structure soaked with electrolyte, used in commercial batteries

The salt bridge is therefore not a simple accessory, but an essential constitutive element that allows the cell to maintain continuous operation by balancing electronic and ionic flows.

Compensatory migration (typical case):

- The **anions** from the salt bridge migrate toward the **anode** to neutralize the excess of positive charges due to cation formation by oxidation.
- The **cations** from the salt bridge migrate toward the **cathode** to compensate for the disappearance of positive charges linked to reduction.

Overall balance: In a continuous operating regime, each electron transfer in the external circuit must be compensated by an ionic charge transfer in the internal circuit; it is this synergy that ensures **charge conservation** at the system scale and prevents blocking polarization.

8.2.4.2 Cell representation (notation):

An electrochemical cell is often described by an **abbreviated notation** (cell notation), which summarizes the two half-cells and their ionic connection. For the Daniell cell, one writes for example:



By **convention**, the half-cell written to the left of the double bar is the **anode** (where oxidation occurs) and the one written to the right is the **cathode** (where reduction occurs).

Meaning of separators.

- The single bar $\mid$ represents a **phase boundary** (for example between a solid metal and an aqueous solution).
- The double bar $\parallel$ represents the **electrolytic junction** (salt bridge, diaphragm): it allows ionic conduction between the two compartments and prevents charge accumulation that would block the cell.

So in general:

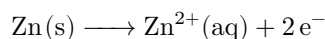


Examples of notations:

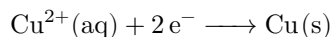
- a) **Cell with hydrogen electrode:** $\text{Pt} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M}) \parallel \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \mid \text{Cu}$
- b) **Cell with different concentrations:** $\text{Ag} \mid \text{Ag}^+(\text{aq}, 0.1 \text{ M}) \parallel \text{Ag}^+(\text{aq}, 0.01 \text{ M}) \mid \text{Ag}$

Physicochemical reading from left to right.

- On the left: $\text{Zn(s)} \longrightarrow \text{Zn}^{2+}(\text{aq})$ corresponds to the zinc electrode immersed in a solution containing Zn^{2+} ; it is the **anode** and the half-equation (written as oxidation) is:



- On the right: $\text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)}$ corresponds to the copper electrode immersed in a solution containing Cu^{2+} ; it is the **cathode** and the half-equation (written as reduction) is:



Experimental consequences. Electrons flow in the external circuit **from the anode to the cathode** (here from zinc to copper), while ions in the salt bridge move to maintain electroneutrality (anions toward the anode, cations toward the cathode). The electromotive force measured in open circuit is then written:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

8.2.4.3 Fundamental quantitative relationships

The operation of an electrochemical cell is governed by precise thermodynamic relationships that link the **electromotive force** (EMF) to state functions — Gibbs free energy, reaction quotient, equilibrium constant — and allow prediction of the influence of temperature and medium composition (activities) on the measured potential.

a. Link between free energy and electromotive force

For an overall redox reaction involving a transfer of n electrons, the change in Gibbs free energy $\Delta_r G$ is related to the cell EMF E_{cell} by:

$$\Delta_r G = -nFE_{\text{cell}}$$

where $F = 96485 \text{ C/mol}$ is the **Faraday constant** (charge of one mole of electrons).

- If $E_{\text{cell}} > 0$, then $\Delta_r G < 0$: the overall reaction is **spontaneous**.
- If $E_{\text{cell}} < 0$, then $\Delta_r G > 0$: the reaction is not spontaneous in this direction (case of **electrolysis**).

EMF and electrode potentials. The EMF of a cell is calculated from the potentials of the two electrodes:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The cathode is the site of reduction, the anode the site of oxidation. A positive EMF confirms spontaneity in the chosen direction.

At equilibrium. When the cell is completely discharged, $E_{\text{cell}} = 0$ and $\Delta_r G = 0$. The medium composition then corresponds to the thermodynamic equilibrium constant K° . By combining the fundamental relationships:

$$\Delta_r G^\circ = -RT \ln K^\circ = -nF E_{\text{cell}}^\circ$$

we obtain:

$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K^\circ \quad \text{or, at } 25^\circ \text{C:} \quad \log_{10} K^\circ = \frac{n E_{\text{cell}}^\circ}{0.06}$$

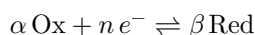
These relationships allow calculation of K° from tabulated standard potentials, or vice versa.

b. From standard potential to the Nernst equation

The standard potential E° of a redox couple characterizes its intrinsic tendency to be reduced, measured under reference conditions (unit activities, 1 bar, 298 K). Under real conditions, the potential E depends on the composition of the medium through the **Nernst equation**.

Fundamental convention. One *always* writes the half-reaction in the **direction of reduction**. This convention definitively fixes the sign in the Nernst equation and avoids errors.

For a general half-reaction:

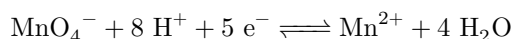


the reaction quotient is:

$$Q = \frac{a_{\text{Red}}^\beta}{a_{\text{Ox}}^\alpha}$$

where electrons and species with unit activity (pure solids, pure liquids, solvent) do not appear. When other species participate (protons, water, etc.), they appear in Q with their stoichiometric coefficient as exponent.

Example. For the $\text{MnO}_4^-/\text{Mn}^{2+}$ couple in acidic medium:



$$Q = \frac{a_{\text{Mn}^{2+}}}{a_{\text{MnO}_4^-} a_{\text{H}^+}^8} = \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] [\text{H}^+]^8} \quad (\text{dilute solution})$$

Liquid water, as solvent, has an activity of 1 and does not appear in Q .

Thermodynamic derivation. For any reaction:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

In electrochemistry, the maximum electrical work gives $\Delta_r G = -nFE$ and $\Delta_r G^\circ = -nFE^\circ$. Substituting:

$$-nFE = -nFE^\circ + RT \ln Q \quad \Rightarrow \quad E = E^\circ - \frac{RT}{nF} \ln Q$$

Operational form at 25 °C. Converting to decimal logarithm ($\ln x = 2.303 \log_{10} x$) and evaluating the prefactor, we obtain:

$$\frac{RT}{F} = \frac{8.314 \text{ J}/(\text{mol} \cdot \text{K}) \times 298.15 \text{ K}}{96485 \text{ C/mol}} = 0.02569 \text{ V}$$

Consequently, the Nernst constant (for $n = 1$) is:

$$\frac{2.303 RT}{F} = 2.303 \times 0.02569 \text{ V} = 0.05916 \text{ V}$$

This value is often rounded to 0.059 V for precise calculations, or to 0.06 V to simplify calculations.^{(58),(59)} We obtain the working formula, valid at 25 °C:

$$E = E^\circ - \frac{0.06}{n} \log_{10} Q$$

Activities and concentrations. In sufficiently dilute solution, the activity coefficient $\gamma \approx 1$ and one assimilates activity to concentration, so $a \approx C$. For a simple couple $\text{Ox} + n e^- \rightleftharpoons \text{Red}$, this gives:

$$E = E^\circ - \frac{0.06}{n} \log_{10} \left(\frac{[\text{Red}]}{[\text{Ox}]} \right)$$

Physical interpretation. The potential E of a redox couple measures its tendency to capture electrons. The Nernst equation formalizes this idea:

- **Excess of oxidant** $\left(\frac{[\text{Red}]}{[\text{Ox}]} \ll 1 \right)$:

The logarithm is negative, the corrective term $-\frac{0.06}{n} \log_{10} \left(\frac{[\text{Red}]}{[\text{Ox}]} \right)$ becomes **positive**. Thus $E > E^\circ$: reduction is favored.

- **Excess of reductant** $\left(\frac{[\text{Red}]}{[\text{Ox}]} \gg 1 \right)$:

The logarithm is positive, the corrective term is negative. Thus $E < E^\circ$: oxidation is favored.

In other words: the richer a couple is in oxidized form, the higher its potential and the more it "demands" electrons. Conversely, an excess of reductant lowers the potential and favors oxidation. **Application:**

concentration cells. Two half-cells containing the *same* redox couple, but at different concentrations, have different E potentials (according to Nernst). The cell EMF then arises **solely** from the composition gradient, without any new overall chemical reaction occurring.

c. Cell EMF and evolution with reaction progress

A cell consists of two half-cells. Its electromotive force is the potential difference between the cathode (site of reduction) and the anode (site of oxidation):

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\oplus} - E_{\ominus}$$

Applying the Nernst equation to each electrode (at 298 K):

$$E_{\text{cell}} = \left(E_{\oplus}^\circ - \frac{0.06}{n} \log_{10} Q_{\oplus} \right) - \left(E_{\ominus}^\circ - \frac{0.06}{n} \log_{10} Q_{\ominus} \right)$$

where $Q_{\oplus}$ and $Q_{\ominus}$ are the quotients of the half-reactions written as reductions. Grouping terms:

$$E_{\text{cell}} = (E_{\oplus}^\circ - E_{\ominus}^\circ) - \frac{0.06}{n} \log_{10} \left(\frac{Q_{\oplus}}{Q_{\ominus}} \right)$$

We recognize the compact form of the **Nernst equation for the cell**:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{n} \log_{10} Q$$

with:

- $E_{\text{cell}}^\circ = E_{\oplus}^\circ - E_{\ominus}^\circ$: standard EMF of the cell.
- $Q = \frac{Q_{\oplus}}{Q_{\ominus}} = \frac{\prod a_{\text{products}}^\nu}{\prod a_{\text{reactants}}^\nu}$: reaction quotient of the balanced overall reaction.
- n : number of electrons exchanged in the overall reaction (after equalization of half-reactions).

Equilibrium and equilibrium constant. As the cell discharges, reactants are consumed and Q increases. The potential E_{cell} gradually decreases until it reaches zero at thermodynamic equilibrium

($E_{\text{cell}} = 0$, $Q = K$). We thus recover the expression already established in (a):

$$E_{\text{cell}}^{\circ} = \frac{0.06}{n} \log_{10} K$$

Historical context

The equation bears the name of the German chemist **Walther Hermann Nernst** (1864–1941), Nobel Prize in Chemistry in 1920.^{(60),(61)} Established in 1889, it unified thermodynamics and electrochemistry by showing how the potential of an electrode quantitatively depends on the concentration or activities of species. At a time when these fields were still distinct, Nernst introduced a fundamental relationship linking electromotive force and free energy, paving the way for modern electrochemistry.

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$



Transition to practice. If thermodynamic laws set the theoretical EMF and the direction of evolution of a cell, the actual performance (voltage under load, deliverable current, lifespan) strongly depends on the material design: nature of electrodes, cell architecture, electrolyte conductivity, management of reaction products, etc. To address common generators and their fields of application, it is therefore necessary to classify them not only by their electrochemical quantities, but according to their structure and their operating mode.

8.2.4.4 Classification of cells according to design

As shown in Table 8.3, the different families of cells differ only in how they organize the reaction space, the electrolyte, and the delivery of reactants. Behind this apparent diversity are actually a few simple guiding ideas that govern the operation of any electrochemical cell and can be formulated generally.

Conceptual principles of an electrochemical cell The operation of a cell is based on three structuring ideas, found in all the architectures previously described:

- Spatial separation of half-reactions:** The overall redox reaction is decomposed into two physically separated half-reactions (anode and cathode), which prevents direct electron transfer between reductant and oxidant and makes it possible to recover this electron flow as usable electric current.
- Imposed electron circulation:** Electrons released at the anode are forced to flow through an external circuit (metallic conductor, load, electronic device), where they perform electrical work before being consumed at the cathode; it is this imposed path that gives the cell its role as a generator.
- Ionic compensation and electrical neutrality:** For electron flow to continue without charge accumulation, the medium must maintain its overall neutrality; this condition is ensured by ion migration in the electrolyte and, where applicable, through a salt bridge or ion-exchange membrane, which close the ionic circuit.

This conceptual trinity thus transforms a spontaneous chemical reaction, which would naturally be dissipative, into an electrochemical generator capable of delivering controlled and usable electrical work.

8.2.5 Fundamental classification: galvanic and electrolytic cells

8.2.5.1 Thermodynamic classification principle

The fundamental difference between the two major families of electrochemical cells is based on the spontaneity of the overall redox reaction and on the direction of energy conversion. Thermodynamically, the criterion is given by the relationship

$$\Delta G = -nFE$$

The sign of the electromotive force E_{cell} directly reflects the spontaneous character ($\Delta G < 0$) of a galvanic cell, or the non-spontaneous character ($\Delta G > 0$) of the electrolytic cell reaction.

Table 8.3 Classification of cells according to design and electrochemical structure. The Nernst equation is the theoretical foundation of several of these categories, notably concentration cells.

Cell type	Structural characteristics	Typical example
Separated liquids cell	Two compartments containing distinct electrolyte solutions, brought into ionic contact by a salt bridge or porous membrane, to allow ion flow while preventing direct mixing of solutions.	Daniell cell: $\text{Zn} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}$
Common electrolyte cell	Both electrodes are immersed in the same electrolyte, simplifying the cell structure; separation of half-reactions then relies solely on the nature and potential of the solid electrodes.	$\text{Zn} \mid \text{Zn}^{2+}(\text{aq}) / \text{Ag}^{+}(\text{aq}) \mid \text{Ag}$ cell in a solution containing the inert anion NO_3^- .
Concentration cell	Both half-cells involve the same redox couple , but at different ionic concentrations; the electromotive force then arises exclusively from the concentration gradient, according to the Nernst equation which predicts at 25 °C: $E_{\text{cell}} = \frac{0.06}{n} \log_{10} \left(\frac{a_2}{a_1} \right)$	$\text{Ag} \mid \text{Ag}^{+}(c_1) \parallel \text{Ag}^{+}(c_2) \mid \text{Ag}$ with $c_1 \neq c_2$.
Fuel cell	Reactants (often gaseous) are continuously supplied from an external source, allowing prolonged operation as long as fuel and oxidant supply is maintained; the cell thus functions as an open electrochemical reactor.	Hydrogen-oxygen cell (H_2/O_2) with aqueous alkaline or acidic electrolyte and catalytic electrodes (Pt).
Dry cell	The electrolyte is immobilized as a paste or gel, making the cell compact, portable, and less prone to liquid leakage; this principle underlies many common primary batteries.	Leclanché cell (Zn–C) with pasty NH_4Cl and ZnCl_2 electrolyte.

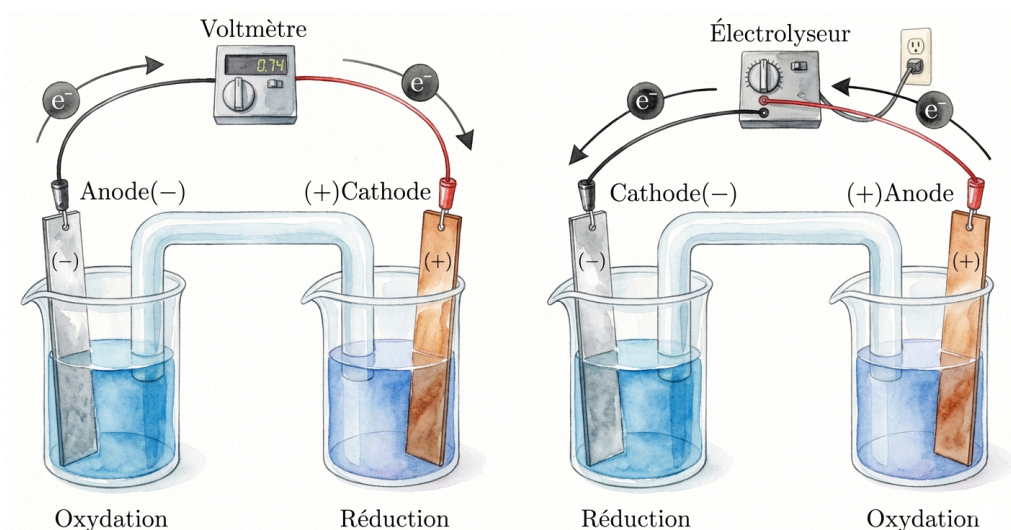


Figure 8.4 Comparison between a galvanic cell (left) and an electrolytic cell (right)

1. Galvanic (or voltaic) cells

- A **galvanic cell** is an electrochemical cell in which a **spontaneous** overall redox reaction ($\Delta G < 0$) occurs, which results in a **positive** electromotive force $E > 0$.
- Part of the energy released by the reaction is converted into useful electrical work, the rest is lost as heat.
- The cell (the **system**) performs **work on the environment**: it provides a current that can power a load (lamp, motor, electronic circuit, etc.), as long as the reactants are not exhausted.
- From the point of view of charge flow, electrons are produced at the **anode** (oxidation) and move, via the external circuit, toward the **cathode** (reduction), while ions flow in the electrolyte and/or the salt bridge to maintain electrical neutrality.
Note: conventional current flows in the opposite direction to electron flow.
- All common commercial cells and batteries (Daniell cell, alkaline cell, lead-acid accumulator, Li-ion batteries, Ni-MH, etc.) are based on galvanic cells, possibly assembled in series or parallel.

2. Electrolytic cells

- An **electrolytic cell** is an electrochemical cell in which an external electrical energy source imposes a **non-spontaneous** redox reaction ($\Delta G > 0$), which corresponds to a **negative** cell electromotive force if the reaction is written in the imposed direction ($E < 0$).
- The external supply provides electrical work that is converted into an **increase in chemical free energy**: thermodynamically unfavored reactants are transformed into higher-energy products (e.g., separation of compounds, metal deposition, water decomposition).
- In this case, it is the **environment** (generator, power supply) that performs **work on the system** (the cell), forcing current to flow in the opposite direction to that it would take spontaneously.
- Electrons are always transferred from the **anode** to the **cathode**, but here their movement is **forced** by the external source: the anode is connected to the positive pole and the cathode to the negative pole of the generator.
- Many industrial operations rely on electrolytic cells: electrodeposition (plating metals on objects), electrolytic refining (Cu, Al), production of Cl_2 , NaOH, water electrolysis, formation or regeneration of certain accumulators.

Caution

Electrode sign and polarity reversal

It is crucial to note that the definitions of anode and cathode are **independent of the electrical sign**: the immutable rule is **Oxidation = Anode** and **Reduction = Cathode**. Conventional current flows in the opposite direction to electron flow.

However, polarity reverses according to the operating mode:

- ▷ **Galvanic cell (Generator):** The anode is the **negative** (–) pole because it is the source of electrons (released by spontaneous oxidation) that feeds the external circuit. The cathode is the **positive** (+) pole.
- ▷ **Electrolytic cell (Receiver):** The anode is connected to the **positive** (+) pole of the external generator (it receives electrons), and the cathode to the **negative** (–) pole (it provides electrons). The anode therefore becomes **positive** and the cathode **negative**.

Table 8.4 Systematic comparison of galvanic cells and electrolytic cells.

Aspect	Galvanic (voltaic) cell	Electrolytic cell
Nature of reaction	Spontaneous ($\Delta G < 0$)	Non-spontaneous ($\Delta G > 0$)
Sign of EMF	$E_{\text{cell}} > 0$	$E_{\text{cell}} < 0$ (for the reaction written in the imposed direction)
Energy conversion	Chemical $\rightarrow$ Electrical	Electrical $\rightarrow$ Chemical
Direction of work	System $\rightarrow$ Environment	Environment $\rightarrow$ System
Anode polarity	Negative	Positive
Cathode polarity	Positive	Negative
Electron direction	From anode to cathode (spontaneous current)	From anode to cathode (current imposed by the source)
Typical architecture	Two half-cells connected by a salt bridge	Often two electrodes in the same electrolyte, or similar setup
Common examples	Daniell cell, alkaline cell, Li-ion batteries, lead-acid accumulator	Water electrolysis, Cl_2/NaOH production, electrodeposition, electrolytic refining of metals

8.2.6 Characteristic quantities of a cell

Three fundamental quantities characterize the electrical and energy behavior of a cell: the electromotive force (EMF), which represents its "ideal voltage"; the current and power it can deliver under load; and its capacity, which measures its total *charge* reserve (and therefore the recoverable energy via voltage). Understanding them allows linking the thermodynamics of redox reactions to the practical performance of an electrochemical generator.

8.2.6.1 Electromotive force (EMF):

definition, measurement conditions, and interpretation:

The Electromotive Force (denoted E or EMF) is the key thermodynamic quantity that quantifies the tendency of a cell to drive electrons through a circuit.

The EMF is the **maximum potential difference** between the terminals of the cell when it delivers **no current** (open circuit). It is therefore the "no-load" voltage of the generator, determined by the redox couples involved and the state of the medium (activities, often approximated as concentrations), where each electrode potential obeys the **Nernst** equation (at least as a first approximation in dilute solutions).

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\oplus} - E_{\ominus}$$

8.2.6.2 Current, power, and capacity: real discharge regime

In practice, when a cell powers a closed circuit, its performance is governed not only by thermodynamics (the EMF), but also by **ohmic** (resistances) and **kinetic** factors (polarization, transport limitations).

Delivered current: why does voltage drop? (simplified model) A cell can be viewed as:

- an **ideal source** of voltage E (the EMF, "no-load" voltage),
- **in series** with an **internal resistance** r (electrolyte, electrodes, contacts, interfaces).

As soon as a load is connected and a current I flows, part of the voltage is "consumed" inside the cell. This is exactly an ohmic voltage drop: rI . Therefore, the voltage actually measured at the terminals becomes:

$$U_{\text{terminals}} = E - rI$$

If the load is a resistance R_{load} , the total seen by the source is $R_{\text{load}} + r$, hence:

$$I = \frac{E}{R_{\text{load}} + r}$$

Caution

The paradox of the "tired" battery

On a voltmeter, a battery may seem "good" because the voltmeter draws almost zero current: $I \approx 0$, so $U_{\text{terminals}} \approx E$.

But as soon as a device is connected (non-zero current), the voltage drops: $U_{\text{terminals}} = E - rI$.

A battery at the end of its life often has a larger r (and/or polarization losses), so the drop rI becomes very significant and the voltage **collapses under load**.

Delivered power: what the load receives The load receives the power:

$$P = U_{\text{terminals}} I = (E - rI)I$$

Two important ideas:

- If I is very small: $U_{\text{terminals}} \approx E$ but the power P is small (since $P \approx EI$).
- If I is very large: the drop rI becomes significant, $U_{\text{terminals}}$ drops, and the useful power may decrease again.

In the simple ohmic model, the power transferred to the load is maximum when:

$$R_{\text{load}} = r$$

But this is **not** the best choice for efficiency, since a significant fraction of the power is lost as internal heat.

Internal losses (heating):

$$P_{\text{lost}} = rI^2$$

Energy efficiency:

$$\eta = \frac{W_{\text{real}}}{W_{\text{max}}} = \frac{\int_0^t U_{\text{terminals}} I dt}{\int_0^t E I dt} < 1$$

Interpretation: the maximum energy corresponds to " E multiplied by the charge transferred," while the energy actually recovered is limited by the voltage under load $U_{\text{terminals}}$.

Capacity: the charge reserve (and recoverable energy) Capacity C (in A · h or C) is the **total amount of charge** that the cell can supply before being considered discharged.

- **Theoretical capacity C_{th} (ideal chemistry):** it depends on the amount of reactants actually available. If the maximum extent is ξ_{max} (mol) for the limiting reactant, then the total transferable charge is:

$$C_{\text{th}} = nF\xi_{\text{max}}$$

- **Practical capacity (reality):** it is lower than C_{th} because part of the chemistry is not fully exploited:
 - ▷ self-discharge (side reactions),
 - ▷ partially inaccessible reactants (porosity, passivation),
 - ▷ limitations at high current (diffusion, polarization).

- **Why capacity depends on discharge current:** at high current, the voltage under load drops more (rI drop + polarization), the cutoff voltage is reached sooner, so the "measured" capacity decreases. This is why manufacturers specify capacity for a given regime (e.g., "C/10").

Synthesis: from ideal (chemistry) to real (usage). A cell can be understood in three "levels":

- a) **What chemistry can give (thermodynamic ideal).** The redox reaction sets an **ideal voltage** called the **EMF E** (no-load voltage, no current) and a **total possible quantity of electricity** called **theoretical capacity (C_{th})**.

Key idea: this is the **maximum** the cell could deliver if everything were perfect.

- b) **What the cell gives when current is drawn (real electrical).** As soon as a device is connected, a current I flows. Then part of the voltage is "lost" due to **internal resistance r** (drop rI) and **polarization** (losses related to slow reactions, ion transport, etc.). The voltage measured at the terminals therefore becomes a **voltage under load $U_{terminals}$** , smaller than E .

- c) **What is actually recovered (usable practical).** Since there are losses, the **practical capacity** is lower than C_{th} , the **delivered power** is limited, and the **efficiency** is $< 100\%$.

Key idea: these are the **effective** performances during use.

Conclusion: the ideal (chemistry) sets a ceiling, the real (electrical) imposes losses, and the practical (usage) describes what is actually obtained.

8.2.7 Electrode potential: a relative quantity

One of the fundamental conceptual difficulties in electrochemistry is that the **electrode potential** of a redox couple cannot be measured absolutely. This limitation is not technical but physical; it stems from the very nature of the electrode-electrolyte interface. Understanding this relativity is essential for correctly interpreting standard potential tables and their applications.

8.2.7.1 The physical impossibility of measuring an absolute potential

When a metal electrode **M** is immersed in a solution containing its ions M^{n+} , a potential difference establishes at the electrode/solution interface. This difference, often denoted **Galvani potential $\Delta\phi$** , results from charge separation until a dynamic equilibrium is established.

The experimental dilemma: measuring a voltage always requires **two terminals**.

- a) The first terminal is the M electrode.
- b) The second terminal must be in electrical contact with the solution, which requires introducing a **second conductor** (another electrode).
- c) However, this second electrode inevitably creates **its own** electrode/solution interface, hence its own $\Delta\phi$, uncontrolled a priori.

Thus, a voltmeter can never give "the potential of M": it measures a **potential difference** between two electrodes (to which junction potentials may be added).

Caution

Analogy (one sentence). Like altitude, one does not measure an absolute value without a reference: one only measures **differences** between two points.

8.2.7.2 The solution: the Standard Hydrogen Electrode (SHE) as a universal reference:

Faced with the impossibility of measuring an electrode potential in isolation, the scientific community adopted an international convention: defining a **conventional zero** for the potential scale. This zero is set by the **Standard Hydrogen Electrode (SHE)**, whose standard potential is arbitrarily defined as:

$$E_{SHE}^{\circ} \equiv 0.0 \text{ V} \quad \text{at all temperatures.}$$

This means that the SHE serves as a *reference* (origin) for the potential scale, not that any electrochemical measurement would be temperature-independent: as soon as conditions are not strictly standard (activities, pressures, etc.), the Nernst equation introduces an explicit dependence on T via the term $\frac{RT}{nF}$.

Thus, any tabulated standard potential E° is read as a potential difference measured relative to the SHE.

- a) **Convention:** $E_{H^+/H_2}^{\circ} \equiv 0.0 \text{ V}$ (zero of the scale)
- b) **Standard conditions:** $a_{H^+} = 1$, $P_{H_2} = 1 \text{ bar}$, platinized platinum electrode, 25°C

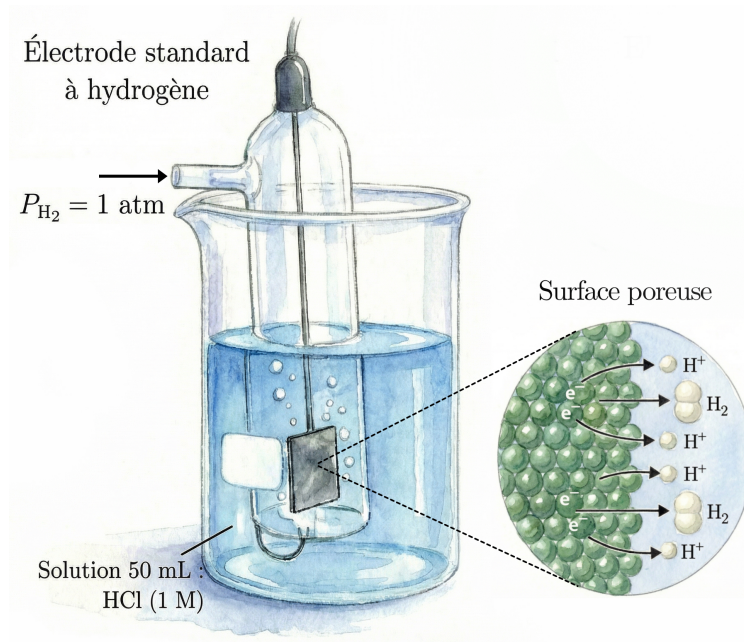


Figure 8.5 Detailed diagram of the Standard Hydrogen Electrode (SHE)

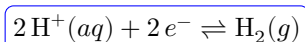
- c) **Meaning:** An $E^\circ = +0.80 \text{ V}$ means "0.80 V more oxidizing than H^+ under standard conditions"

Construction and rigorous conditions: A functional SHE requires highly controlled experimental conditions:

- Platinized platinum electrode:** A Pt wire (or plate) coated by electrodeposition with a layer of **platinum black** (finely divided and porous Pt). This structure significantly increases the real contact surface compared to the geometric surface, improving the kinetics of electron transfer. It lowers the activation overpotential of the H^+/H_2 couple, promoting (quasi)-reversible behavior and a reproducible potential.
- Standard acid solution:** An aqueous solution where the thermodynamic activity of protons is fixed at $a_{\text{H}^+} \approx 1$ (often approximated as an acid solution $\approx 1.0 \text{ mol L}^{-1}$ under dilute conditions). A supporting electrolyte as *inert* as possible with respect to the Pt/solution interface is chosen, to limit potential perturbations and preserve the reversibility of the electrode.
- Standard hydrogen gas:** High-purity dihydrogen $\text{H}_2(\text{g})$ maintained at a standard partial pressure of $P^\circ = 1 \text{ bar}$ (10^5 Pa). Continuous bubbling ensures two critical functions: it imposes the activity of H_2 near the electrode (in the Nernst expression) and removes dissolved oxygen that could induce side reactions.
- Controlled temperature:** The system must be thermostated, generally at $T = 298.15 \text{ K}$. Although the standard potential of the SHE is defined as zero by convention, the term $\frac{RT}{nF}$ in the Nernst law depends on T ; an uncontrolled thermal variation can therefore affect measurement reproducibility.

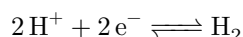
A platinized platinum electrode (platinum black, porous surface) is immersed in an acidic solution with $a(\text{H}^+) = 1$. Ultra-pure $\text{H}_2(\text{g})$ bubbles at $P_{\text{H}_2} = 1 \text{ bar}$ to establish equilibrium at the interface. The zoom or enlargement in the figure above (8.5) illustrates a clear direction; the half-reaction $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ is reversible.

Operation and electrochemical equilibrium The half-reaction at the platinum/solution interface is:



Platinum does not participate in the redox reaction; it serves as an inert conductor and catalyst to rapidly establish dynamic equilibrium.

Why $E^\circ(\text{SHE}) = 0 \text{ V}$: a *convention* For the H^+/H_2 couple, written in the reduction direction:



the Nernst equation at 298 K gives:

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^\circ - \frac{0.06}{2} \log_{10} \left(\frac{a_{\text{H}_2}}{a_{\text{H}^+}^2} \right)$$

For an ideal gas, activity is approximated by relative pressure:

$$a_{\text{H}_2} \simeq \frac{P_{\text{H}_2}}{P^\circ} \quad \text{with} \quad P^\circ = 1 \text{ bar},$$

hence:

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^\circ - \frac{0.06}{2} \log_{10} \left(\frac{P_{\text{H}_2}/P^\circ}{a_{\text{H}^+}^2} \right)$$

By **convention**, the standard potential of the Standard Hydrogen Electrode (SHE) is defined as:

$$E_{\text{H}^+/\text{H}_2}^\circ \equiv 0 \text{ V}$$

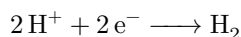
Thus, under standard conditions ($a_{\text{H}^+} = 1$ and $P_{\text{H}_2} = P^\circ = 1 \text{ bar}$), the Nernst expression gives:

$$E_{\text{H}^+/\text{H}_2} = 0 \text{ V}.$$

Outside standard conditions, the SHE potential deviates from zero according to the Nernst equation.

The SHE can operate in both directions The SHE is not intrinsically a cathode or an anode: its role depends on the couple it is paired with.

- If it **receives** electrons: it is a **cathode** (reduction):



- If it **donates** electrons: it is an **anode** (oxidation):



The direction depends on the couple it is paired with in the measurement cell.

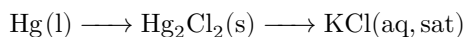
Why was hydrogen chosen? Justifications The H^+/H_2 couple was chosen as the basis of the potential scale because it defines a simple, well-characterized reaction that can be brought close to equilibrium on a suitable platinum surface.

- **Reversibility:** On platinized platinum, the exchange kinetics of the H^+/H_2 couple are high, minimizing polarization and promoting a stable reference potential.
- **Simplicity and universality:** The proton is involved in a large part of acid-base and redox equilibria in aqueous media, making the reference very general.
- **Reproducibility:** Controlled contact between $\text{H}_2(\text{g})$ and an acidic solution allows fixing defined activities/pressures, improving inter-laboratory comparability.
- **Well-established data:** The thermodynamic quantities associated with H_2 and H^+ are among the most documented, which facilitated its adoption as a standard.

Practical limitations and secondary reference electrodes Although fundamental for defining the scale, the SHE is cumbersome to implement (need for a hydrogen cylinder (H_2), explosion risk, easy poisoning of Pt). In the laboratory, **secondary reference electrodes**, more robust and easier to use, are preferred, with stable and known potential relative to the SHE.

At 25°C, the most common are:

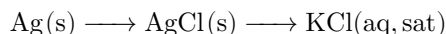
- **Saturated Calomel Electrode (SCE):**



Consisting of liquid mercury in contact with calomel (Hg_2Cl_2 , solid mercurous chloride) and a saturated solution of KCl. This was the most common historical reference, very stable, but now less used due to mercury toxicity.

$$E_{\text{SCE}} \approx +0.244 \text{ V} \quad \text{relative to SHE (at } 25^\circ\text{C)}.$$
⁽⁶²⁾

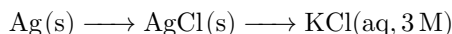
- **Silver-Silver Chloride Electrode (saturated KCl):**



Composed of a chlorided silver wire (AgCl) immersed in an internal saturated KCl solution. This is the modern standard reference electrode: robust, non-toxic, and compact.

$$E_{\text{Ag/AgCl}} \approx +0.197 \text{ V} \quad \text{relative to SHE (at } 25^\circ\text{C)}$$

- **Silver-Silver Chloride Electrode (KCl, 3M):**



Variant of the previous one using a non-saturated KCl concentration (3 mol/L). It avoids salt crystallization at the junction (frit) during temperature variations, offering better thermal stability.

$$E_{\text{Ag/AgCl}} \approx +0.210 \text{ V} \quad \text{relative to SHE (at } 25^\circ\text{C)}$$

Note: These values depend on temperature and the exact concentration of the internal electrolyte.

Summary: Electrode potential is a **relative** quantity because:

- Only **potential differences** between two electrodes can be measured.
- The community assigned the value **zero** to the standard potential of the SHE. $E_{\text{SCE}} \approx +0.241 \text{ V/SHE}$
- The **standard potential** E° of a couple = EMF of the cell:
[studied couple (standard conditions)] || SHE
- This convention transforms an impossibility of absolute measurement into a **coherent, universal, and exploitable** reference system.

8.2.7.3 Definition and determination of the standard potential E°

The **standard potential** E° of a redox couple is defined operationally.

The standard potential $E_{\text{Ox/Red}}^\circ$ of a redox couple is the **Electromotive Force** (EMF) of the cell formed by:

- A half-cell containing the studied couple **in its standard conditions** (all species at activity 1, specified temperature, generally 298 K).
- A **Standard Hydrogen Electrode** (SHE) as the other half-cell.

The cell is assembled so that reduction occurs on the electrode of the studied couple (if $E^\circ > 0$) or on the SHE (if $E^\circ < 0$).

Experimental setup for determining E° : Figure 8.6 well illustrates the experimental tool for determining the standard potential value. The setup consists of two half-cells connected by a salt bridge (typically a concentrated KCl solution gelled in agar-agar). The left half-cell is the Standard Hydrogen Electrode (SHE), which serves as a universal reference. It is maintained under rigorous conditions: a platinized platinum electrode is immersed in an acidic solution where $a_{\text{H}^+} = 1$, while continuous bubbling of ultra-pure hydrogen at a pressure of 1 bar ($P_{\text{H}_2} = 1$) ensures equilibrium at the interface. The right half-cell is the working electrode, here a metallic silver electrode ($\text{Ag}_{(\text{s})}$) immersed in a silver nitrate solution (AgNO_3) with an activity of Ag^+ ions exactly equal to 1 ($a_{\text{Ag}^+} = 1$). A high-impedance voltmeter measures the electromotive force (EMF) of the cell in open circuit, avoiding any current that would disturb equilibrium. By schematic convention (often adopted in electrochemistry), the Standard Hydrogen Electrode (SHE), taken as a reference, is represented on the left. In this measurement setup, the voltage read on the voltmeter is then written:

$$E_{\text{meas}} = E_{\text{right}} - E_{\text{left}}$$

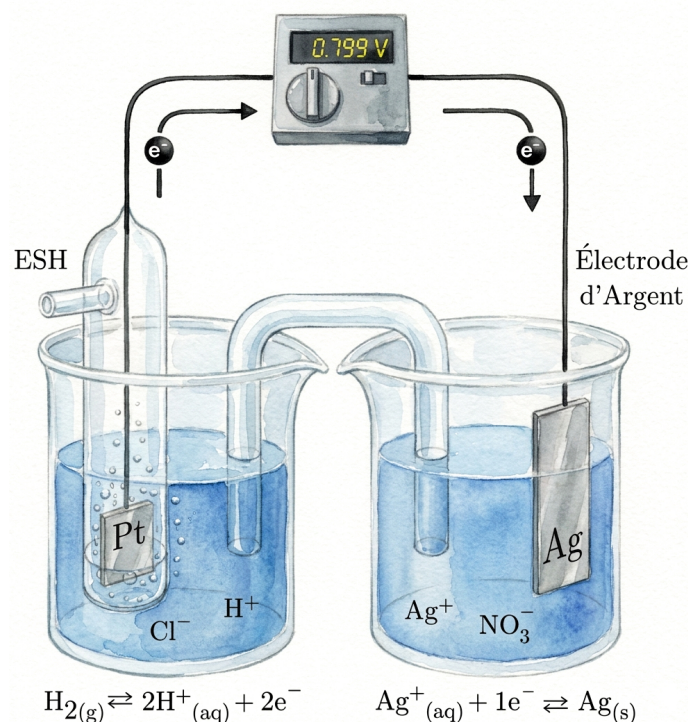


Figure 8.6 Experimental setup for determining the standard potential of the Ag^+/Ag couple.

This **right-left** writing therefore depends on the drawing convention (placement of the SHE) and does not by itself define the nature of the electrodes.

The general physical relationship to remember is:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

with **Oxidation at the anode** and **Reduction at the cathode**. Thus, in the example where the silver electrode has a standard potential $E^\circ > 0$, the SHE plays the role of anode (oxidation) facing this couple; this role would reverse facing a couple with a negative standard potential.

Thermodynamic demonstration and calculation: The measured voltage E_{meas} corresponds to the potential difference between the cathode and the anode. Applying the Nernst law to each half-cell under their respective conditions, we obtain:

$$\begin{aligned} E_{\text{meas}} &= E_{\text{cathode}} - E_{\text{anode}} = E_{(\text{Ag}^+/\text{Ag})} - E_{\text{SHE}} \\ &= \left[E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{0.06}{1} \log \left(\frac{a_{\text{Ag}^+}}{a_{\text{Ag(s)}}} \right) \right] - \left[\underbrace{E_{\text{H}^+/\text{H}_2}^\circ}_0 + \frac{0.06}{2} \log \left(\frac{(a_{\text{H}^+})^2}{\frac{P_{\text{H}_2}}{P^\circ}} \right) \right] \end{aligned}$$

Under the imposed standard conditions ($T = 298.15 \text{ K}$, $a_{\text{Ag}^+} = 1$, $a_{\text{Ag(s)}} = 1$, $a_{\text{H}^+} = 1$, $P_{\text{H}_2} = P^\circ = 1 \text{ bar}$), all logarithmic terms become zero ($\ln(1) = 0$). The equation then reduces to:

$$E_{\text{meas}} = E_{\text{Ag}^+/\text{Ag}}^\circ - 0$$

Thus, the electromotive force measured in open circuit directly gives access to the standard potential of the studied couple:

$$E_{\text{Ag}^+/\text{Ag}}^\circ = E_{\text{meas}} = +0.799 \text{ V}$$

Meaning and scale of standard potentials The sign and value of E° are intrinsic thermodynamic quantities that quantify the relative tendency of an oxidizing/reducing couple to capture electrons compared to the

reference couple H^+/H_2 . This scale allows a predictive classification of redox properties:

- $E^\circ > 0$: The couple is **more oxidizing** than H^+/H_2 . The oxidized species (e.g., Ag^+) has a higher affinity for electrons than H^+ . Its reducing agent (e.g., Ag(s)) is therefore a **weaker** reducing agent than H_2 and does not react with non-oxidizing acids to release dihydrogen. This is the case of so-called **noble** metals.
- $E^\circ < 0$: The couple is **more reducing** than H^+/H_2 . The reducing agent (e.g., Zn(s)) donates its electrons more easily than H_2 and can therefore reduce H^+ to H_2 . These metals are attacked by acids with gas evolution.

The classification of all couples by decreasing E° constitutes the **standard potential scale**, a true scale of oxidizing power. It allows applying the **gamma rule** (or diagonal rule) to predict the spontaneous direction of redox reactions: the oxidant of the couple with the highest E° reacts with the reducing agent of the couple with the lowest E° .

Limitations and precautions for use

- Relativity:** An $E^\circ = +0.80 \text{ V}$ for Ag^+/Ag does not mean that the absolute potential of silver is 0.80 V, but that it is 0.80 V **relative to the SHE**.
- Standard conditions:** E° is defined for unit activities, which differs from 1 M concentrations for non-ideal solutions.
- pH dependence:** For couples involving H^+ or OH^- , E° depends on pH. One often defines a formal standard potential at a given pH.
- Secondary references:** In practice, the SHE is bulky and impractical. More stable reference electrodes such as the saturated calomel electrode (SCE, $E \approx +0.24 \text{ V /SHE}$) or the Ag/AgCl electrode, whose potential relative to the SHE is perfectly known, are used.

Summary: Electrode potential is a **relative** quantity because:

- Experimentally, only a **potential difference** between two electrodes can be measured.
- The community conventionally assigned the value **zero** to the potential of the Standard Hydrogen Electrode (SHE).
- The **standard potential** E° of a couple is therefore the EMF of the cell formed by this couple (in its standard conditions) and an SHE.
- This convention allows establishing a **coherent and universal scale** of oxidizing powers, essential for predicting the direction and equilibrium of redox reactions.

This relativity is not a weakness but a strength: it transforms an impossibility of absolute measurement into a practical and universally accepted reference system.

8.2.7.4 Predicting the direction of reactions:

The gamma rule (or diagonal rule) is a simple graphical tool for predicting the spontaneous direction of a redox reaction from the standard potentials of the couples involved.

The principle of the gamma rule is simple: On a vertical axis of increasing potentials (from bottom to top), the two redox couples involved are placed. A diagonal is then drawn connecting the strongest oxidant (highest potential) to the strongest reductant (lowest potential). This diagonal forms a "γ" with the potential axis and indicates the spontaneous direction of the reaction: the strongest oxidant reacts with the strongest reductant.

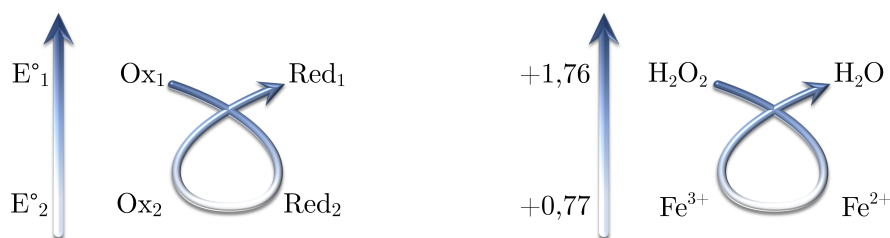


Figure 8.7 Predicting reaction direction with the gamma rule

Practical example: Can Fe^{2+} be oxidized to Fe^{3+} with H_2O_2 ?

- Couple 1: $\text{Fe}^{3+}/\text{Fe}^{2+}$ $E^\circ = +0.77 \text{ V}$
- Couple 2: $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ $E^\circ = +1.76 \text{ V}$

Table 8.5 Scale of standard potentials E° at 25 °C (relative to the SHE). Data from. ^{(63),(64)}

No.	Element	Redox couple	Reduction half-equation	E° (V)
Extremely Strong Oxidants ($E^\circ > +1.8$ V)				
1	F	F_2/F^-	$F_2(g) + 2e^- \rightleftharpoons 2F^-$	+2.866
2	O	O_3/O_2	$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	+2.075
3	S	$S_2O_8^{2-}/SO_4^{2-}$	$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.010
4	Ag	Ag^{2+}/Ag^+	$Ag^{2+} + e^- \rightleftharpoons Ag^+$	+1.980
5	Co	Co^{3+}/Co^{2+}	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.920
6	Pb	Pb^{4+}/Pb^{2+}	$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.455
Strong Oxidants ($+1.2 < E^\circ < +1.8$ V)				
7	Mn	MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.507
8	Au	Au^{3+}/Au	$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	+1.498
9	Ce	Ce^{4+}/Ce^{3+}	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	+1.440
10	Cl	Cl_2/Cl^-	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.358
11	Cr	$Cr_2O_7^{2-}/Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.332
12	Mn	MnO_2/Mn^{2+}	$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.224
13	O	O_2/H_2O	$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
Moderate Oxidants ($+0.8 < E^\circ < +1.2$ V)				
14	Br	Br_2/Br^-	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.087
15	N	NO_3^-/NO	$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO(g) + 2H_2O$	+0.957
16	Hg	Hg_2^{2+}/Hg	$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	+0.796
17	Ag	Ag^+/Ag	$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
18	Fe	Fe^{3+}/Fe^{2+}	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
19	O	O_2/H_2O_2	$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695
Weak Oxidants ($0 < E^\circ < +0.8$ V)				
20	I	I_2/I^-	$I_2(s) + 2e^- \rightleftharpoons 2I^-$	+0.536
21	Cu	Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.342
22	Ag	$AgCl/Ag$	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
23	S	SO_4^{2-}/SO_2	$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2(aq) + 2H_2O$	+0.158
24	Cu	Cu^{2+}/Cu^+	$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.153
25	Sn	Sn^{4+}/Sn^{2+}	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.151
26	S	S/H_2S	$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S(g)$	+0.142
27	H	H^+/H_2	$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0
Weak Reductants ($0 < E^\circ < -0.8$ V)				
28	Pb	Pb^{2+}/Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.126
29	Sn	Sn^{2+}/Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	-0.138
30	Ni	Ni^{2+}/Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	-0.257
31	Co	Co^{2+}/Co	$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	-0.277
32	Cd	Cd^{2+}/Cd	$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	-0.403
33	Fe	Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	-0.440
34	Cr	Cr^{3+}/Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr(s)$	-0.740
35	Zn	Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.762
Strong Reductants ($-0.8 < E^\circ < -2.5$ V)				
36	Mn	Mn^{2+}/Mn	$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	-1.185
37	V	V^{2+}/V	$V^{2+} + 2e^- \rightleftharpoons V(s)$	-1.175
38	Ti	Ti^{2+}/Ti	$Ti^{2+} + 2e^- \rightleftharpoons Ti(s)$	-1.630
39	Al	Al^{3+}/Al	$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	-1.662
40	Be	Be^{2+}/Be	$Be^{2+} + 2e^- \rightleftharpoons Be(s)$	-1.847
41	U	U^{3+}/U	$U^{3+} + 3e^- \rightleftharpoons U(s)$	-1.789
42	Mg	Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	-2.372
Extremely Strong Reductants ($E^\circ < -2.5$ V)				
43	Na	Na^+/Na	$Na^+ + e^- \rightleftharpoons Na(s)$	-2.714
44	Ca	Ca^{2+}/Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	-2.868
45	Sr	Sr^{2+}/Sr	$Sr^{2+} + 2e^- \rightleftharpoons Sr(s)$	-2.899
46	Ba	Ba^{2+}/Ba	$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.912
47	K	K^+/K	$K^+ + e^- \rightleftharpoons K(s)$	-2.936
48	Li	Li^+/Li	$Li^+ + e^- \rightleftharpoons Li(s)$	-3.040

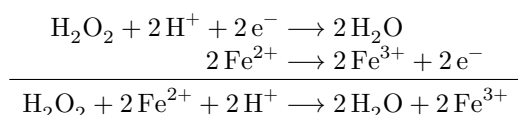
Comparative potential analysis: By comparing the standard potential values, we observe:

$$E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.76 \text{ V} > E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$$

This potential difference allows us to identify:

- **The strongest oxidant:** H_2O_2 because its potential is the highest, so it has the greatest tendency to capture electrons.
- **The strongest reductant:** Fe^{2+} because the potential of its couple is the lowest, so it has the greatest tendency to donate electrons.

Spontaneous reaction: Since H_2O_2 is the strongest oxidant and Fe^{2+} the strongest reductant, their reaction is thermodynamically favored. Hydrogen peroxide can therefore oxidize iron(II) ions to iron(III) ions according to the reaction:



Thermodynamic verification: The driving force of this reaction can be quantified by calculating the standard electromotive force of the corresponding cell:

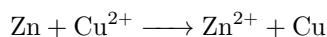
$$\Delta E^\circ = E^\circ(\text{oxidant}) - E^\circ(\text{reductant}) = 1.76 - 0.77 = 0.99 \text{ V} > 0$$

A positive ΔE° value confirms that the reaction is indeed spontaneous in the direction written.

Example 2: Reduction of Cu^{2+} by Zn (basic electrochemistry). Couples:

- Cu^{2+}/Cu : +0.34 V
- Zn^{2+}/Zn : -0.76 V

$\Delta E^\circ = 0.34 - (-0.76) = +1.10 \text{ V}$. Diagonal: Cu^{2+} (strong oxidant) oxidizes Zn (strong reductant). Reaction:



Conventions:

- **Tabulated potentials:** the E° values are **standard reduction potentials**.
- **Nernst (at 25 °C):** for a half-equation written as reduction $\text{Ox} + n\text{e}^- \rightleftharpoons \text{Red}$,

$$E = E^\circ - \frac{0.05916}{n} \log Q, \quad Q = \frac{a(\text{products})}{a(\text{reactants})}$$

- **Activities:** in dilute solution,

$$a_i \approx \frac{[i]}{c^\circ}, \quad c^\circ = 1 \text{ mol/L}$$

Thus if $[i]$ is expressed in mol/L, one can numerically write $a_i \simeq [i]$.

- **Pure condensed phases:** pure solids and liquid water have $a = 1$ and do not appear in Q .

Exercises with solutions:

Exercise

Ag^+/Ag electrode (Nernst + interpretation)

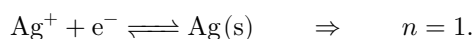
Statement A silver electrode Ag(s) is immersed in a silver nitrate AgNO_3 solution. Assume a dilute solution: $a_{\text{Ag}^+} \approx [\text{Ag}^+]/c^\circ$ with $c^\circ = 1 \text{ mol} \cdot \text{L}^{-1}$, and $a_{\text{Ag(s)}} = 1$.

- Calculate E for $[\text{Ag}^+] = 10^{-2} \text{ mol/L}$.
- Calculate E for $[\text{Ag}^+] = 10^{-6} \text{ mol/L}$.
- Interpret: what happens if the Ag^+ solution is **diluted**?

Data: $E^\circ(\text{Ag}^+/\text{Ag}) = +0.799 \text{ V}$.

Solution

Half-equation (reduction):



Reaction quotient (products / reactants):

$$Q = \frac{a_{\text{Ag(s)}}}{a_{\text{Ag}^+}} = \frac{1}{a_{\text{Ag}^+}}$$

Nernst at 25 °C:

$$E = E^\circ - 0.059 \log \left(\frac{1}{a_{\text{Ag}^+}} \right) = E^\circ + 0.059 \log(a_{\text{Ag}^+})$$

In dilute solution, $a_{\text{Ag}^+} \approx [\text{Ag}^+]/c^\circ$ with $c^\circ = 1 \text{ mol} \cdot \text{L}^{-1}$ (c° is the standard reference concentration used to define a dimensionless activity), therefore:

$$E \simeq 0.799 + 0.059 \log [\text{Ag}^+]$$

a) $[\text{Ag}^+] = 10^{-2} \rightarrow \log(10^{-2}) = -2$

$$E = 0.799 + 0.059(-2) = 0.6807 \text{ V}$$

b) $[\text{Ag}^+] = 10^{-6} \rightarrow \log(10^{-6}) = -6$

$$E = 0.799 + 0.059(-6) = 0.4440 \text{ V}$$

c) **Interpretation:** upon dilution, $[\text{Ag}^+]$ decreases $\Rightarrow a_{\text{Ag}^+}$ decreases $\Rightarrow Q = 1/a_{\text{Ag}^+}$ increases $\Rightarrow E$ decreases (Nernst). The electrode becomes **less oxidizing** (lower reduction potential).

Exercise

Gamma rule (spontaneity): Fe^{2+} and H_2O_2

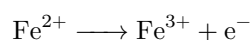
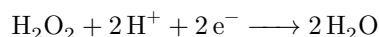
Statement Can Fe^{2+} be oxidized to Fe^{3+} with H_2O_2 in acidic medium?

- Couple A: $\text{Fe}^{3+}/\text{Fe}^{2+}$ $E^\circ = +0.77 \text{ V}$
 - Couple B: $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ $E^\circ = +1.76 \text{ V}$
- a) Use **only** the gamma rule to predict the spontaneous direction.
b) Write the two half-equations in the spontaneous direction.
c) Write the overall equation.
d) Calculate ΔE° and conclude.

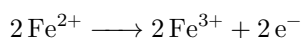
Solution

a) **Gamma:** since $E^\circ_{(\text{H}_2\text{O}_2/\text{H}_2\text{O})} > E^\circ_{(\text{Fe}^{3+}/\text{Fe}^{2+})}$, the strongest oxidant is H_2O_2 (it is **reduced**) and the strongest reductant is Fe^{2+} (it is **oxidized**).

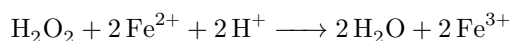
b) Half-equations (acidic medium):



Multiplication of the second by 2:



c) Overall equation:



d) Validation by ΔE° :

$$\Delta E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.76 - 0.77 = +0.99 \text{ V} > 0,$$

therefore the reaction is spontaneous in the direction written.

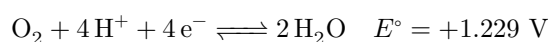
Exercise

Equality pH: $\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{O}_2/\text{H}_2\text{O}$

Statement At 25 °C, assume $P_{\text{O}_2} = 1 \text{ bar}$ and $[\text{MnO}_4^-] = [\text{Mn}^{2+}] = 1$. Determine the pH for which:

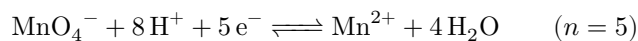
$$E_{(\text{MnO}_4^-/\text{Mn}^{2+})} = E_{(\text{O}_2/\text{H}_2\text{O})}.$$

Data:



Solution

1) **Permanganate couple.** Reduction half-equation:



Reaction quotient:

$$Q_{\text{Mn}} = \frac{a_{\text{Mn}^{2+}} a_{\text{H}_2\text{O}}^4}{a_{\text{MnO}_4^-} a_{\text{H}^+}^8} \approx \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

Therefore:

$$E_{\text{Mn}} = 1.51 - \frac{0.059}{5} \log \left(\frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \right)$$

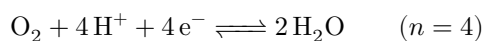
With $[\text{Mn}^{2+}] = [\text{MnO}_4^-] = 1$:

$$E_{\text{Mn}} = 1.51 - \frac{0.059}{5} \log \left(\frac{1}{[\text{H}^+]^8} \right)$$

Since $\log \left(\frac{1}{[\text{H}^+]^8} \right) = 8 \text{ pH}$, therefore:

$$E_{\text{Mn}} = 1.51 - \frac{0.059}{5} \cdot 8 \text{ pH} = 1.51 - 0.094656 \text{ pH}$$

2) **Dioxygen couple.**



$$Q_{\text{O}_2} = \frac{a_{\text{H}_2\text{O}}^2}{a_{\text{O}_2} a_{\text{H}^+}^4} \approx \frac{1}{(P_{\text{O}_2}/P^\circ)[\text{H}^+]^4}$$

With $P_{\text{O}_2} = P^\circ = 1 \text{ bar}$:

$$E_{\text{O}_2} = 1.229 - \frac{0.059}{4} \log \left(\frac{1}{[\text{H}^+]^4} \right) = 1.229 - 0.059 \text{ pH}$$

3) **Equality of potentials.**

$$1.51 - 0.094656 \text{ pH} = 1.229 - 0.059 \text{ pH}$$

$$0.281 = 0.035496 \text{ pH} \quad \Rightarrow \quad \text{pH} \approx 7.92$$

Gamma reading (commentary) When pH increases, $[H^+]$ decreases, so Q increases and reduction potentials decrease (Nernst). Permanganate decreases faster, losing its oxidizing character more quickly in less acidic media.

Exercise

Daniell cell: gamma + $\Delta_r G^\circ$ + K°

Statement Consider the cell (at 25 °C):



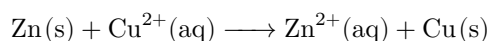
Data:

$$E^\circ_{(\text{Cu}^{2+}/\text{Cu})} = +0.340 \text{ V}, \quad E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.763 \text{ V}$$

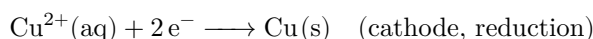
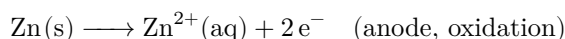
- Use the **gamma rule** to predict the spontaneous direction.
- Identify anode/cathode and write the half-equations.
- Calculate E°_{cell} .
- Deduce $\Delta_r G^\circ$ and then the equilibrium constant K° .

Solution

- a) **Gamma:** $0.340 > -0.763$. The strongest oxidant is Cu^{2+} and the strongest reductant is Zn(s) . Spontaneous reaction:



- b) Half-equations:



- c) Standard cell potential:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.340 - (-0.763) = 1.103 \text{ V}$$

- d) Thermodynamics:

$$\Delta_r G^\circ = -nFE^\circ_{\text{cell}}, \quad n = 2.$$

$$\Delta_r G^\circ \approx -2 \times 96485 \times 1.103 \approx -2.13 \times 10^5 \text{ J} \cdot \text{mol}^{-1}.$$

Relationship with equilibrium:

$$\Delta_r G^\circ = -RT \ln K^\circ \quad \Rightarrow \quad \ln K^\circ = \frac{nFE^\circ_{\text{cell}}}{RT}$$

Numerically at $T = 298.15 \text{ K}$:

$$\ln K^\circ \approx \frac{2 \times 96485 \times 1.103}{8.314 \times 298.15} \approx 85.9, \quad K^\circ \approx 10^{37.3}.$$

Conclusion: K° is enormous, the reaction is practically complete to the right.

Exercise

Gamma method and Nernst equation

Statement At 25 °C, the following are mixed:

$$[\text{Fe}^{3+}]_0 = [\text{Fe}^{2+}]_0 = 10^{-2} \text{ mol} \cdot \text{L}^{-1}, \quad [\text{I}_2]_0 = 10^{-3} \text{ mol} \cdot \text{L}^{-1}, \quad [\text{I}^-]_0 = 10^{-1} \text{ mol} \cdot \text{L}^{-1}.$$

Data:

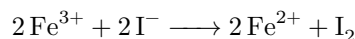
$$E^\circ_{(\text{Fe}^{3+}/\text{Fe}^{2+})} = +0.77 \text{ V}, \quad E^\circ_{(\text{I}_2/\text{I}^-)} = +0.54 \text{ V}.$$

- Predict the spontaneous direction using the gamma rule.
- Calculate the initial potentials E_{Fe} and E_{I} (Nernst).
- Conclude: does the reaction start spontaneously?

Solution

Gamma method then Nernst homogeneous

- Gamma (standard):** $0.77 > 0.54$. The strongest oxidant is Fe^{3+} and the strongest reductant is I^- . Expected reaction:



- Nernst.**

(a) **Iron couple:** $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ ($n = 1$)

$$Q_{\text{Fe}} = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \approx \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E_{\text{Fe}} = 0.77 - 0.059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

Here the ratio is 1, so $E_{\text{Fe}} = 0.77 \text{ V}$

(b) **Iodine couple:** $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$ ($n = 2$)

$$Q_{\text{I}} = \frac{a_{\text{I}^-}^2}{a_{\text{I}_2}} \approx \frac{[\text{I}^-]^2}{[\text{I}_2]}$$

$$E_{\text{I}} = 0.54 - \frac{0.059}{2} \log \left(\frac{[\text{I}^-]^2}{[\text{I}_2]} \right)$$

Numerically:

$$\frac{[\text{I}^-]^2}{[\text{I}_2]} = \frac{(10^{-1})^2}{10^{-3}} = \frac{10^{-2}}{10^{-3}} = 10^1 \Rightarrow \log(10^1) = 1,$$

therefore:

$$E_{\text{I}} = 0.54 - \frac{0.059}{2} \times 1 = 0.54 - 0.02958 = 0.510 \text{ V}$$

- Conclusion (spontaneous start).** Since $E_{\text{Fe}} > E_{\text{I}}$ ($0.77 > 0.510$), the effective oxidant Fe^{3+} is more oxidizing than I_2 under these conditions: the reaction starts spontaneously in the predicted direction.

Final message (to remember) The gamma rule is the **compass**: it gives the spontaneous direction from E° . The Nernst equation is the **magnifying glass**: it quantifies the effect of concentrations, pH, and pressures.

Exercise

Study of a $\text{Zn}/\text{Cr}_2\text{O}_7^{2-}$ cell

A cell is formed by two compartments:

Compartment 1: A zinc plate immersed in a solution (50 mL) of ZnSO_4 (0.01 M).

Compartment 2: A platinum wire immersed in a solution (50 mL) containing potassium dichromate (0.02 M) and chromium chloride CrCl_3 (0.01 M) in acidic medium. A salt bridge containing potassium sulfate connects the two compartments.

- Write the half-equations of the reactions and the overall equation.
- Draw a diagram of the cell setup and indicate the polarity, the direction of electron flow, current, and ions. What is the role of the salt bridge?
- Calculate the initial electromotive force, knowing that the pH of compartment 2 is maintained at pH = 1.

- d) Calculate the concentration of species at equilibrium. Can the reaction be considered complete?
 e) Compartment 1 is buffered at pH = 8, the voltmeter indicates an electromotive force equal to 2.12 V. Calculate the solubility product of $\text{Zn}(\text{OH})_2$.
 Data: $E^\circ(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.33 \text{ V}$, $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$.

Solution

Data from the statement

Compartment 1:

- Electrode: zinc plate
- Solution: 50 mL of ZnSO_4 0.01 M
- $[\text{Zn}^{2+}]_0 = 0.01 \text{ M}$

Compartment 2:

- Electrode: platinum wire (inert)
- Solution: 50 mL with $\text{K}_2\text{Cr}_2\text{O}_7$ 0.02 M and CrCl_3 0.01 M
- $[\text{Cr}_2\text{O}_7^{2-}]_0 = 0.02 \text{ M}$, $[\text{Cr}^{3+}]_0 = 0.01 \text{ M}$
- Acidic medium (imposed pH)

Salt bridge: Potassium sulfate (K_2SO_4) connecting the two compartments.

Standard potentials: $E^\circ(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.33 \text{ V}$ and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$

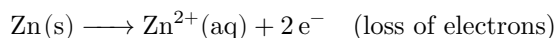
a) Half-equations and overall reaction:

Methodology: Determining the spontaneous direction Gamma rule: The strongest oxidant (highest standard potential) reacts with the strongest reductant (lowest standard potential).

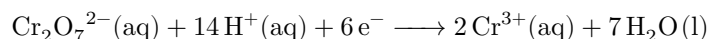
- Strongest oxidant: $\text{Cr}_2\text{O}_7^{2-}$ ($E^\circ = 1.33 \text{ V}$)
- Strongest reductant: Zn ($E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V} \Rightarrow \text{Zn metal is the reductant}$)

Therefore: The spontaneous reaction is the oxidation of zinc and the reduction of dichromate.

Balanced half-equations At the anode (compartment 1) - Oxidation:



At the cathode (compartment 2) - Reduction: Dichromate is reduced in acidic medium. Oxygen atoms must be balanced with H_2O and charges with e^- .

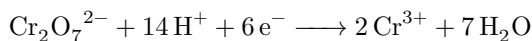
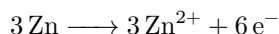


Tip: Balancing a half-equation in acidic medium

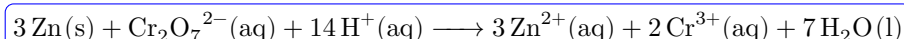
- Balance atoms other than O and H
- Balance O with H_2O and H with H^+
- Balance charges with e^-

Overall equation

To add the half-equations, the number of electrons exchanged must be identical. The LCM (2,6) is 6.



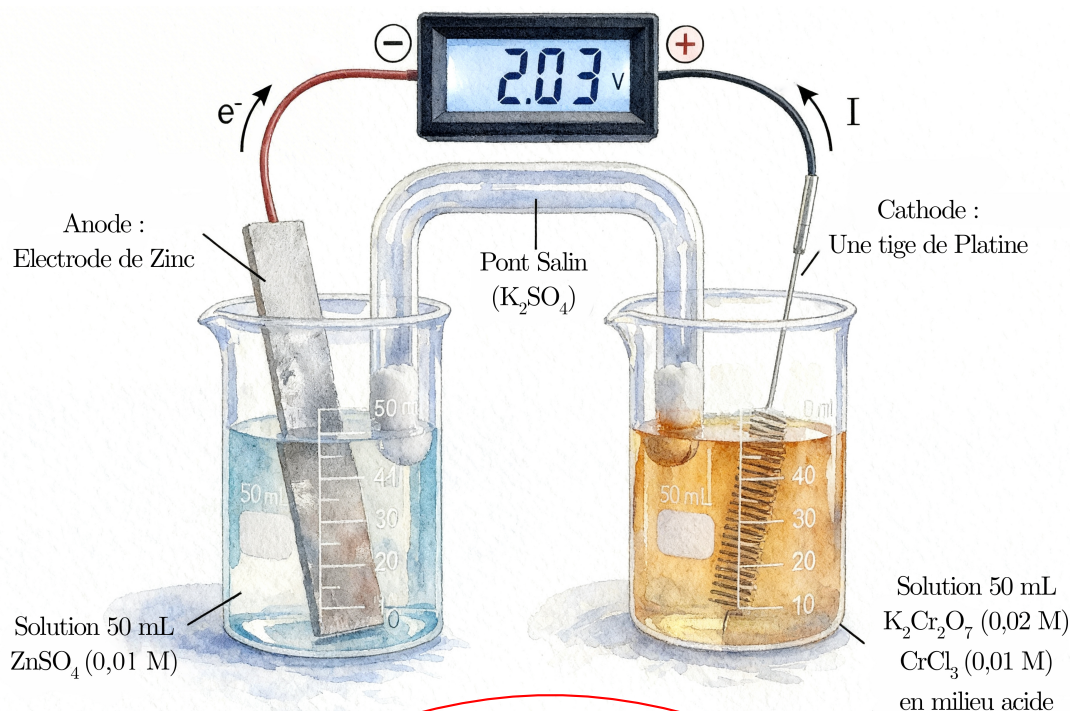
Adding term by term (electrons cancel):



Role of the salt bridge

- **Ensuring electrical continuity** by closing the circuit (ion circulation)
- **Maintaining electroneutrality** in each compartment:
 - At the anode: production of $\text{Zn}^{2+} \Rightarrow$ arrival of SO_4^{2-} anions
 - At the cathode: consumption of $\text{H}^+ \Rightarrow$ arrival of K^+ cations
- **Avoiding mixing** of the solutions from the two compartments

b) Draw a diagram of the cell setup with polarity and electron direction.



From the two half-equations, the direction of electron movement can be distinguished. Electrons are produced at the anode (by oxidation of Zinc) and consumed at the cathode (by reduction of $Cr_2O_7^{2-}$) and through the conducting wire, they move from:

Anode (left compartment, Zn electrode) $\longrightarrow$ Cathode (right compartment, Pt electrode)

c) **Initial electromotive force (pH = 1)**

Anode potential (compartment 1): The Nernst law for the Zn^{2+}/Zn couple is:

$$E = E^\circ + \frac{0.06}{n} \log[Zn^{2+}]$$

With $n = 2$ and $[Zn^{2+}]_0 = 10^{-2}$ M:

$$\begin{aligned} E_{Zn} &= -0.76 + \frac{0.06}{2} \log(10^{-2}) \\ &= -0.76 - 0.06 = -0.82 \text{ V} \end{aligned}$$

Cathode potential (compartment 2): For the $Cr_2O_7^{2-}/Cr^{3+}$ couple, the Nernst law is:

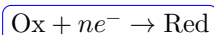
$$E = E^\circ + \frac{0.06}{n} \log \left(\frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2} \right)$$

With $pH = 1 \Rightarrow [H^+] = 10^{-1}$ M, and $n = 6$:

$$\begin{aligned} E_{Cr} &= 1.33 + \frac{0.06}{6} \log \left(\frac{0.02 \times (10)^{-14}}{(0.01)^2} \right) \\ &= 1.33 + 0.01 \log(2 \times 10^{-12}) = 1.213 \text{ V} \end{aligned}$$

Caution

Caution with the Nernst formula: For a reduction half-equation:



The Nernst formula is written:

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{Oxidant}]}{[\text{Reductant}]}$$

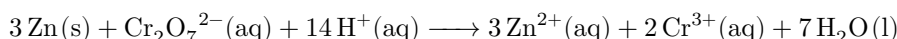
Do not invert numerator and denominator: the oxidant (oxidized form) is always in the numerator, the reductant (reduced form) in the denominator. This does not depend on the direction of the reaction in which the couple intervenes.

Initial electromotive force:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Cr}} - E_{\text{Zn}}$$

$$E_{\text{cell}} = 1.213 - (-0.82) = 2.033 \text{ V}$$

Second method: using the reaction quotient Q : Another way to determine the electromotive force of the cell is to directly use the overall reaction and the reaction quotient Q . This method is often faster and highlights the role of the initial composition of the system. For the overall reaction:



the reaction quotient Q is defined by:

$$Q = \frac{[\text{Zn}^{2+}]^3 \cdot [\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}^+]^{14}}$$

excluding pure condensed phases (solids and liquids). The electromotive force of the cell is then expressed by the relation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{n} \log Q$$

where:

- $E_{\text{cell}}^\circ = E_{\text{Cr}}^\circ - E_{\text{Zn}}^\circ = 1.33 - (-0.76) = 2.09 \text{ V}$ is the standard EMF of the cell,
- $n = 6$ is the number of electrons exchanged in the overall reaction,
- Q is the reaction quotient calculated from initial concentrations.

The initial reaction quotient Q is written:

$$Q = \frac{[\text{Zn}^{2+}]^3 \cdot [\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}^+]^{14}} = \frac{(0.01)^3 \cdot (0.01)^2}{0.02 \cdot (0.1)^{14}}$$

The electromotive force is given by:

$$E_{\text{cell}} = 2.09 - \frac{0.06}{6} \times \log \frac{(0.01)^3 \cdot (0.01)^2}{0.02 \cdot (0.1)^{14}} = 2.09 - 0.01 \times 5.70 = 2.033 \text{ V}$$

Both methods give the same result:

$$E_{\text{cell}} = 2.033 \text{ V}$$

This confirms the consistency of the two approaches and validates the use of the global formula from the reaction.

d) **Concentrations of species at equilibrium:**

Calculation of the equilibrium constant

At equilibrium, $E_{\text{cell}} = 0$, so $E_{\text{Cr}} = E_{\text{Zn}}$. The equilibrium constant K is calculated from the standard potentials:

$$\log K = \frac{n\Delta E^\circ}{0.06} = \frac{6 \times (1.33 - (-0.76))}{0.06} = 209$$

$$K = 10^{209} \quad (\text{extremely large value})$$

Therefore: The reaction is **completely shifted** to the right.

Determination of the limiting reactant: Let us work with the amounts of substance in 0.05 L:

- $n_{\text{Zn}^{2+}}^0 = 0.01 \times 0.05 = 5 \times 10^{-4} \text{ mol}$
- $n_{\text{Cr}_2\text{O}_7^{2-}}^0 = 0.02 \times 0.05 = 10^{-3} \text{ mol}$
- $n_{\text{Cr}^{3+}}^0 = 0.01 \times 0.05 = 5 \times 10^{-4} \text{ mol}$
- $n_{\text{H}^+}^0 = 0.1 \times 0.05 = 5 \times 10^{-3} \text{ mol}$ (at pH = 1)

Advancement table

	3 Zn	+	Cr ₂ O ₇ ²⁻	+	14 H ⁺	→	3 Zn ²⁺	+	2 Cr ³⁺	+	7 H ₂ O
$t_0(\text{mol})$	excess		$1 \cdot 10^{-3}$		$5 \cdot 10^{-3}$		$5 \cdot 10^{-4}$		$5 \cdot 10^{-4}$		solvent

Determination of x_{max} :

The limiting reactant is the one that disappears first. Let us test the two reactants in solution:

- If Cr₂O₇²⁻ were limiting ($x = 1.0 \times 10^{-3} \text{ mol}$): it would require $14 \times 1.0 \times 10^{-3} = 1.4 \times 10^{-2} \text{ mol}$ of H⁺. But $n_{\text{H}^+}^0 = 5.0 \times 10^{-3} \text{ mol} < 1.4 \times 10^{-2} \text{ mol} \rightarrow$ impossible.
- If H⁺ is limiting:

$$x_{\text{max}} = \frac{n_{\text{H}^+}^0}{14} = \frac{5.0 \times 10^{-3}}{14} \approx 3.57 \times 10^{-4} \text{ mol}$$

Compared to Cr₂O₇²⁻: $n_{\text{Cr}_2\text{O}_7^{2-}}^0 = 1.0 \times 10^{-3} \text{ mol} > x_{\text{max}} \rightarrow$ consistent.

Final state (mol) with $x_{\text{max}} = 3.57 \times 10^{-4} \text{ mol}$:

	3 Zn	+	Cr ₂ O ₇ ²⁻	+	14 H ⁺	→	3 Zn ²⁺	+	2 Cr ³⁺	+	7 H ₂ O
$t_{\text{eq}}(\text{mol})$	excess		$6.43 \cdot 10^{-4}$		$2 \cdot 10^{-6}$		$1.57 \cdot 10^{-3}$		$1.21 \cdot 10^{-3}$		solvent

Concentrations at equilibrium ($V = 0.050 \text{ L}$):

$$[\text{Zn}^{2+}]_{\text{eq}} = \frac{1.57 \times 10^{-3}}{0.050} = \boxed{0.0314 \text{ M}}$$

$$[\text{Cr}_2\text{O}_7^{2-}]_{\text{eq}} = \frac{6.43 \times 10^{-4}}{0.050} = \boxed{0.0129 \text{ M}}$$

$$[\text{Cr}^{3+}]_{\text{eq}} = \frac{1.214 \times 10^{-3}}{0.050} = \boxed{0.0243 \text{ M}}$$

$$[\text{H}^+]_{\text{eq}} \approx \boxed{4 \cdot 10^{-5} \text{ M}} \quad (\text{final pH} \approx 4.4 \text{ at real equilibrium})$$

Note: If the exact value $x_{\text{max}} = \frac{5}{14} \times 10^{-3}$ were used, one would find $n_{\text{H}^+}^{\text{eq}} = 0$ (theoretical), but in reality, equilibrium always leaves an infinitesimal amount of H⁺, hence a weakly acidic pH.

Can the reaction be considered complete? The answer is **yes**, for several reasons:

- The limiting reactant H^+ is almost completely consumed:

$$n_{\text{H}^+}^{\text{eq}} \approx 2 \times 10^{-6} \text{ mol} \quad \text{so} \quad [\text{H}^+]_{\text{eq}} \approx 4 \times 10^{-5} \text{ M}$$

This quantity is negligible compared to the concentrations of the other species.

- The equilibrium constant is extremely large ($K = 10^{209} \gg 1$), meaning that the reaction is thermodynamically very favorable and completely shifted toward products.
- Redox reactions between a metal (here Zinc) and a strong oxidant such as dichromate ion in acidic medium are generally quantitative (i.e., the transformation is complete and the limiting reactant is entirely consumed).

The reaction can therefore be considered **quasi-complete**.

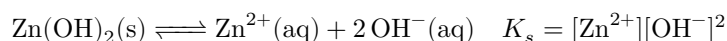
e) **Solubility product of $\text{Zn}(\text{OH})_2$ (pH = 8)**

New experimental condition

Compartment 1 is now buffered at pH = 8, so:

$$[\text{H}^+] = 10^{-8} \text{ M} \quad \Rightarrow \quad [\text{OH}^-] = \frac{K_e}{[\text{H}^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6} \text{ M}$$

At this pH, Zn^{2+} precipitates as $\text{Zn}(\text{OH})_2$ according to the equilibrium:



Expression of the anode potential

The Zn^{2+} concentration is now controlled by K_s :

$$[\text{Zn}^{2+}] = \frac{K_s}{[\text{OH}^-]^2}$$

The potential of the zinc electrode becomes:

$$\begin{aligned} E_{\text{Zn}} &= E_{\text{Zn}^{2+}/\text{Zn}}^\circ + \frac{0.06}{2} \log[\text{Zn}^{2+}] \\ &= -0.76 + 0.03 \log \left(\frac{K_s}{[\text{OH}^-]^2} \right) \\ &= -0.76 + 0.03 (\log K_s - 2 \log[\text{OH}^-]) \end{aligned}$$

With $\log[\text{OH}^-] = \log(10^{-6}) = -6$:

$$E_{\text{Zn}} = -0.76 + 0.03(\log K_s + 12)$$

Using the measured EMF

The voltmeter indicates $E_{\text{cell}} = 2.12 \text{ V}$. The conditions of compartment 2 have not changed (pH = 1), so $E_{\text{Cr}} = 1.213 \text{ V}$.

$$E_{\text{cell}} = E_{\text{Cr}} - E_{\text{Zn}} \quad \Rightarrow \quad E_{\text{Zn}} = 1.213 - 2.12 = \boxed{-0.907 \text{ V}}$$

Determination of K_s

Equating the two expressions for E_{Zn} :

$$\begin{aligned} -0.907 &= -0.76 + 0.03(\log K_s + 12) \\ 0.03(\log K_s + 12) &= -0.907 + 0.76 = -0.147 \\ \log K_s + 12 &= \frac{-0.147}{0.03} = -4.9 \\ \log K_s &= -4.9 - 12 = -16.9 \\ \Rightarrow K_s &= 10^{-16.9} \approx 1.26 \times 10^{-17} \end{aligned}$$

$$K_s(\text{Zn}(\text{OH})_2) \approx 1.26 \cdot 10^{-17}$$

The value found for K_s is in good agreement with tabulated data (about 3×10^{-17}). This validates the consistency of the measurement and the use of the EMF to determine a solubility product.

Exercise

Permanganate/oxalic acid titration

A volume of 20 mL of potassium permanganate solution is titrated with oxalic acid. The reaction is carried out in acidic medium and the solution decolorizes when 13.6 mL of oxalic acid 0.1 N is added.

- Write the half-reactions and the overall reaction equation.
- Calculate the normality and molarity of the potassium permanganate.

Couples: $\text{MnO}_4^-/\text{Mn}^{2+}$; $\text{CO}_2/\text{C}_2\text{H}_2\text{O}_4$.

Solution

Data

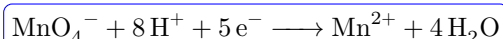
Quantity	Value
Volume of KMnO_4	$V_1 = 20 \text{ mL}$
Volume of oxalic acid at equivalence	$V_2 = 13.6 \text{ mL}$
Normality of oxalic acid	$N_2 = 0.1 \text{ N}$

Redox couples: $\text{MnO}_4^-/\text{Mn}^{2+}$; $\text{CO}_2/\text{C}_2\text{H}_2\text{O}_4$.

Half-reactions and overall equation

Reduction half-reaction ($\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$) Manganese goes from oxidation state **+VII** to **+II**: it therefore gains **5 electrons**.

- Balance oxygen with H_2O : $\text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$
- Balance hydrogen with H^+ : $\text{MnO}_4^- + 8 \text{H}^+ \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$
- Balance charges with electrons:

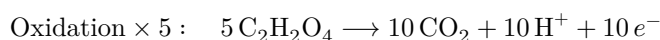
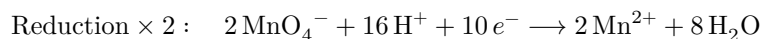


Oxidation half-reaction ($\text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{CO}_2$) Each carbon atom goes from oxidation state **+III** to **+IV**; the molecule therefore donates **2 electrons** in total.

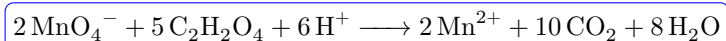
- Balance carbon: $\text{C}_2\text{H}_2\text{O}_4 \rightarrow 2 \text{CO}_2$
- Balance hydrogen with H^+ : $\text{C}_2\text{H}_2\text{O}_4 \rightarrow 2 \text{CO}_2 + 2 \text{H}^+$
- Balance charges with electrons:



Overall reaction equation The number of electrons exchanged must be equalized. The LCM of 5 and 2 is 10, hence:



Adding term by term and simplifying ($16 \text{H}^+ - 10 \text{H}^+ = 6 \text{H}^+$ and the 10e^- cancel):



Calculation of normality and molarity of potassium permanganate

Normality of KMnO_4

At the **equivalence**, the fundamental law of titrations in normality is written:

$$N_1 V_1 = N_2 V_2$$

Hence:

$$N_1 = \frac{N_2 \times V_2}{V_1} = \frac{0.1 \times 13.6}{20}$$

$$N_1 = 0.068 \text{ N} = 6.8 \cdot 10^{-2} \text{ N}$$

Molarity of KMnO_4

The relationship between normality and molarity involves the number n_e of electrons exchanged per entity:

$$N = n_e \times C$$

For MnO_4^- , $n_e = 5$ (5 electrons gained during reduction), so:

$$C_1 = \frac{N_1}{n_e} = \frac{0.068}{5}$$

$$C_1 = 1.36 \cdot 10^{-2} \text{ mol/L}$$

Verification by stoichiometry

a) Amount of oxalic acid:

$$n(\text{C}_2\text{H}_2\text{O}_4) = \frac{N_2}{2} \times V_2 = 0.05 \times 13.6 \times 10^{-3} = 6.80 \cdot 10^{-4} \text{ mol}$$

(N_2 is divided by 2 because oxalic acid exchanges 2 electrons)

b) From the stoichiometric coefficients of the overall equation:

$$\frac{n(\text{KMnO}_4)}{2} = \frac{n(\text{C}_2\text{H}_2\text{O}_4)}{5} \implies n(\text{KMnO}_4) = \frac{2}{5} \times 6.80 \cdot 10^{-4} = 2.72 \cdot 10^{-4} \text{ mol}$$

c) Molar concentration:

$$C_1 = \frac{n(\text{KMnO}_4)}{V_1} = \frac{2.72 \times 10^{-4}}{20 \times 10^{-3}} = 1.36 \cdot 10^{-2} \text{ mol/L}$$

Exercise

A solution of volume 200 mL contains 0.01 mol of copper nitrate $\text{Cu}(\text{NO}_3)_2$, 0.025 mol of aluminum chloride AlCl_3 , and 81 mg of FeCl_3 .

- What is the maximum concentration of silver that can be dissolved without precipitation?
- Classify in increasing order the precipitation pH of the metal cations.

pK_s : $\text{Al}(\text{OH})_3=33.52$; $\text{Cu}(\text{OH})_2=19.32$; $\text{Fe}(\text{OH})_3=38.70$; $\text{AgCl}=9.73$. $M(\text{FeCl}_3)=162 \text{ g/mol}$.

Solution

Data

- Volume of solution: $V = 200 \text{ mL} = 0.200 \text{ L}$
- Copper nitrate: $n_{\text{Cu}} = 0.010 \text{ mol}$ of $\text{Cu}(\text{NO}_3)_2$

- Aluminum chloride: $n_{\text{Al}} = 0.025 \text{ mol}$ of AlCl_3
- Iron(III) chloride: $m = 81 \text{ mg} = 0.081 \text{ g}$ of FeCl_3 , $M = 162 \text{ g/mol}$
- Solubility product constants:

$$\text{p}K_s(\text{Al}(\text{OH})_3) = 33.52$$

$$\text{p}K_s(\text{Cu}(\text{OH})_2) = 19.32$$

$$\text{p}K_s(\text{Fe}(\text{OH})_3) = 38.70$$

$$\text{p}K_s(\text{AgCl}) = 9.73$$

1. Maximum silver concentration without precipitation

We seek the maximum concentration of Ag^+ that can be added without AgCl precipitating. This requires knowing the chloride ion concentration in the initial solution.

Chloride ion concentration

- AlCl_3 : $n_{\text{Cl}} = 3 \times 0.025 = 0.075 \text{ mol}$
- FeCl_3 :

$$n_{\text{Fe}} = \frac{0.081}{162} = 5.0 \times 10^{-4} \text{ mol}$$

$$n_{\text{Cl}} = 3 \times 5.0 \times 10^{-4} = 1.5 \times 10^{-3} \text{ mol}$$

- $\text{Cu}(\text{NO}_3)_2$ does not provide Cl^- .

Total:

$$n_{\text{Cl}^-} = 0.075 + 0.0015 = 0.0765 \text{ mol}$$

Concentration:

$$[\text{Cl}^-] = \frac{0.0765}{0.200} = 0.3825 \text{ mol/L}$$

Condition for non-precipitation of AgCl

The solubility product:

$$K_s(\text{AgCl}) = 10^{-9.73} \approx 1.86 \times 10^{-10}$$

Precipitation begins when:

$$[\text{Ag}^+] \cdot [\text{Cl}^-] = K_s$$

Hence the maximum concentration before precipitation:

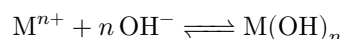
$$[\text{Ag}^+]_{\text{max}} = \frac{K_s}{[\text{Cl}^-]} = \frac{1.86 \times 10^{-10}}{0.3825} \approx 4.86 \times 10^{-10} \text{ mol/L}$$

Answer:

$$[\text{Ag}^+]_{\text{max}} \approx 4.86 \times 10^{-10} \text{ mol/L}$$

2. Classification in increasing order of precipitation pH of metal cations

The cations are: Al^{3+} , Cu^{2+} , Fe^{3+} . Their precipitation as hydroxides follows the reaction:



The onset of precipitation occurs when:

$$[\text{OH}^-] = \left(\frac{K_s}{[\text{M}^{n+}]} \right)^{1/n}$$

with $[\text{M}^{n+}]$ the initial concentration of the cation.

Initial concentrations

$$[\text{Cu}^{2+}] = \frac{0.010}{0.200} = 0.050 \text{ mol/L}$$

$$[\text{Al}^{3+}] = \frac{0.025}{0.200} = 0.125 \text{ mol/L}$$

$$[\text{Fe}^{3+}] = \frac{5.0 \times 10^{-4}}{0.200} = 2.5 \times 10^{-3} \text{ mol/L}$$

For Fe^{3+}

$$K_s = 10^{-38.70} \approx 2.00 \times 10^{-39}$$

$$[\text{OH}^-] = \left(\frac{2.00 \times 10^{-39}}{2.5 \times 10^{-3}} \right)^{1/3} = (8.0 \times 10^{-37})^{1/3}$$

$$[\text{OH}^-] \approx 9.28 \times 10^{-13} \text{ mol/L}$$

$$\text{pOH} \approx -\log(9.28 \times 10^{-13}) \approx 12.03$$

$$\text{pH} = 14 - 12.03 \approx 1.97$$

For Al^{3+}

$$K_s = 10^{-33.52} \approx 3.02 \times 10^{-34}$$

$$[\text{OH}^-] = \left(\frac{3.02 \times 10^{-34}}{0.125} \right)^{1/3} = (2.42 \times 10^{-33})^{1/3}$$

$$[\text{OH}^-] \approx 1.34 \times 10^{-11} \text{ mol/L}$$

$$\text{pOH} \approx -\log(1.34 \times 10^{-11}) \approx 10.87$$

$$\text{pH} \approx 3.13$$

For Cu^{2+}

$$K_s = 10^{-19.32} \approx 4.79 \times 10^{-20}$$

$$[\text{OH}^-] = \left(\frac{4.79 \times 10^{-20}}{0.050} \right)^{1/2} = (9.58 \times 10^{-19})^{1/2}$$

$$[\text{OH}^-] \approx 9.79 \times 10^{-10} \text{ mol/L}$$

$$\text{pOH} \approx -\log(9.79 \times 10^{-10}) \approx 9.01$$

$$\text{pH} \approx 4.99$$

Increasing order of precipitation onset pH

$$\text{Fe}^{3+} (1.97) < \text{Al}^{3+} (3.13) < \text{Cu}^{2+} (4.99)$$

Answer:

$$\text{Fe}^{3+} < \text{Al}^{3+} < \text{Cu}^{2+}$$

Exercise

Cu/Ag and $\text{Cu}(\text{OH})_2$ cell

Consider the following cell:



Therefore:

- **Anodic compartment:** copper metal electrode immersed in 50 mL of a $\text{Cu}(\text{OH})_2$ solution with $[\text{Cu}^{2+}] = 0.05 \text{ mol/L}$ (assuming all copper is in Cu^{2+} form).
- **Cathodic compartment:** platinum electrode immersed in 50 mL of a solution containing:

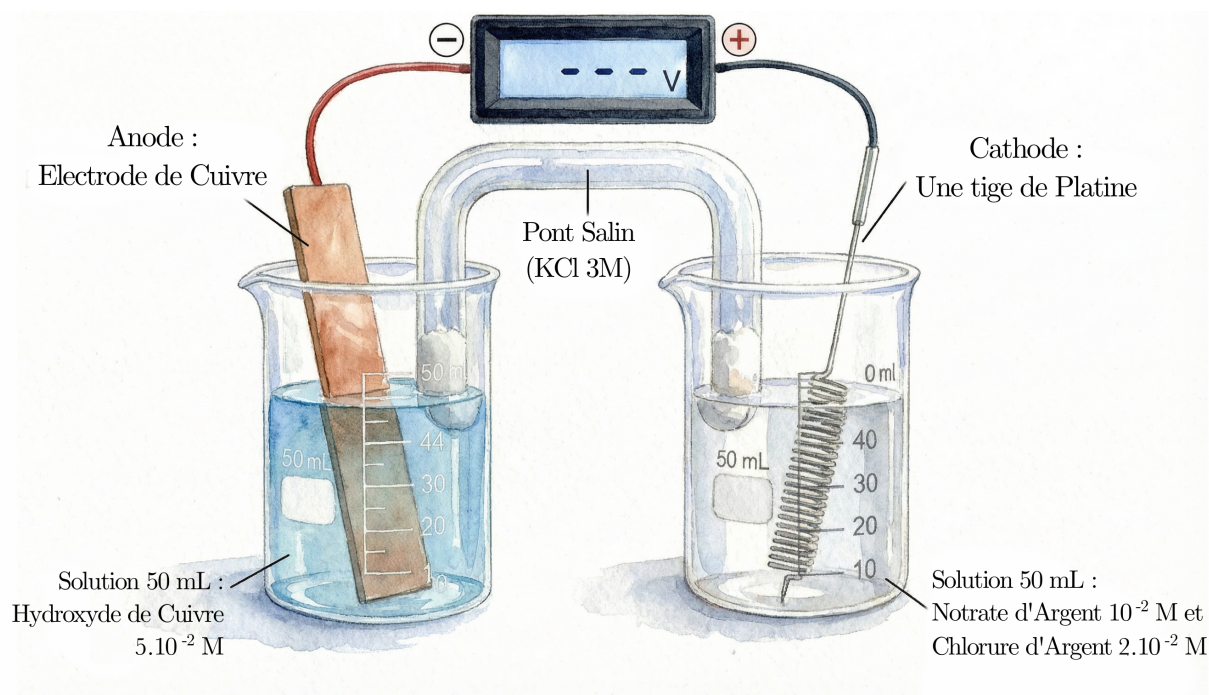
$$[\text{Ag}^+]_{\text{total}} = 0.01 \text{ mol/L} \quad \text{and} \quad [\text{Cl}^-]_{\text{total}} = 0.02 \text{ mol/L}$$

In the presence of chloride ions, part of the Ag^+ ions precipitates as AgCl(s) .

- Salt bridge: KCl at 3 M concentration.

The digital voltmeter displays a value V to be determined.

Standard potentials at 25°C : $E^0(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$ $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$
Solubility constants: $K_s(\text{AgCl}) = 10^{-9.75}$ $K_s(\text{Cu}(\text{OH})_2) = 10^{-19.32}$



Questions

- Write the half-equations and the overall equation of the cell in operation. Specify the anode and cathode, as well as the oxidation and reduction reactions.
- From the diagram, indicate the direction of electric current and that of electrons in the external circuit, justifying.
- Calculate the effective concentration of free Ag^+ ions in the cathodic compartment, taking into account the precipitation of AgCl . (Data: $K_s(\text{AgCl}) = 10^{-9.75}$).
- Calculate the electromotive force of the cell (value displayed by the voltmeter) under initial conditions? Would there be an impact on the EMF if there were no precipitation of AgCl ?
- The cell discharges until exhaustion (equilibrium). Determine the concentrations of species at equilibrium with:
 - Calculate the equilibrium constant K of the overall reaction.
 - Establish the reaction advancement table.
- The anodic compartment is now modified: it is buffered at $\text{pH} = 10$. The new measured EMF is 1.05 V. Deduce an experimental value of the solubility product K_s of $\text{Cu}(\text{OH})_2$.

Solution

Solution: Cu/Ag and Cu(OH)₂ cell

Before starting, let us recall some key concepts:

- **Standard potential (E°):** Tendency of a species to gain electrons (to be reduced). The larger E° , the better the oxidant.
- **Nernst law (at 25°C):**

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{Oxidant}]}{[\text{Reductant}]}$$

where n is the number of electrons exchanged.

- **Cell operation:** The anode is the site of oxidation (negative pole), the cathode the site of reduction (positive pole). The electromotive force (EMF) is:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} > 0$$

- **Solubility product (K_s):**
 - For $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$: $K_s = [\text{Ag}^+][\text{Cl}^-]$
 - For $\text{Cu(OH)}_2\text{(s)} \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-$: $K_s = [\text{Cu}^{2+}][\text{OH}^-]^2$

Answer (a): The two half-equations and the overall equation:

Objective: Determine the spontaneous direction of the reaction and write the equations.

Identification of redox couples:

- Anodic compartment (left): Cu electrode in $\text{Cu}^{2+} \Rightarrow$ couple Cu^{2+}/Cu
- Cathodic compartment (right): Pt electrode in $\text{Ag}^+ \Rightarrow$ couple Ag^+/Ag

Comparison of standard potentials:

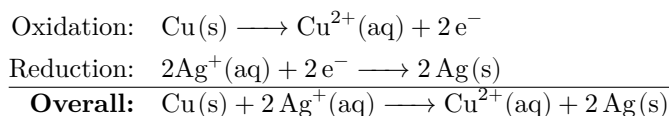
$$E^\circ(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V} > E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$$

Note: The couple with the higher standard potential gains electrons and is reduced. It constitutes the **cathode** (positive pole). The other couple is oxidized at the **anode** (negative pole).

Half-reactions:

- **At the anode (oxidation):** $\text{Cu(s)} \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$
- **At the cathode (reduction):** $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}$

Overall equation: To balance electrons, multiply the reduction by 2:

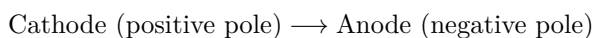


Answer (b): Direction of current and direction of electrons: an essential distinction

Conventional current (I)

By historical convention (Franklin, 18th century), electric current is said to flow from the **positive** (+) terminal to the **negative** (−) terminal outside the generator. This is a practical convention that allows applying electrical laws (Ohm, Kirchhoff) without worrying about the nature of charges.

In our case, current flows in the opposite direction to electron motion. It therefore goes from:



Electron direction:

Physically, in a metallic wire, it is the **electrons** (negative charges) that actually move. Since they are negative, they are repelled by the negative terminal (where they are in excess) and attracted by the positive terminal (where they are lacking). They therefore flow in the opposite direction to conventional current:

Electrons: negative terminal $(-)$ $\longrightarrow$ positive terminal $(+)$

In our case, electrons are produced at the anode (by oxidation of Cu) and consumed at the cathode (by reduction of Ag^+). In the external circuit, they therefore move from:

Anode (left compartment, Cu electrode) $\longrightarrow$ Cathode (right compartment, Pt electrode)

What to remember for cells

- **Anode** = oxidation = produces electrons = **negative** terminal $(-)$
- **Cathode** = reduction = consumes electrons = **positive** terminal $(+)$

In the external circuit:

Current I: cathode $(+)$ $\longrightarrow$ anode $(-)$
Electrons: anode $(-)$ $\longrightarrow$ cathode $(+)$

Answer (c): Calculation of $[\text{Ag}^+]_{\text{free}}$:

Precipitation of AgCl: The precipitation reaction is: $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl(s)}$

Calculation of initial amounts:

$$n_{\text{Ag}^+}^0 = 0.010 \times 0.050 = 5.0 \times 10^{-4} \text{ mol}$$

$$n_{\text{Cl}^-}^0 = 0.020 \times 0.050 = 1.0 \times 10^{-3} \text{ mol}$$

State	Ag^+	+	Cl^-	$\rightleftharpoons$	AgCl(s)
Initial (mol)	5.0×10^{-4}		1.0×10^{-3}		0
In progress (mol)	$5.0 \times 10^{-4} - x$		$1.0 \times 10^{-3} - x$		x
Equilibrium (mol)	ε		5.0×10^{-4}		$\approx 5.0 \times 10^{-4}$

With:

- x : volumetric advancement (in mol)
- $\varepsilon \ll 5.0 \times 10^{-4}$ (residual quantity)

Resolution: Since $K_s = 1.78 \times 10^{-10}$ is very small, precipitation is almost complete. Ag^+ ions are limiting compared to Cl^- ions.

At equilibrium:

- $[\text{Cl}^-]_{\text{free}} \approx \frac{5.0 \times 10^{-4}}{0.050} = 0.01 \text{ M}$
- The K_s relation gives:

$$[\text{Ag}^+]_{\text{free}} = \frac{K_s}{[\text{Cl}^-]_{\text{free}}} = \frac{1.78 \times 10^{-10}}{0.01} = 1.78 \times 10^{-8} \text{ M}$$

Therefore: $\varepsilon = 1.78 \times 10^{-8} \ll 0.01$

$$[\text{Ag}^+]_{\text{free}} = 1.78 \times 10^{-8} \text{ M}$$

Exact method (for the curious): For students wishing a rigorous resolution without approximation, here is the exact resolution of the quadratic equation.

From the K_s expression:

$$\begin{aligned}(5.0 \times 10^{-4} - x)(1.0 \times 10^{-3} - x) &= K_s \\ x^2 - 1.5 \times 10^{-3}x + 5.0 \times 10^{-7} &= 1.78 \times 10^{-10} \\ x^2 - 1.5 \times 10^{-3}x + 4.999822 \times 10^{-7} &= 0\end{aligned}$$

$$\sqrt{\Delta} \approx 5.000712 \times 10^{-4} \Rightarrow \begin{cases} x_1 = \frac{1.5 \times 10^{-3} - 5.000712 \times 10^{-4}}{2} \approx 4.999644 \times 10^{-4} \\ x_2 = \frac{1.5 \times 10^{-3} + 5.000712 \times 10^{-4}}{2} \approx 1.0000356 \times 10^{-3} \end{cases}$$

Therefore the equation admits two distinct real solutions, but only one has physical meaning:

- x_1 is physically acceptable because $x_1 \leq n_{\text{Ag}^+}^0$.
- x_2 is rejected because $x_2 > n_{\text{Ag}^+}^0$ (impossible to precipitate more Ag^+ ions than were initially present).

Ag^+ is the limiting reactant. After complete precipitation:

$$n_{\text{Cl}^-}^{\text{final}} = 1.0 \times 10^{-3} - 5.0 \times 10^{-4} = 5.0 \times 10^{-4} \text{ mol}$$

$$[\text{Cl}^-] = \frac{5.0 \times 10^{-4}}{0.050} = 0.01 \text{ M}$$

Application of the solubility product: At equilibrium with the precipitate: $K_s = [\text{Ag}^+][\text{Cl}^-]$

$$[\text{Ag}^+] = \frac{K_s}{[\text{Cl}^-]} = \frac{10^{-9.75}}{0.01} = \frac{10^{-9.75}}{10^{-2}}$$

$$[\text{Ag}^+]_{\text{free}} \approx 1.78 \cdot 10^{-8} \text{ mol}$$

Note: This rigorous resolution via the quadratic equation confirms that the approximation made in the simplified method ($x \approx 5.0 \times 10^{-4}$) is excellent. The difference between the two methods is completely negligible.

Note: The concentration of free Ag^+ ions is extremely low because precipitation with Cl^- is almost complete (K_s very small).

Answer (d): Calculation of EMF:

Principle: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Anode potential (couple Cu^{2+}/Cu):

$$E_{\text{anode}} = E^\circ(\text{Cu}^{2+}/\text{Cu}) + \frac{0.059}{2} \log[\text{Cu}^{2+}]$$

$$E_{\text{anode}} = 0.34 + \frac{0.059}{2} \log(0.05)$$

$$\log(0.05) = \log(5 \times 10^{-2}) = \log 5 - 2 \approx 0.70 - 2 = -1.30$$

$$E_{\text{anode}} = 0.34 + 0.0295 \times (-1.30) = 0.34 - 0.03835 \approx 0.3017 \text{ V}$$

Cathode potential (couple Ag^+/Ag):

$$E_{\text{cathode}} = E^\circ(\text{Ag}^+/\text{Ag}) + 0.059 \log[\text{Ag}^+]$$

With $[\text{Ag}^+] = 10^{-7.75}$ M (question c):

$$E_{\text{cathode}} = 0.80 + 0.059 \log(10^{-7.75}) = 0.80 + 0.059 \times (-7.75)$$

$$E_{\text{cathode}} = 0.80 - 0.45725 \approx 0.3428 \text{ V}$$

Electromotive force:

$$E_{\text{cell}} = 0.3428 - 0.3017 = 0.041 \text{ V (i.e., 41 mV)}$$

Impact of the absence of AgCl precipitation:

Without precipitation, $[\text{Ag}^+] = 0.01$ M:

$$E'_{\text{cathode}} = 0.80 + 0.059 \log(0.01) = 0.80 + 0.059 \times (-2) = 0.682 \text{ V}$$

$$E'_{\text{cell}} = 0.682 - 0.3017 = 0.380 \text{ V}$$

Note: Precipitation of AgCl considerably lowers the cathode potential and therefore the cell voltage (from 0.38 V to 0.041 V).

Answer (e): Calculation of species concentrations at equilibrium:

i) Calculation of the equilibrium constant K

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.80 - 0.34 = 0.46 \text{ V}$$

$$\text{Relationship with } K: \log K = \frac{n \times E_{\text{cell}}^{\circ}}{0.059} = \frac{2 \times 0.46}{0.059} \approx 15.59$$

$$K = 10^{15.59} \approx 3.89 \times 10^{15}$$

Note: K is enormous, so the reaction $\text{Cu(s)} + 2 \text{Ag}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{Ag(s)}$ is complete in the forward direction.

ii) Advancement table:

Initial data

- Common volume: $V = 50 \text{ mL} = 0.050 \text{ L}$
- Anode (Cu^{2+}): $n_{\text{Cu}^{2+}}^0 = 0.05 \times 0.050 = 2.5 \times 10^{-3} \text{ mol}$
- Cathode (Ag^+ total dissolved): $n_{\text{Ag}^+}^0 = 0.01 \times 0.050 = 5.0 \times 10^{-4} \text{ mol}$

State	Cu	+	2Ag^+	$\rightleftharpoons$	Cu^{2+}	+	2Ag
Initial (mol)	excess		5.0×10^{-4}		2.5×10^{-3}		0
In progress (mol)	excess		$5.0 \times 10^{-4} - 2\xi$		$2.5 \times 10^{-3} + \xi$		2ξ
Equilibrium (mol)	excess		ε		$2.5 \times 10^{-3} + \xi_{\text{max}}$		5.0×10^{-4}

With:

- ξ : advancement in mol
- $\xi_{\text{max}} = \frac{5.0 \times 10^{-4}}{2} = 2.5 \times 10^{-4} \text{ mol}$ (maximum advancement if complete reaction)
- ε : residual amount of Ag^+ ions at equilibrium (very small)

Equilibrium constant The cell reaction has the constant:

$$K = \frac{[\text{Cu}^{2+}]_{\text{eq}}}{[\text{Ag}^+]_{\text{eq}}^2} = 3.89 \times 10^{15}$$

In terms of amounts of substance:

$$K = \frac{\frac{n_{\text{Cu}^{2+}}^{\text{eq}}}{V}}{\left(\frac{n_{\text{Ag}^+}^{\text{eq}}}{V}\right)^2} = \frac{n_{\text{Cu}^{2+}}^{\text{eq}} \times V}{(n_{\text{Ag}^+}^{\text{eq}})^2}$$

Approximation of quasi-complete reaction, since K is very large ($> 10^{15}$), Ag^+ ions are almost completely consumed:

$$\xi_{\text{eq}} \approx \xi_{\text{max}} = 2.5 \times 10^{-4} \text{ mol}$$

Amount of Cu^{2+} at equilibrium

$$n_{\text{Cu}^{2+}}^{\text{eq}} = n_{\text{Cu}^{2+}}^0 + \xi_{\text{eq}} = 2.5 \times 10^{-3} + 2.5 \times 10^{-4} = 2.75 \times 10^{-3} \text{ mol}$$

$$n_{\text{Cu}^{2+}}^{\text{eq}} = 2.75 \times 10^{-3} \text{ mol}$$

Calculation of residual amount of Ag^+ ions We know that the residual amount of Ag^+ ions at equilibrium (very small) is $\varepsilon = n_{\text{Ag}^+}^{\text{eq}}$, and from the expression of K :

$$\begin{aligned} \varepsilon^2 &= \frac{n_{\text{Cu}^{2+}}^{\text{eq}} \times V}{K} \\ \varepsilon^2 &= \frac{(2.75 \times 10^{-3}) \times 0.050}{3.89 \times 10^{15}} = \frac{1.375 \times 10^{-4}}{3.89 \times 10^{15}} = 3.53 \times 10^{-20} \\ \varepsilon &= \sqrt{3.53 \times 10^{-20}} = 1.88 \times 10^{-10} \text{ mol} \end{aligned}$$

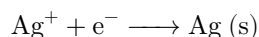
Therefore the concentrations at equilibrium are:

$$\begin{aligned} [\text{Cu}^{2+}]_{\text{eq}} &= \frac{n_{\text{Cu}^{2+}}^{\text{eq}}}{V} = \frac{2.75 \times 10^{-3}}{0.050} = 0.055 \text{ M} \\ [\text{Ag}^+]_{\text{eq}} &= \frac{\varepsilon}{V} = \frac{1.88 \times 10^{-10}}{0.050} = 3.76 \times 10^{-9} \text{ M} \end{aligned}$$

Equilibrium state of the galvanic cell At equilibrium, the cell no longer delivers current and the electromotive force measured by the voltmeter is zero. In the anodic compartment, the copper electrode shows **localized corrosion** only on its immersed part in the $\text{Cu}(\text{OH})_2$ solution, while the non-immersed part remains almost intact. The solution has turned dark blue, reflecting a significant increase in the concentration of Cu^{2+} ions due to the oxidation of copper metal according to the half-reaction:



In the other compartment, the platinum electrode is now **covered with a deposit** of silver metal. This phenomenon is called a **spontaneous electrolytic deposit** or more precisely spontaneous electrodeposition, resulting from the reduction of the initially present Ag^+ ions:



The concentration of free Ag^+ ions has become extremely low, on the order of 10^{-8} M, due both to their deposition on the cathode and to their precipitation as silver chloride (AgCl) in the presence of chloride ions (Cl^-) whose concentration has decreased to about 0.01 M. The 3 M KCl salt bridge ensures electroneutrality of the two compartments by allowing ion migration without any current flowing in the external circuit. The entire system has thus reached a state of chemical and electrochemical equilibrium

where the potentials of the two electrodes are equal:

$$E_{\text{Ag}^+/\text{Ag}} = E_{\text{Cu}^{2+}/\text{Cu}}$$



Answer (f): Calculation of the solubility product $K_s(\text{Cu}(\text{OH})_2)$ at pH=10:

New conditions: $\text{pH} = 10 \Rightarrow [\text{OH}^-] = 10^{-4} \text{ M}$, $E'_{\text{cell}} = 1.05 \text{ V}$

Calculation of the new anode potential: The cathodic compartment has not changed, so $E_{\text{cathode}} = 0.3428 \text{ V}$ (question d).

$$E'_{\text{cell}} = E_{\text{cathode}} - E'_{\text{anode}} \Rightarrow E'_{\text{anode}} = E_{\text{cathode}} - E'_{\text{cell}}$$

$$E'_{\text{anode}} = 0.3428 - 1.05 = \boxed{-0.7072 \text{ V}}$$

Determination of $[\text{Cu}^{2+}]$ by the Nernst law:

$$E'_{\text{anode}} = E^\circ(\text{Cu}^{2+}/\text{Cu}) + \frac{0.059}{2} \log[\text{Cu}^{2+}]$$

$$-0.7072 = 0.34 + 0.0295 \log[\text{Cu}^{2+}]$$

$$0.0295 \log[\text{Cu}^{2+}] = -1.0472$$

$$\log[\text{Cu}^{2+}] = \frac{-1.0472}{0.0295} \approx -35.5$$

$$[\text{Cu}^{2+}] = 10^{-35.5} = 10^{0.5} \times 10^{-36} \approx \boxed{3.16 \times 10^{-36} \text{ M}}$$

Calculation of the K_s of $\text{Cu}(\text{OH})_2$:

$$K_s(\text{Cu}(\text{OH})_2) = [\text{Cu}^{2+}] \times [\text{OH}^-]^2$$

$$K_s = (3.16 \times 10^{-36}) \times (10^{-4})^2 = 3.16 \times 10^{-36} \times 10^{-8}$$

$$\boxed{K_s(\text{Cu}(\text{OH})_2) \approx 3.16 \times 10^{-44}}$$

Note: This value is extremely low, much lower than the initial data ($10^{-19.32}$). This is explained by the high basicity of the medium (pH=10) which almost completely precipitates Cu^{2+} . The difference with the theoretical value may come from calculation approximations or experimental conditions.

Exercise

Exercise: Zn/Fe cell in ammoniacal medium

Consider the following electrochemical cell:

- **Compartment 1 (anode):** zinc metal electrode immersed in 100 mL of zinc sulfate solution (ZnSO_4) at 0.01 M.
- **Compartment 2 (cathode):** iron metal electrode immersed in 100 mL of a solution containing iron(II) sulfate (FeSO_4) at 0.02 M and ammonia (NH_3) at 0.1 M.
- The two compartments are connected by a potassium chloride (KCl) salt bridge.

Data at 25°C:

$$E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V} \quad ; \quad E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$$

$$K_e = 10^{-14} \quad ; \quad \frac{0.06}{n} \text{ for the Nernst law}$$

- Write the electronic half-equations for the two redox couples involved in this cell, then establish the overall equation of the reaction that occurs when the cell delivers current.
- Calculate the initial electromotive force (EMF) of the cell.
- Draw a labeled diagram of the cell indicating:
 - the polarity of the electrodes,
 - the direction of electron flow in the external circuit,
 - the direction of ion movement in the salt bridge,
 - the role of the salt bridge.
- Determine the equilibrium constant K of the overall reaction. Deduce the concentrations of species at equilibrium assuming that Fe^{2+} is the limiting reactant.
- Calculate the apparent standard potential of the Fe^{2+}/Fe couple in ammoniacal medium knowing that: Compartment 1 is now buffered at pH = 10. Knowing that zinc precipitates as $\text{Zn}(\text{OH})_2$ ($K_s = 10^{-16.8}$), determine the potential of the zinc electrode under these conditions. The measured EMF is then $E_{\text{cell}} = 1.32 \text{ V}$.

Solution

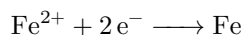
Solution: Zn/Fe cell in ammoniacal medium

a). Half-equations and overall equation:

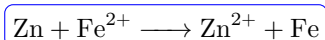
- **Compartment 1 (anode):** oxidation of zinc metal



- **Compartment 2 (cathode):** reduction of iron(II) ions to iron metal



Adding these two half-equations gives the overall equation:



b). Initial electromotive force

Zinc electrode potential (anode):

$$E_{\text{Zn}} = E^\circ(\text{Zn}^{2+}/\text{Zn}) + \frac{0.06}{2} \log[\text{Zn}^{2+}]$$

$$E_{\text{Zn}} = -0.76 + 0.03 \log(0.01) = -0.76 + 0.03 \times (-2) = -0.76 - 0.06 = \boxed{-0.82 \text{ V}}$$

Iron electrode potential (cathode):

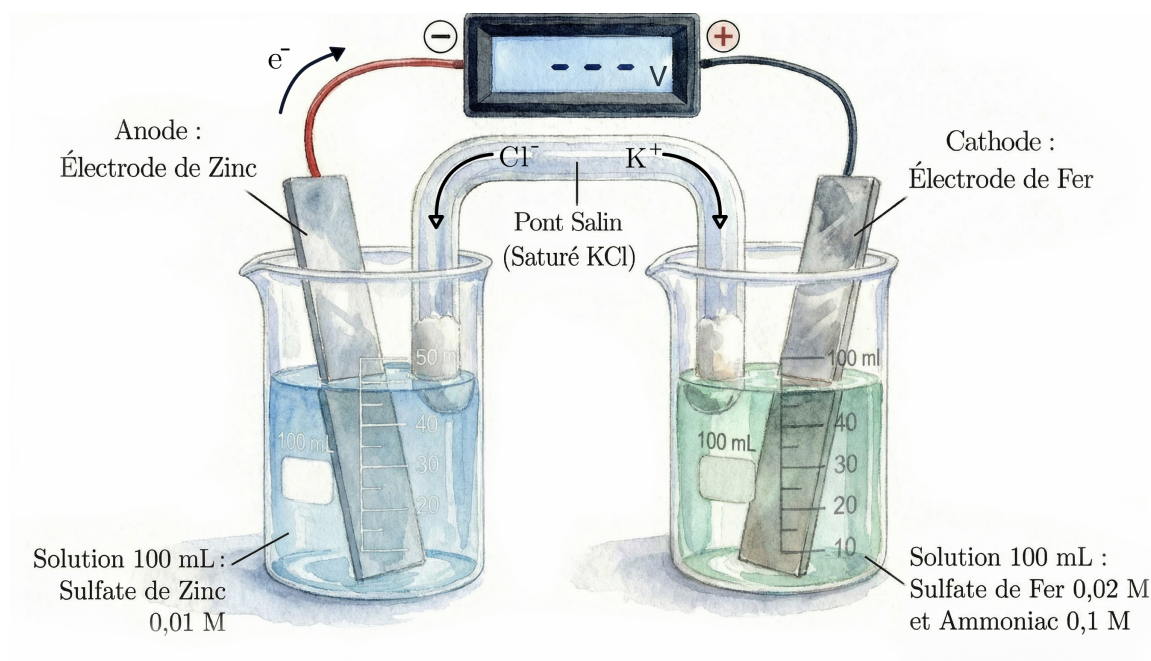
$$E_{\text{Fe}} = E^\circ(\text{Fe}^{2+}/\text{Fe}) + \frac{0.06}{2} \log[\text{Fe}^{2+}]$$

$$E_{\text{Fe}} = -0.44 + 0.03 \log(0.02) = -0.44 + 0.03 \times (-1.70) = -0.44 - 0.051 = \boxed{-0.491 \text{ V}}$$

Initial EMF:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Fe}} - E_{\text{Zn}} = -0.491 - (-0.82) = \boxed{0.329 \text{ V}}$$

c). Diagram of the cell and role of the salt bridge:



Role of the salt bridge:

- Ensuring electrical continuity between the two compartments.
- Maintaining electrical neutrality by allowing ion migration:
 - K^+ ions migrate toward the cathodic compartment (where Fe^{2+} are consumed).
 - Cl^- ions migrate toward the anodic compartment (where Zn^{2+} are produced).

d). Equilibrium constant and final concentrations:

Equilibrium constant:

$$\log K = \frac{n\Delta E^\circ}{0.06} = \frac{2 \times [(-0.44) - (-0.76)]}{0.06} = \frac{0.64}{0.06} \approx 10.67$$

$$\boxed{K = 10^{10.67} \approx 4.7 \times 10^{10}}$$

Concentrations at equilibrium (Fe^{2+} limiting):

Initial amounts in 0.1 L:

$$n_{\text{Zn}^{2+}}^0 = 0.01 \times 0.1 = 10^{-3} \text{ mol}$$

$$n_{\text{Fe}^{2+}}^0 = 0.02 \times 0.1 = 2 \times 10^{-3} \text{ mol}$$

If Fe^{2+} is limiting, $x_{\max} = 2 \times 10^{-3}$ mol. Then:

$$n_{\text{Zn}^{2+}}^{\text{eq}} = 10^{-3} + x_{\max} = 3 \times 10^{-3} \text{ mol}$$

$$n_{\text{Fe}^{2+}}^{\text{eq}} \approx 0$$

Concentrations:

$$[\text{Zn}^{2+}]_{\text{eq}} = \frac{3 \times 10^{-3}}{0.1} = 0.03 \text{ M}$$

$$[\text{Fe}^{2+}]_{\text{eq}} \approx 0$$

e). Influence of $\text{Zn}(\text{OH})_2$ precipitation at pH = 10

At pH = 10, $[\text{OH}^-] = 10^{-4}$ M. The solubility product:

$$K_s = [\text{Zn}^{2+}][\text{OH}^-]^2 = 10^{-16.8}$$

$$[\text{Zn}^{2+}] = \frac{K_s}{[\text{OH}^-]^2} = \frac{10^{-16.8}}{(10^{-4})^2} = \frac{10^{-16.8}}{10^{-8}} = 10^{-8.8} \approx 1.58 \times 10^{-9} \text{ M}$$

Zinc potential under these conditions:

$$E'_{\text{Zn}} = E^\circ(\text{Zn}^{2+}/\text{Zn}) + \frac{0.06}{2} \log[\text{Zn}^{2+}] = -0.76 + 0.03 \log(1.58 \times 10^{-9})$$

$$\log(1.58 \times 10^{-9}) = \log 1.58 - 9 \approx 0.20 - 9 = -8.80$$

$$E'_{\text{Zn}} = -0.76 + 0.03 \times (-8.80) = -0.76 - 0.264 = -1.024 \text{ V}$$

Apparent standard potential of the Fe^{2+}/Fe couple in ammoniacal medium:

The measured EMF is $E_{\text{cell}} = 1.32$ V. We have:

$$E_{\text{cell}} = E''_{\text{Fe}} - E'_{\text{Zn}} \Rightarrow E''_{\text{Fe}} = E_{\text{cell}} + E'_{\text{Zn}} = 1.32 + (-1.024) = 0.296 \text{ V}$$

This potential E''_{Fe} is that of the iron electrode under the conditions of compartment 2 (ammoniacal medium). It corresponds to:

$$E''_{\text{Fe}} = E^{\circ'}(\text{Fe}^{2+}/\text{Fe}) + \frac{0.06}{2} \log[\text{Fe}^{2+}]_{\text{free}}$$

We calculated earlier $[\text{Fe}^{2+}]_{\text{free}} \approx 6.32 \times 10^{-7}$ M. Therefore:

$$0.296 = E^{\circ'}(\text{Fe}^{2+}/\text{Fe}) + 0.03 \log(6.32 \times 10^{-7})$$

$$\log(6.32 \times 10^{-7}) = -6.20$$

$$0.296 = E^{\circ'}(\text{Fe}^{2+}/\text{Fe}) + 0.03 \times (-6.20) = E^{\circ'}(\text{Fe}^{2+}/\text{Fe}) - 0.186$$

$$E^{\circ'}(\text{Fe}^{2+}/\text{Fe}) = 0.296 + 0.186 = 0.482 \text{ V}$$

Conclusion

This apparent standard potential (≈ 0.48 V) is very different from the standard potential (-0.44 V) due to the complexation of Fe^{2+} ions by ammonia, which considerably decreases their free concentration and modifies the electrode potential.

Nernst constant: In all exercises of this chapter, and unless the temperature is explicitly stated otherwise, you must imperatively use the value **0.059** (more precisely **0.0591**) as the Nernst constant in the equation:

$$E = E^\circ - \frac{0.059}{n} \log Q$$

This value is the **exact value at 25 °C**,^{(58),(59)} the temperature at which the vast majority of electrochemical experiments and exercises are conducted.

Why not use 0.06?

- The value **0.059** at 298.15 K comes from the rigorous calculation:⁽⁵⁸⁾

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298.15}{96485} = 0.0591 \text{ V}$$

- The value **0.06** is merely an **approximation** commonly used to simplify calculations,^{(58),(59)} but it introduces a systematic error of about 1.7% on the calculated potential.
- In a graded exercise, using 0.06 may lead to a numerical result different from the one expected by the instructor, which may be penalized.

Golden rule:

As long as the temperature is not explicitly specified in the problem statement, you systematically use **0.059** (and not 0.06).

However, a fundamental exception applies:

If the problem statement explicitly imposes the value **0.06** in the data (for example: $\frac{0.06}{n}$ for the Nernst equation), then you must absolutely use this value.

In this case, the instructor has deliberately chosen this approximation to simplify calculations or to familiarize you with working with rounded values. Using 0.059 when the problem statement imposes 0.06 would lead to a **wrong** result compared to the expected answer. The rule is therefore as follows:

- If the problem statement specifies a temperature different from 25 °C use $\frac{2.303RT}{F}$.
- If the problem statement does not specify the temperature and does not mention 0.06 use **0.059**.
- If the problem statement explicitly mentions 0.06 in the data use **0.06** without question.

Important: The Nernst constant is not a fixed value. It depends on temperature according to the relationship:

$$\frac{2.303RT}{F}$$

Thus, at 15 °C, the Nernst coefficient is approximately **0.057 V**, and at 40 °C, it is approximately **0.062 V**.⁽⁶⁵⁾ Consequently, if an exercise gives you a temperature different from 25 °C, you should definitely not use 0.059 or 0.06, but rather calculate the constant using the general formula.

Exercise

Measurement of standard potentials of silver and iron

Objective

Experimentally determine the standard potentials of the Ag^+/Ag and Fe^{2+}/Fe couples using a Standard Hydrogen Electrode (SHE) and verify the Nernst law.

Experimental setup

Description of the setup

- **Beaker 1:** Standard Hydrogen Electrode (SHE)
 - Platinized platinum electrode
 - HCl 1 M solution ($[\text{H}^+] = 1 \text{ M}$)
 - Dihydrogen gas bubbling at $P_{\text{H}_2} = 1 \text{ atm}$
 - $T = 25 \text{ °C}$
- **Beaker 2:** Metal electrode (silver or iron)

- Silver metal electrode for the Ag^+/Ag couple
- Iron metal electrode for the Fe^{2+}/Fe couple
- Solution of the corresponding metal at the indicated concentration
- **Salt bridge:** Tube filled with KCl gelled (using agar-agar) ensuring electrolytic continuity
- **Voltmeter:** Connected between the two electrodes to measure the electromotive force

Questions

- **Diagram and identification**
 - Reproduce the setup diagrammatically, clearly identifying the anode and cathode (silver or iron).
Indication: Polarity depends on the sign of the standard potential of the studied couple relative to the SHE.
 - Indicate the direction of electron flow in the external circuit for each case.
 - Indicate the direction of ion migration in the salt bridge for each case.
- **Electrochemical half-reactions**
 - Write the half-reaction that occurs at the Standard Hydrogen Electrode.
 - Write the half-reaction that occurs at the silver electrode, then at the iron electrode.
 - Write the overall reaction equation that occurs in the cell for each case.
- **Determination of the standard potential of silver**
 - With a 1 M AgNO_3 solution, the voltage measured by the voltmeter is +0.800 V. Deduce the value of the standard potential $E^\circ(\text{Ag}^+/\text{Ag})$. Justify your answer using the relation:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$
 - Recall the physical meaning of this value.
 - Compare with the tabulated value $E^\circ(\text{Ag}^+/\text{Ag}) = +0.799$ V. How can any difference be explained?
- **Determination of the standard potential of iron**
 - The silver electrode is now replaced by an iron electrode immersed in a 1 M FeSO_4 solution. The measured voltage is +0.44 V, but the voltmeter is connected in reverse compared to the silver case: the red (positive) lead is on the SHE and the black (negative) lead on the iron. Explain why and deduce the value of $E^\circ(\text{Fe}^{2+}/\text{Fe})$. Identify the anode and the cathode in this cell.
 - Why is the sign different from that of silver? What is the consequence on the role of the SHE (anode or cathode)?
 - Compare with the tabulated value $E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44$ V. Comment on the agreement or any discrepancy, and clearly identify the anode and the cathode.
- **Further exploration** (bonus questions)
 - Why is a platinized platinum electrode used rather than a simple polished platinum electrode for the SHE?
 - What is the role of the salt bridge? What would happen without it?
 - Why is the SHE difficult to use in routine practice? Cite other more practical reference electrodes.
 - Why is the standard potential of iron negative while that of silver is positive? What consequence does this have on the reactivity of the two metals?

Solution

Experimental determination of anode and cathode

When the value and even the sign of the standard potential of the studied couple are unknown, a "fixed connection convention" is adopted to avoid any ambiguity.

Conventional connection

- The Standard Hydrogen Electrode (SHE) is systematically connected to the negative terminal of the voltmeter.

- The electrode of the couple to be studied is connected to the positive terminal.

Reading and interpretation The voltmeter displays a voltage U (positive or negative) whose sign directly indicates the role of the electrodes (cathode or anode):

Connection convention: SHE on terminal (-), studied electrode on terminal (+)

Case 1: The measured voltage is positive ($U > 0$)

- The studied electrode is more positive than the SHE.
- Electrons flow from the SHE to the studied electrode.
- The studied electrode is the site of a **reduction**: it is the **cathode**.
- The SHE is the site of an **oxidation**: it is the **anode**.
- The standard potential of the couple is **positive**: $E^\circ = +U$.

Case 2: The measured voltage is negative ($U < 0$)

- The studied electrode is more negative than the SHE.
- Electrons flow from the studied electrode to the SHE.
- The studied electrode is the site of an **oxidation**: it is the **anode**.
- The SHE is the site of a **reduction**: it is the **cathode**.
- The standard potential of the couple is **negative**: $E^\circ = -|U|$.

Illustration with examples

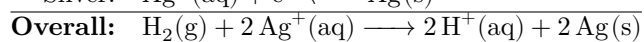
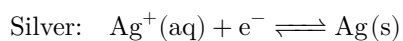
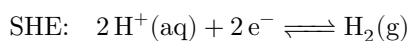
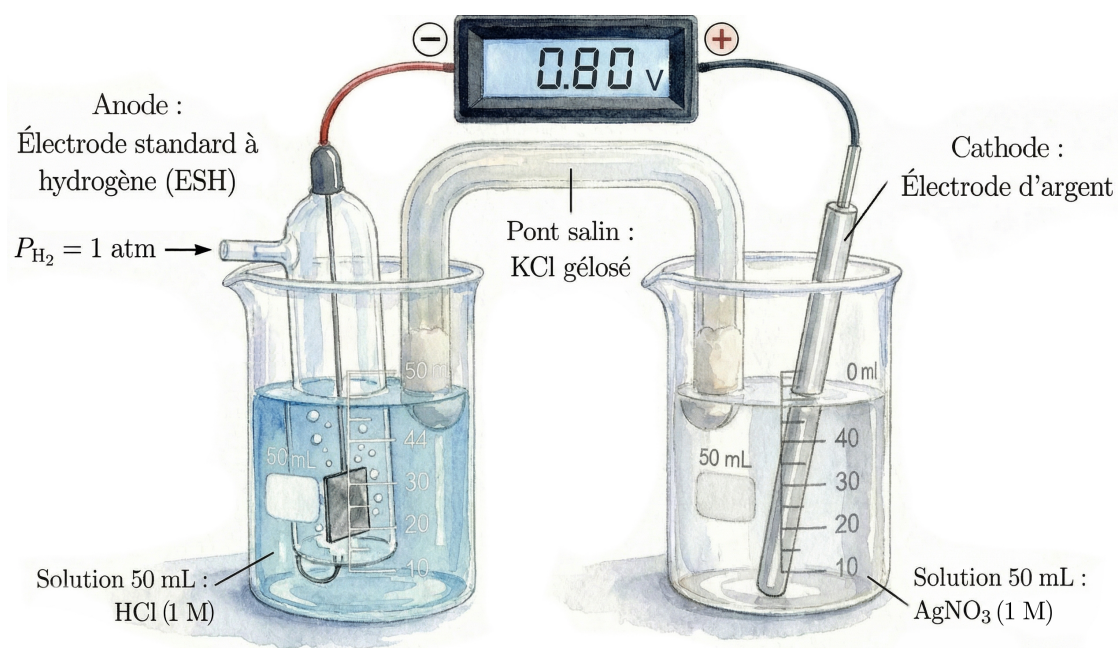
- **With a silver electrode:** $U = +0.80$ V is measured
 - The silver electrode is the cathode.
 - $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80$ V.
- **With an iron electrode:** $U = -0.44$ V is measured
 - The iron electrode is the anode.
 - $E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44$ V.

Fundamental note This interpretation is only valid if the connection convention is respected: the SHE **always** on the negative terminal of the voltmeter. This is the only way to unambiguously deduce the sign of the standard potential from the measurement.

Answer elements (for the teacher)

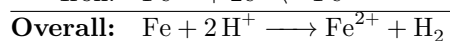
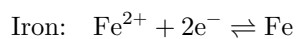
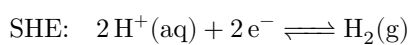
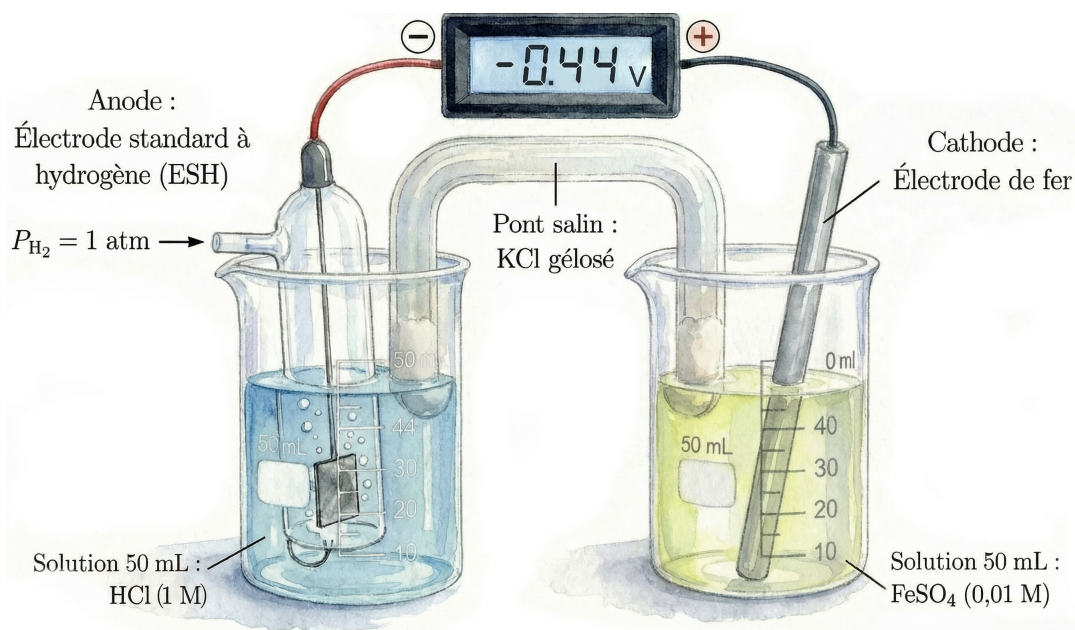
1. Diagram and identification

- **Case of silver:** $E^\circ(\text{Ag}^+/\text{Ag}) > 0$ so silver is more oxidizing than H^+ .
 - Anode: SHE (oxidation of H_2)
 - Cathode: Ag (reduction of Ag^+)
 - Electrons: from SHE to silver
 - Salt bridge: K^+ toward Ag, Cl^- toward SHE



- **Case of iron:** $E^\circ(\text{Fe}^{2+}/\text{Fe}) < 0$ so iron is more reducing than H₂.

- Anode: Fe (oxidation of Fe)
- Cathode: SHE (reduction of H⁺)
- Electrons: from iron to SHE
- Salt bridge: K⁺ toward SHE, Cl[−] toward Fe



2. Half-reactions

- SHE: $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$
- Silver: $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$
- Iron: $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$
- Overall Ag: $2\text{Ag}^+ + \text{H}_2 \longrightarrow 2\text{Ag} + 2\text{H}^+$
- Overall Fe: $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$

3. Standard potential of silver

- a) $E_{\text{cell}} = E_{\text{Ag}} - E_{\text{SHE}} = 0.800 - 0 = 0.800 \text{ V} \Rightarrow E^\circ(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$
- b) Silver tends to exist in metallic form rather than ionic form compared to H^+ .
- c) Very close to the tabulated value (0.799 V). Differences may come from temperature, H_2 pressure, exact concentration.

4. Standard potential of iron

- a) With the iron electrode connected to the + terminal of the voltmeter and the SHE to the – terminal, a **negative** voltage -0.44 V would be measured.
- By reversing the connections (SHE to the + terminal, iron to the – terminal), a positive voltage of 0.44 V is obtained.

Let U' be this voltage measured after reversal:

$$U' = E_{\text{SHE}} - E_{\text{Fe}} = 0 - E_{\text{Fe}} = 0.44 \text{ V} \Rightarrow E_{\text{Fe}} = -0.44 \text{ V}$$

Thus, the standard potential of the Fe^{2+}/Fe couple is $E^\circ = -0.44 \text{ V}$ relative to the SHE.

- b) Iron is more reducing than H_2 , so its standard potential is negative. Consistent with the tabulated value.

5. Further exploration

- a) Platinum black increases the active surface and catalyzes the electron exchange reaction, allowing rapid attainment of equilibrium.
- b) The salt bridge ensures electrical continuity while minimizing junction potential. Without it, the cell cannot function (open circuit).
- c) The SHE is difficult to use because it requires H_2 gas, a special electrode, and delicate handling. More practical reference electrodes: saturated calomel electrode (SCE), silver chloride electrode (Ag/AgCl).

Conclusion

This setup allows experimental determination of the standard potential of a redox couple and verification of the Nernst law. The precision of measurements depends on the care taken in preparing solutions and stabilizing temperature.

General Conclusion

*To my students:
Never stop asking the why of the how.*

Chemistry is not a series of isolated chapters. It is a language — and like all languages, its strength lies not in its individual words, but in the way they are put together, combined, and made to converse.

This book was written with a single, recurring question in mind — the question I have always asked my students, and that I hope they will continue to ask themselves long after they have closed these pages: **the why of the how**. Not just: *how does this reaction happen?* But: *why does it happen this way, and not another? Under what conditions would it change? What principle governs its direction, its speed, its outcome?*

This is the question that separates the scientist from the technician, the clinician from the automaton. It is the question that transforms memorization into understanding, and understanding into wisdom. It is the question I hope you will carry with you — not only through your examinations, but through every patient you encounter, every prescription you write, every diagnosis you make.

It has been a journey from the infinitely small to the measurably large, from the first page of this book to the last. From the structure of the atom to the voltage across an electrochemical cell. From the probabilistic cloud of an electron orbital to the pH of a biological buffer that keeps a patient alive. It's been a long road, and on purpose.

It started with the **atom** — not as an abstract concept, but as the fundamental building block of all chemical reasoning. Quantum numbers, atomic orbitals, electronic configurations — these are not things to memorize, they are the foundation that makes everything else meaningful. The periodic table is not a list. It is a map of how matter behaves. Electronegativity, atomic radius, ionization energy — these are all inevitable, natural outcomes of the arrangement of electrons about a nucleus.

From the atom, we moved to the **chemical bond**: the force which turns isolated atoms into the molecules of life. Lewis structures gave us a first language of connectivity; the VSEPR model gave that connectivity a geometry; molecular orbital theory showed us that electrons don't belong to individual atoms but are delocalized over the whole molecule. Hybridization rounded out the picture, explaining why carbon — the backbone of biochemistry — forms four equivalent bonds in methane, three in ethylene, and two in acetylene.

Water, a single, quiet medium, dominated the second part of this book. The aqueous solution is not just a stage for chemical reactions, but a participant — a structured, polar, hydrogen-bonded environment that dissolves, ionizes, carries, and controls. If there is no water, there is no biochemistry. If we don't understand water, we don't understand medicine.

Acid-base equilibria have shown us that the simplest of chemical acts — proton transfer — is the basis for some of the most important physiological processes: respiratory regulation, renal compensation, drug absorption through membranes. The Henderson-Hasselbalch equation is more than an equation; it is the mathematical heart of the bicarbonate buffer, the reason why a small dose of sodium bicarbonate given intravenously can correct metabolic acidosis.

Titration extended this logic into analytical practice: to be able to *quantify* is to be able to diagnose. The equivalence point of a titration is the clinical equivalent of a threshold: at this point the reaction is complete, at that point the diagnosis begins. Every test in a hospital laboratory is based on the same quantitative logic explored in the titration chapters.

Solubility equilibria introduced the concept of **threshold**: below a certain ionic product dissolution occurs, above it precipitation occurs. Kidney stones develop when this threshold is exceeded. Fluoride protects against dental caries by shifting this threshold in favour of a more insoluble mineral phase. Radiological contrast agents are chosen because barium sulfate is practically insoluble in biological fluids. Chemistry sets the limit; biology works around it.

Redox equilibria and electrochemistry complete this journey naturally: the **conversion of chemical energy into electrical energy**, and vice versa. Oxidation state is a bookkeeping tool for electron transfer. The Nernst equation relates thermodynamic potential with the actual concentrations existing in solution, and the Standard Hydrogen Electrode provides the universal reference against which all electrode potentials are measured. These

are not abstractions: cardiac pacemakers, pH electrodes, glucose biosensors, the electrochemical gradients that drive nerve impulses — all stand on the same theoretical foundations explored in the final chapters.

The Unifying Thread

One principle has been constant through all the chapters: macroscopic properties are the manifestation of microscopic structure. The acidity of a molecule is a measure of the stability of its conjugate base. The solubility of a salt depends on the balance between lattice energy and hydration energy. The spontaneity of a redox reaction is decided by the difference in standard potentials. In each case the observable — measurable in the laboratory, consequential in the clinic — has its explanation at the atomic or molecular scale.

This is what chemistry gives to the future health professional: not a collection of formulas to be remembered under pressure, but a coherent framework for *understanding why*.

You who have worked through this book, whether as a first-year student of medicine, pharmacy, dentistry or life sciences, have now acquired something that no single examination can fully measure: the habit of reasoning from first principles. You've learned to ask not only *what* happens but *why* it happens, and under what conditions it might happen differently.

This is a demanding, sometimes uncomfortable but always rewarding scientific discipline — and it is what the practice of medicine and pharmacy will require of you throughout your career. Drug interactions, metabolic disorders, diagnostic assays, pharmacokinetics, toxicology: all of these areas require the same rigorous chemical thinking that this book has tried to build.

This book has been written with the sole conviction that the healthcare professional of the future need not be a chemist. But they must think like one — rigorously and systematically, with the humility of knowing that every molecule has a story.

Chemistry is not a subject you complete. It is a language that you speak increasingly fluently, more accurately, more confidently, with every patient you meet, every drug you prescribe, every result you interpret.

The atoms remain. The bonds are still there. The equilibria still move. And the question remains — always: *the why of the how*.

This book began with an atom.

It ends with a circuit.

Between them: the whole of chemistry.

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Oran, Algeria, 2026

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