Chemistry and Introduction to Biochemistry

Electrochemistry

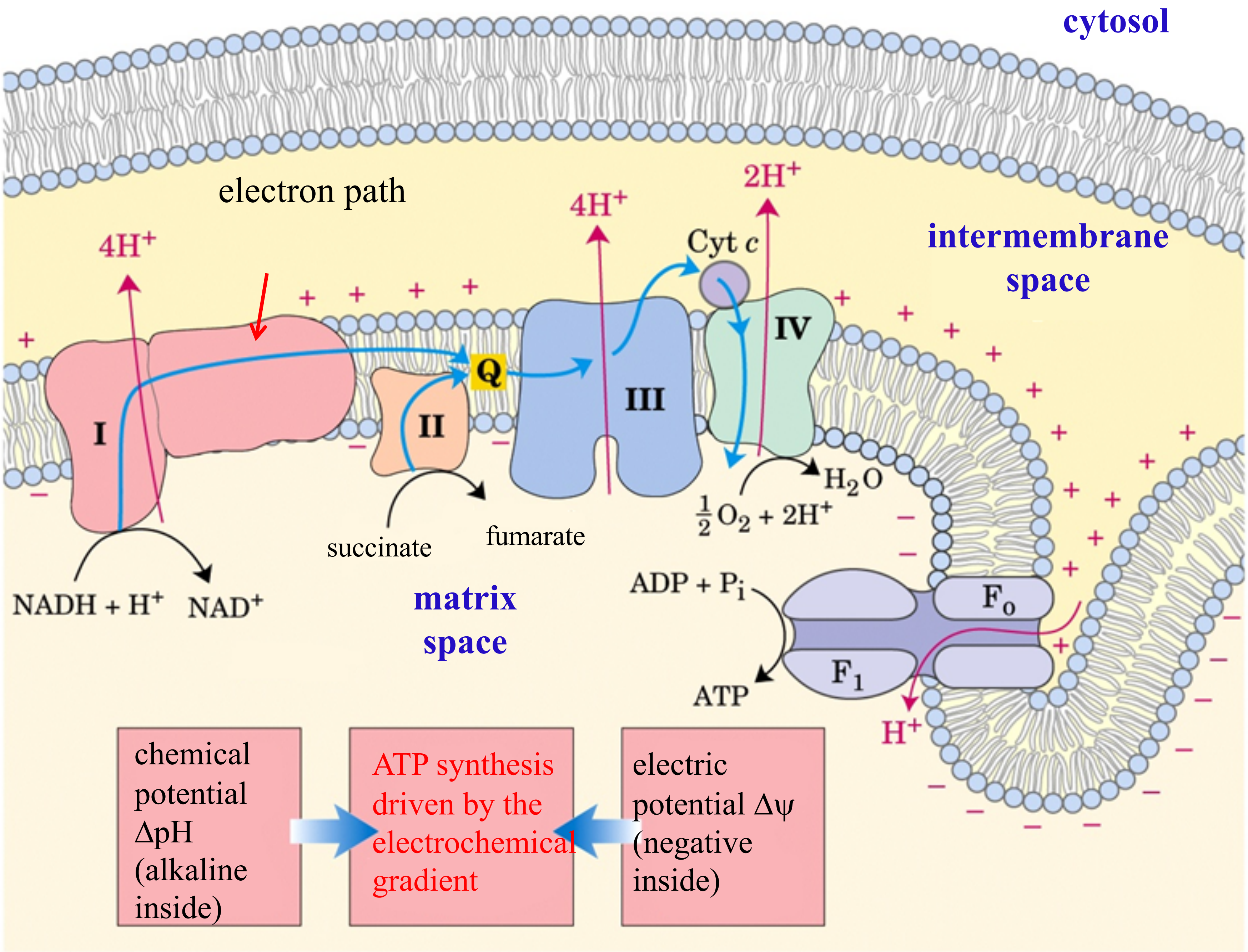
Luigi Galvani
(1737 – 1798)

Alessandro Volta
(1745– 1827)

Walther H. Nernst
(1864 – 1941)

Alcune immagini sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

Electron transport chains



chemical potential ΔpH (alkaline inside)

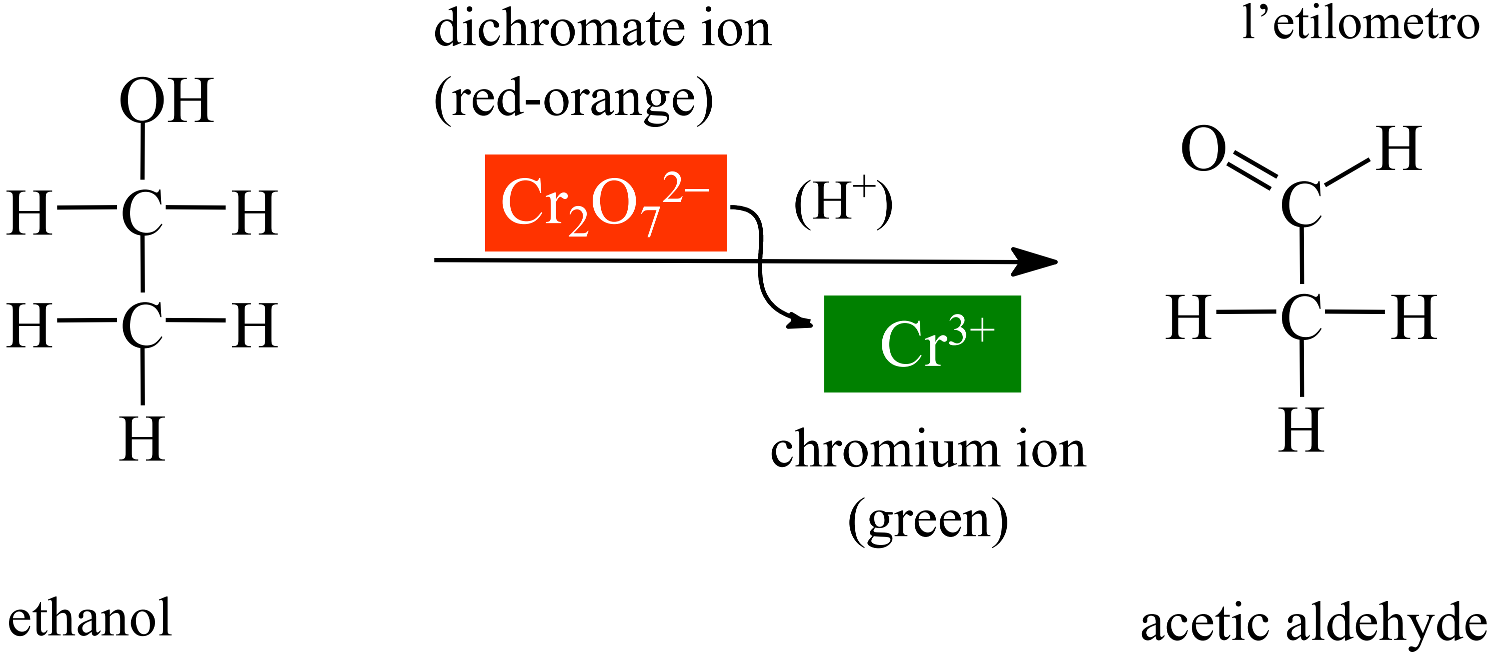
ATP synthesis driven by the electrochemical gradient

electric potential Δψ (negative inside)

Alcol Test

The color change of the dichromate ion in the oxidation reaction of alcohols (and aldehydes) is exploited in the extemporaneous examination of the ethanol concentration in the breath (balloon test).

l'etilometro



dichromate ion (red-orange)

$Cr_2O_7^{2-}$

(H^+)

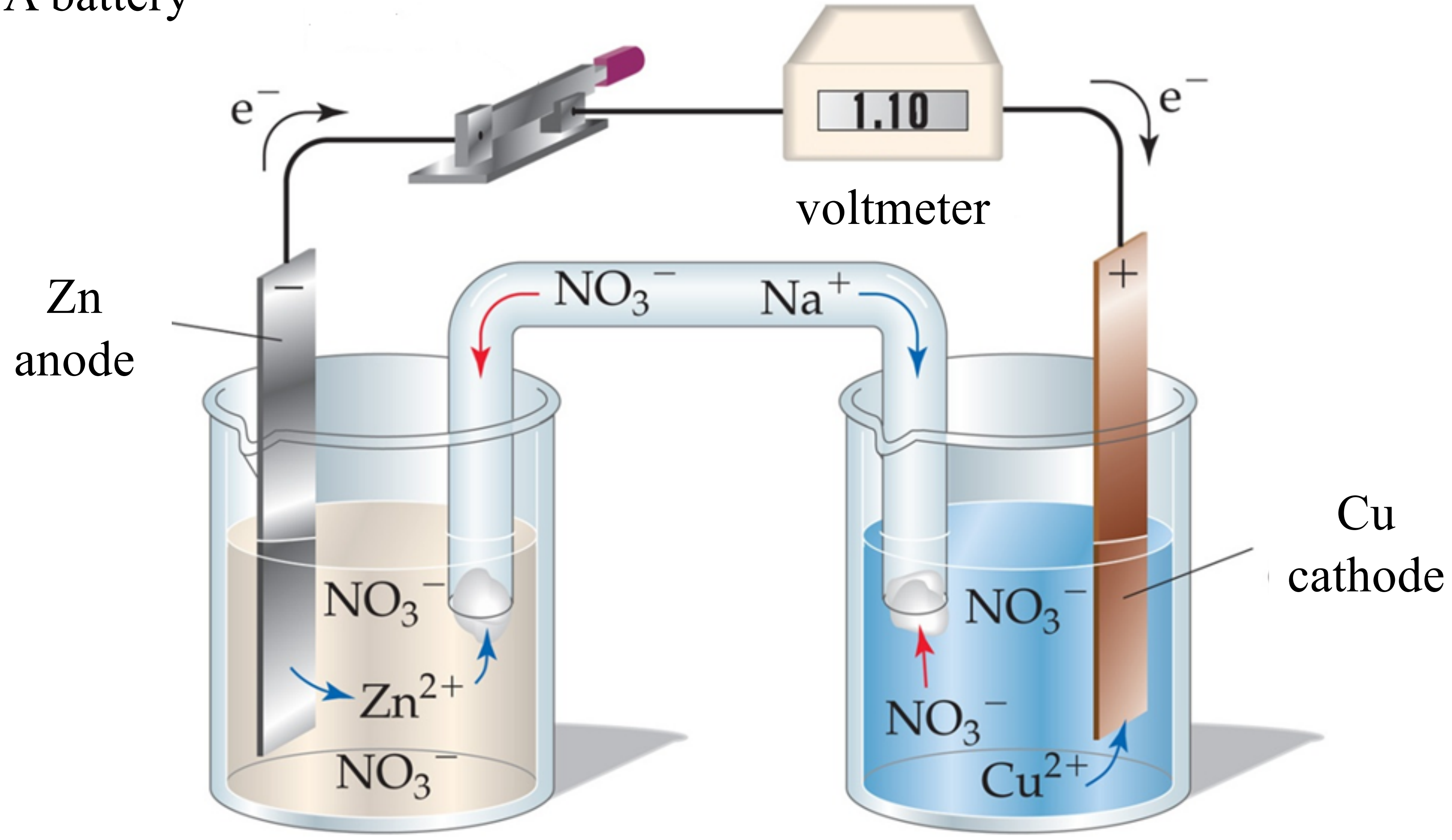
Cr^{3+}

chromium ion (green)

ethanol

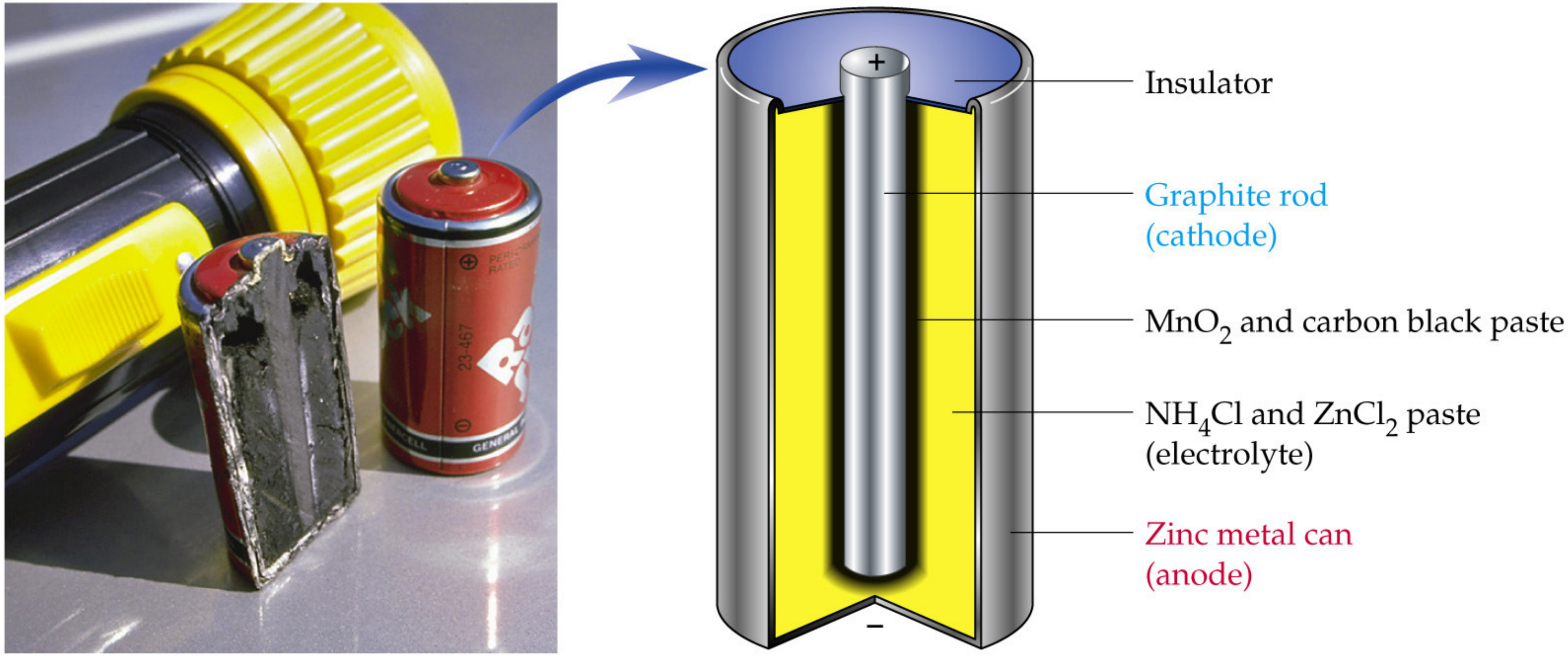
acetic aldehyde

A battery



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Alcaline battery (common, manganese-zinc)



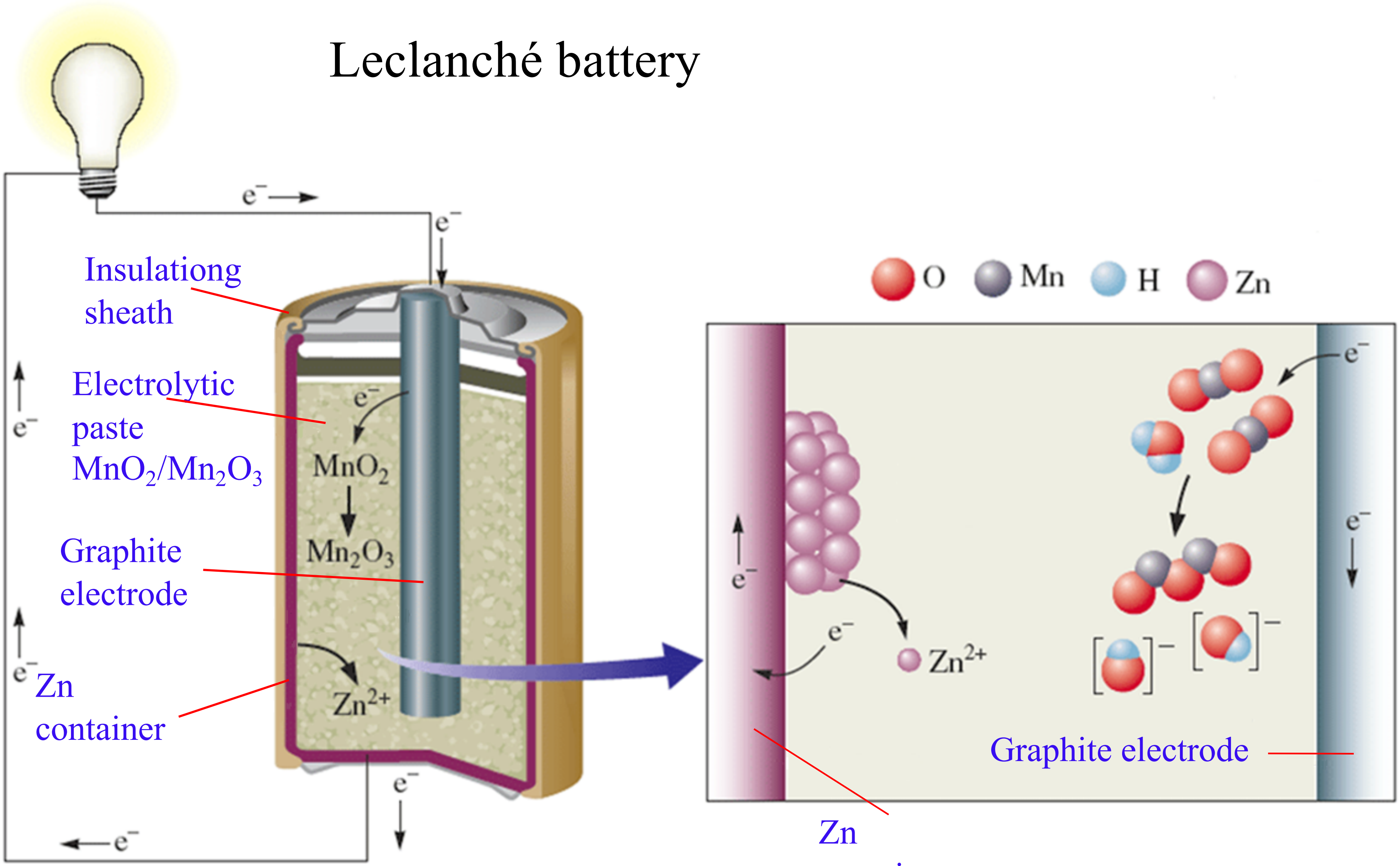
anode cathode

$$\mathrm{Zn} \;\Big|\; \mathrm{Zn}^{2+} \;\Big\|\; \mathrm{Mn}^{2+}, \mathrm{Mn} \;\Big|\; \mathrm{C\ (s)\ graphite}$$

$$E^0_{Zn/Zn^{2+}} = -0.76\ V \qquad E^0_{Mn/Mn^{2+}} = +1.51\ V$$

$$\Delta E^0 = 1.51 - (-0.76) = 2.27\ V$$

Leclanché battery



Insulationg sheath

Electrolytic paste MnO_2/Mn_2O_3

Graphite electrode

Zn container

Graphite electrode

Zn container

anode: $Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

catode: $2\ NH_4^+ (aq) + 2\ MnO_2\ (s) + 2e^- \rightarrow Mn_2O_3\ (s) + 2NH_3\ (aq) + H_2O\ (l)$

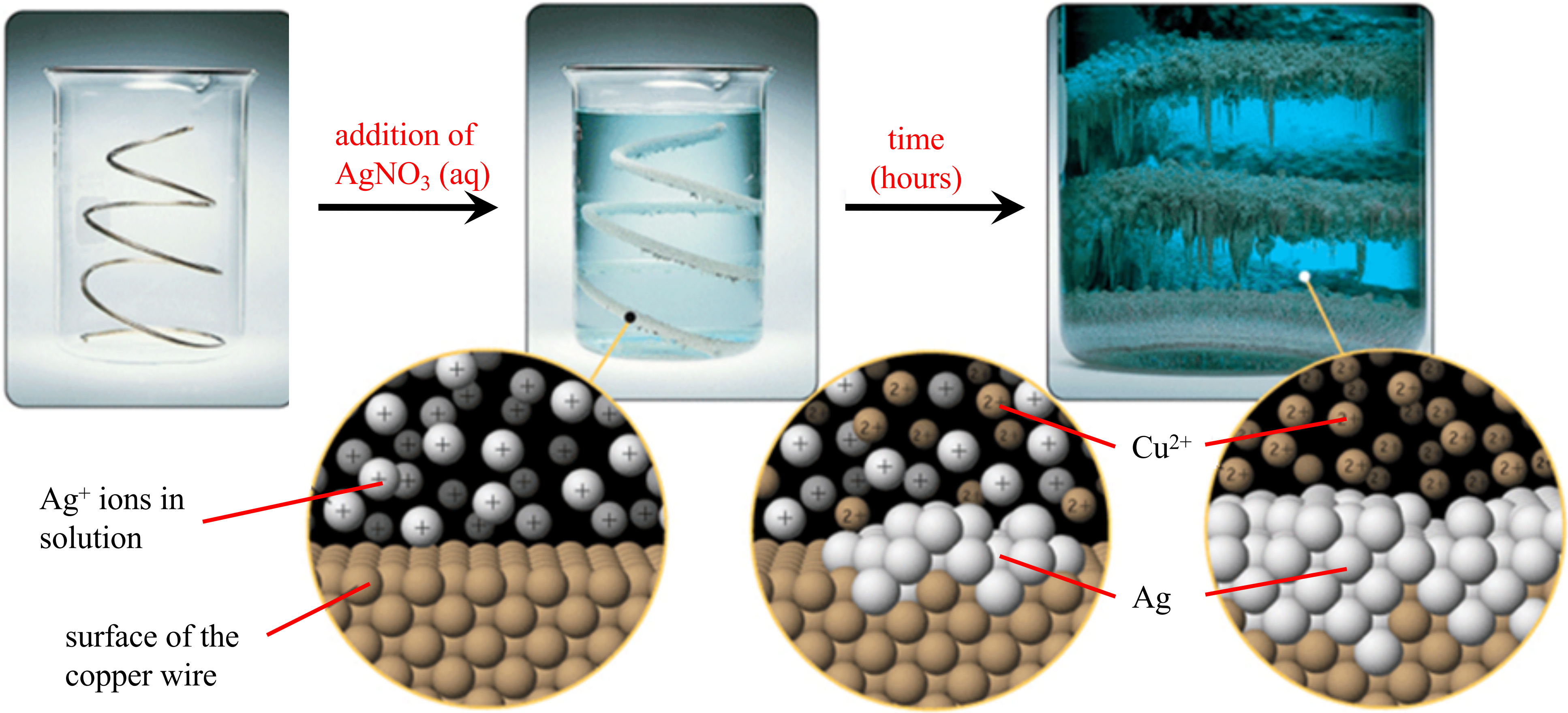
$Zn\ (s) + 2\ NH_4^+\ (aq) + 2\ MnO_2\ (s) \rightarrow Zn^{2+}\ (aq) + 2NH_3\ (aq) + H_2O\ (l) + Mn_2O_3\ (s)$

Redox reactions

A silver nitrate ($AgNO_3$) solution is added to a piece of copper

Over time, copper reduces Ag^+ ions to metallic Ag crystals, and copper oxidizes to Cu^{2+} cupric ions

The blue color of the solution is due to the presence of Cu^{2+} cupric ions



addition of $AgNO_3$ (aq)

time (hours)

Ag^+ ions in solution

surface of the copper wire

Cu^{2+}

Ag

$$Cu\ (s) + 2\ Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$$

Formation of Silver Crystals

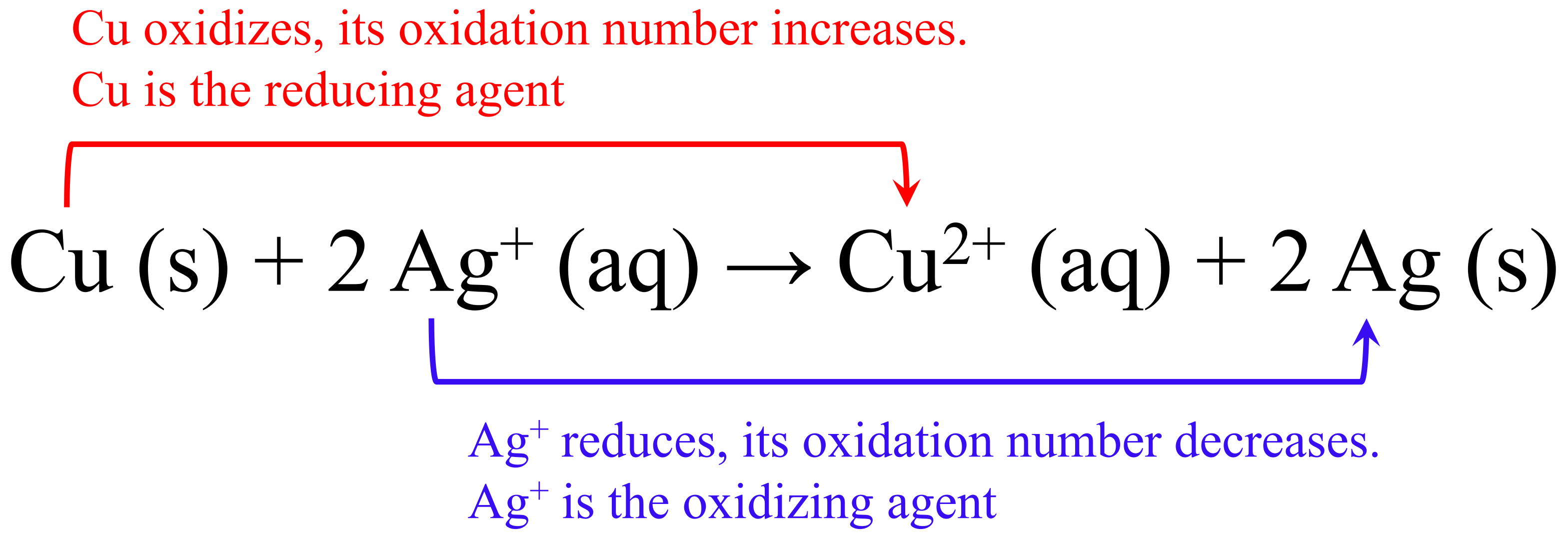
$$Cu\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$$

$$Cu\ (s) + 2\ AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + 2\ Ag\ (s)$$

Oxidation-reduction reactions (redox)

In an oxidation-reduction reaction electron transfer occurs between a reducing agent and an oxidizing agent. The essential characteristics of all redox reactions are as follows:

- one reagent oxidizes and the other is reduced
- the two oxidation and reduction reactions are coupled and must be balanced
- the oxidizing agent (the chemical species that causes oxidation) is **reduced**
- the reducing agent (the chemical species that causes the reduction) is **oxidized**
- the **oxidation numbers** are used to determine whether a substance oxidises or is reduced: an element oxidizes if its oxidation number increases, and is reduced if its oxidation number decreases

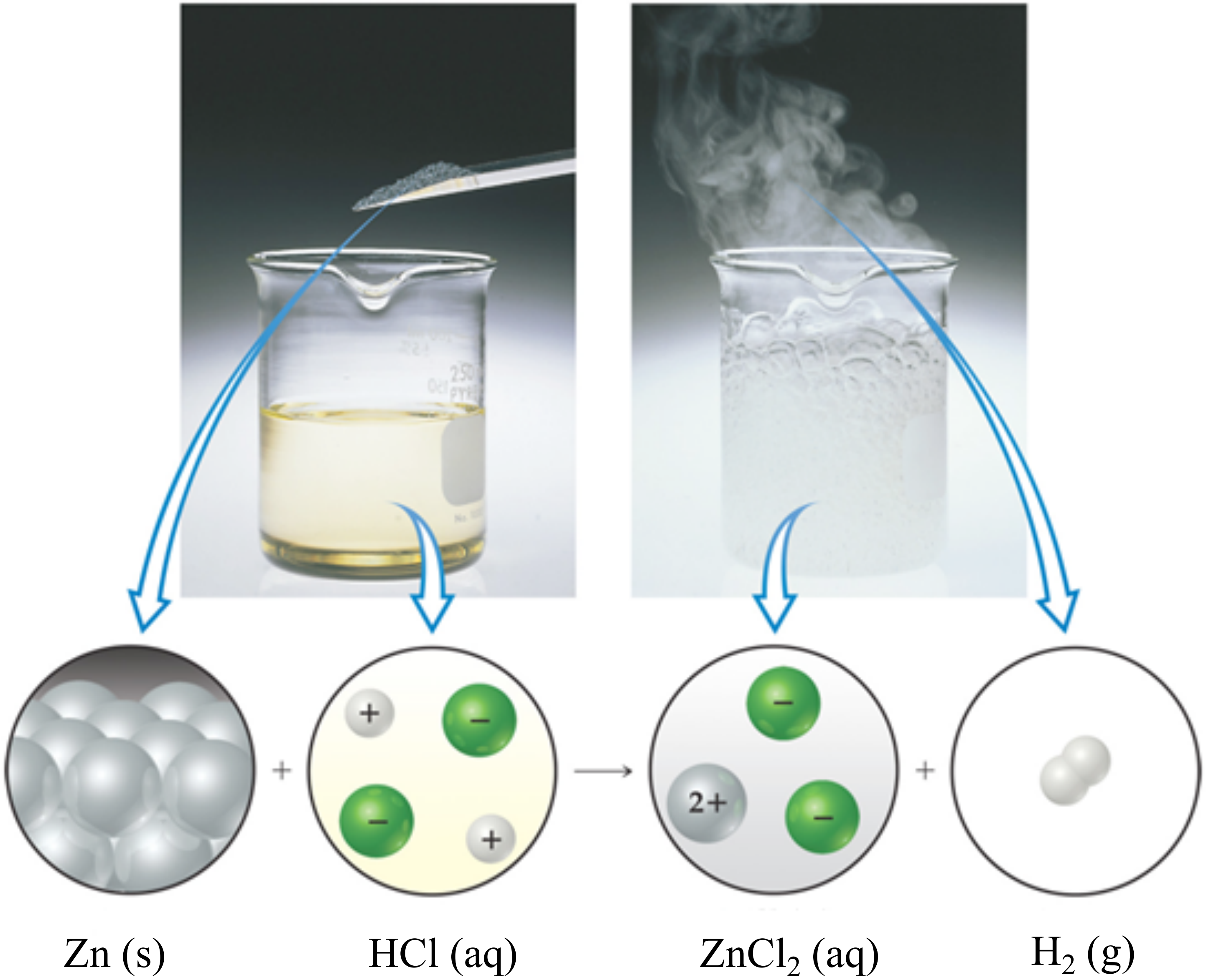


Cu oxidizes, its oxidation number increases.
Cu is the reducing agent

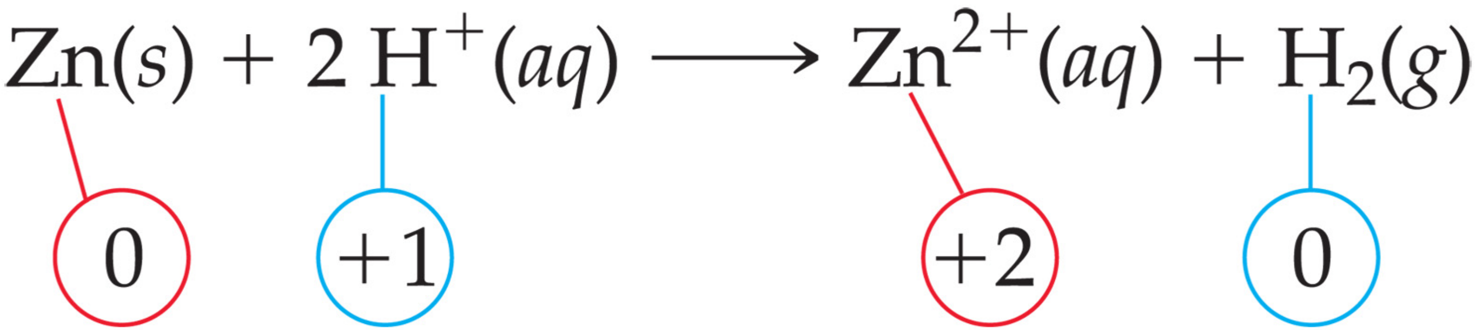
$$Cu\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$$

Ag^{+} reduces, its oxidation number decreases.
Ag^{+} is the oxidizing agent

In redox reactions, electrons are transferred from one species to another



Oxidation and reduction



$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

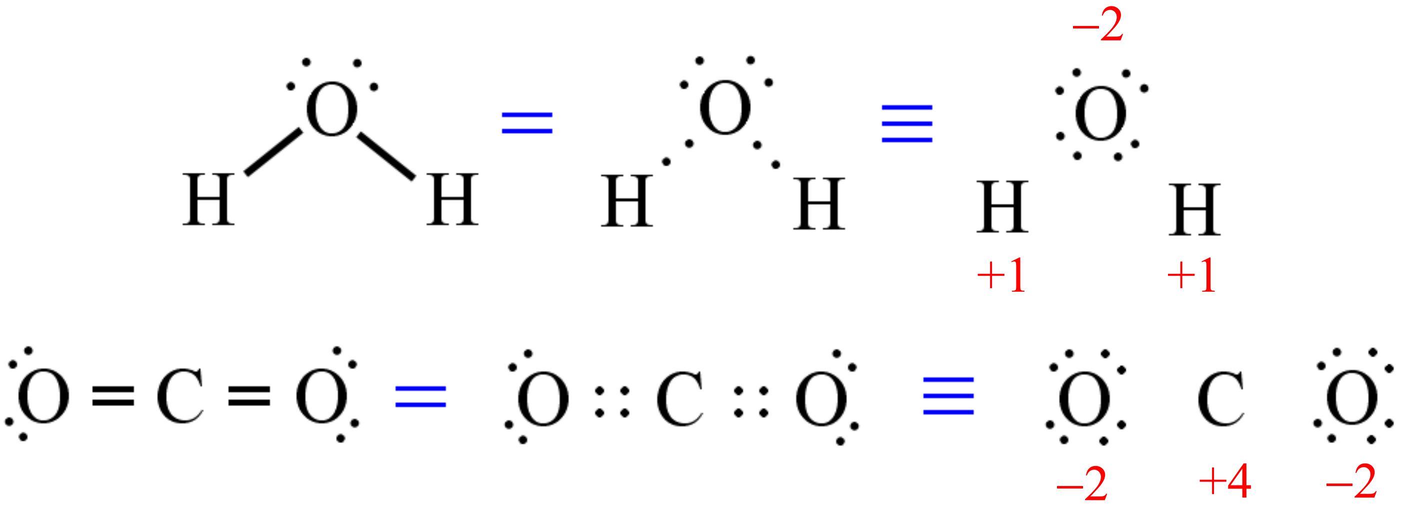
- a species oxidizes when it loses electrons
  - The zinc loses 2 electrons $Zn \rightarrow Zn^{2+} + 2\,e^-$
- a species is reduced when it acquires electrons
- each of the H^+ gains an electron and by combining they form H_2

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

- the species that is reduced is called the oxidizing agent
- H^+ oxidizes Zn by removing its electrons
- the species that is oxidized is called the reducing agent
  - Zn reduces H^+ giving off it electrons

Oxidation number

The oxidation number is the **charge** that an element in a compound would take if the bonding electrons were attributed to the most electronegative element. The charge that the element "assumes" is determined by the comparison with the external electronic configuration of the element, in its fundamental state.



The oxidation number is not a real charge, but a fictitious one, formally attributed to each element in a compound.

Rules to assign the oxidation number, in brief:

- in the elementary state the oxidation number is 0
- the oxidation number of a monoatomic ion equals its charge
- non-metals tend to have negative oxidation numbers (with exceptions)
- oxygen has oxidation number –2, except for peroxides where it is – 1
- hydrogen has an oxidation number – 1 when bound to a metal and +1 when combined with a non-metal
- the sum of the oxidation numbers in a neutral compound is equal to 0
- the sum of the oxidation numbers in a polyatomic ion equals the charge of the ion

Balancing redox reactions

In redox reactions the mass **and** charge must be balanced. The same **number of atoms** must appear in the products and reagents of a chemical equation, and the sum of the **electrical charges** of all species on both sides of the arrow must be equal.

Balancing ensures that the electrons produced in the oxidation reaction are the same as those consumed in the reduction reaction.

Semireactions method

The reduction and oxidation processes "the semireactions", are written separately and are balanced (mass + charge). Eg. in the reduction of silver (I) by copper

reduction semirection: $Ag^+ (aq) + e^- \rightarrow Ag (s)$

oxidation semireaction: $Cu (s) \rightarrow Cu^{2+} (aq) + 2\ e^-$

Since each mole of Cu yields 2 moles of electrons, and to accept them 2 moles of Ag^+ are needed:

$$2\ Ag^+ (aq) + \cancel{2}\ e^- \rightarrow 2\ Ag (s)$$

$$Cu (s) \rightarrow Cu^{2+} (aq) + \cancel{2}\ e^-$$

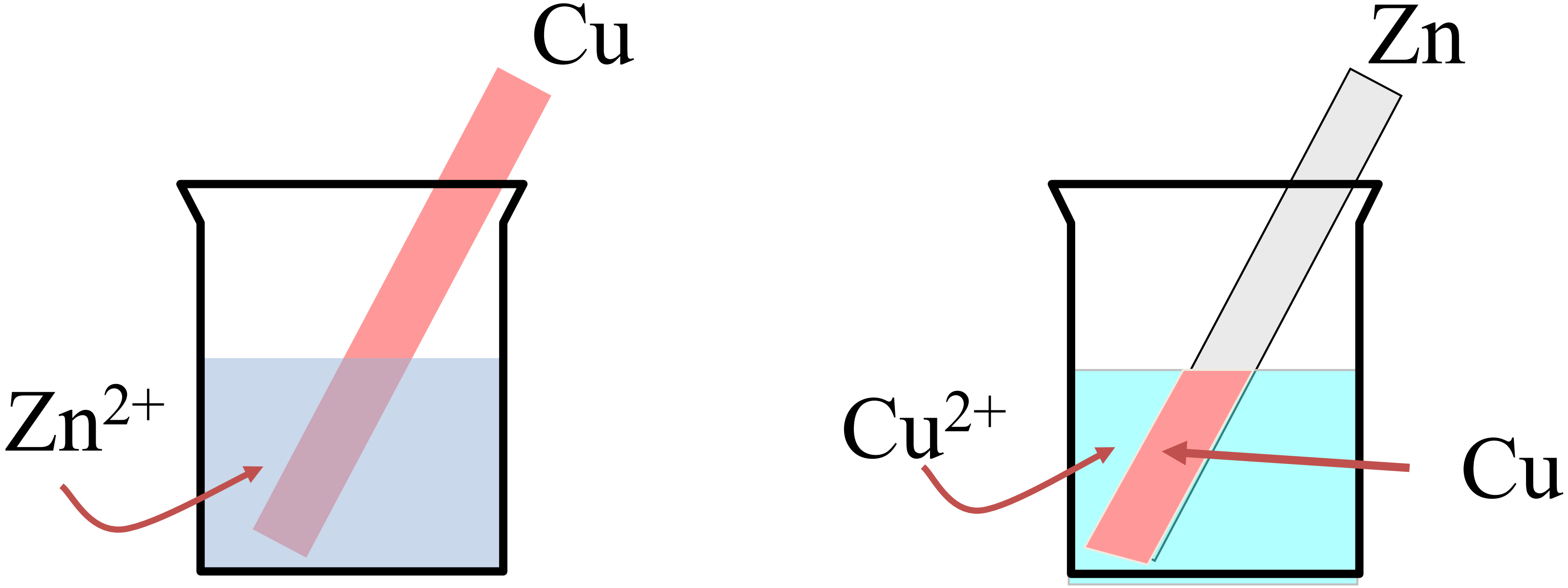
- -

$$Cu (s) + 2\ Ag^+ (aq) \rightarrow Cu^{2+} (aq) + 2\ Ag (s)$$

Lets consider the two possible reactions:

~~$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$~~

$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$



Reducing power of Cu^{2+}/Cu < Reducing power of Zn^{2+}/Zn

Only the second reaction is spontaneous

Voltaic cells

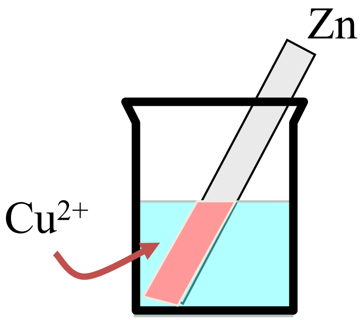
We can therefore devise a **device** that uses the **spontaneous redox** reactions to move electrons (hence electrical current) and therefore **produce electricity**. Such devices are known as voltaic cells or galvanic cells or batteries.

All galvanic cells are built so that the electrons of the reducing agent are transferred through an electric circuit to the oxidizing agent.

In a voltaic cell, the chemical energy is converted into electricity. In the opposite process, known as electrolysis, electricity is used to drive a chemical reaction in a non-spontaneous direction.

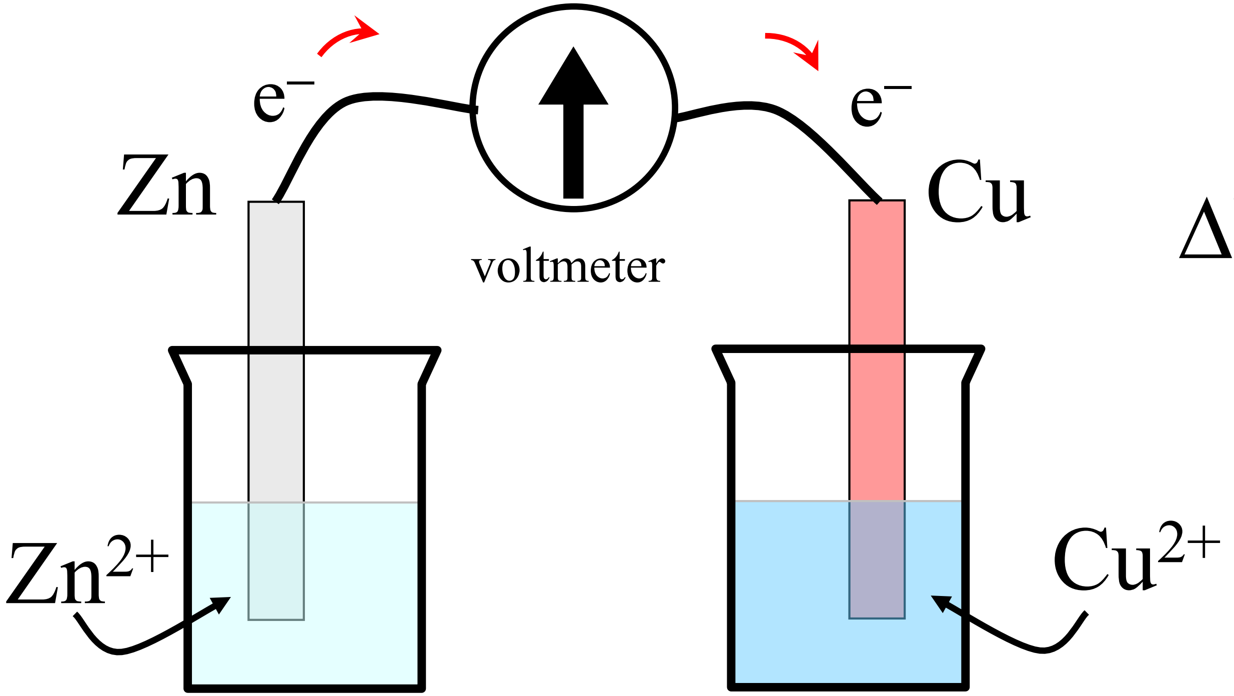
How do we build a battery?

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$



oxidation	$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$
reduction	$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

Electrons move spontaneously from zinc to copper.



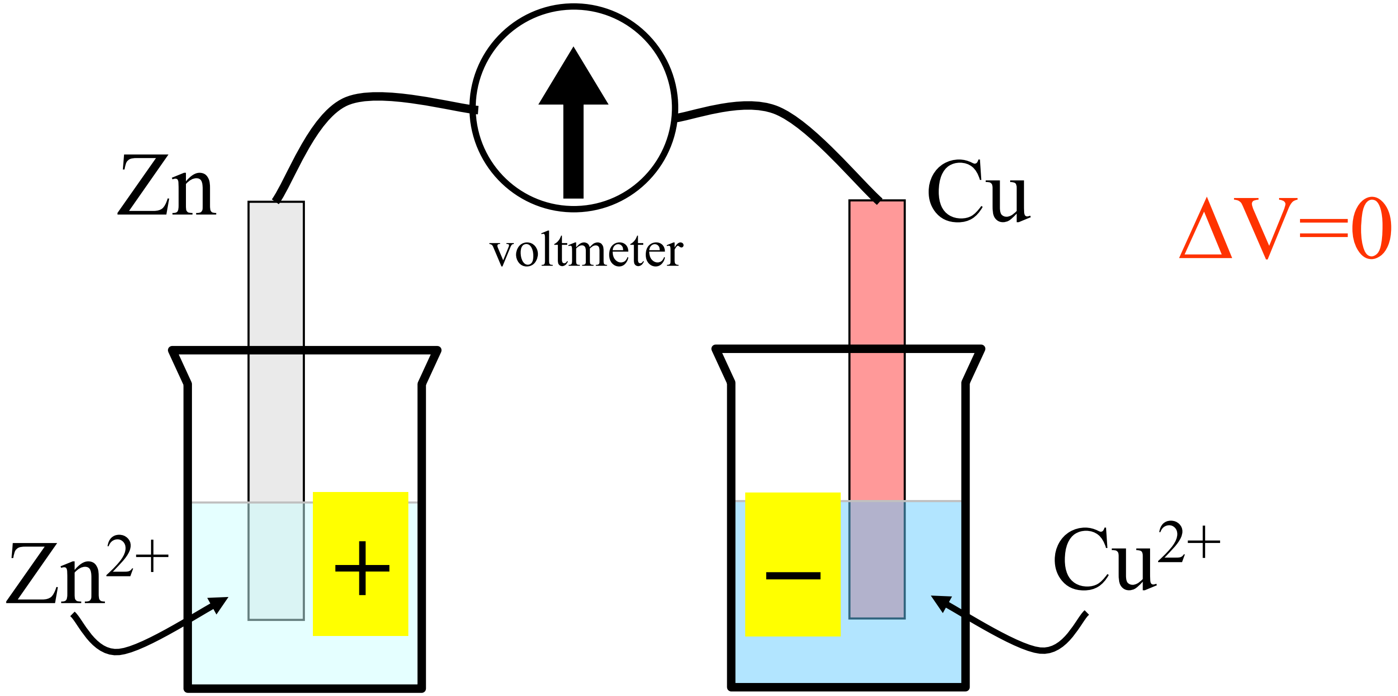
$\Delta V=0$

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

oxidation $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$

reduction $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$

Since electrons move from left to right, if the neutrality of the solutions is not maintained, a + charge is built to the left and a – charge is built to the left
This blocks a further transfer of elecrons.

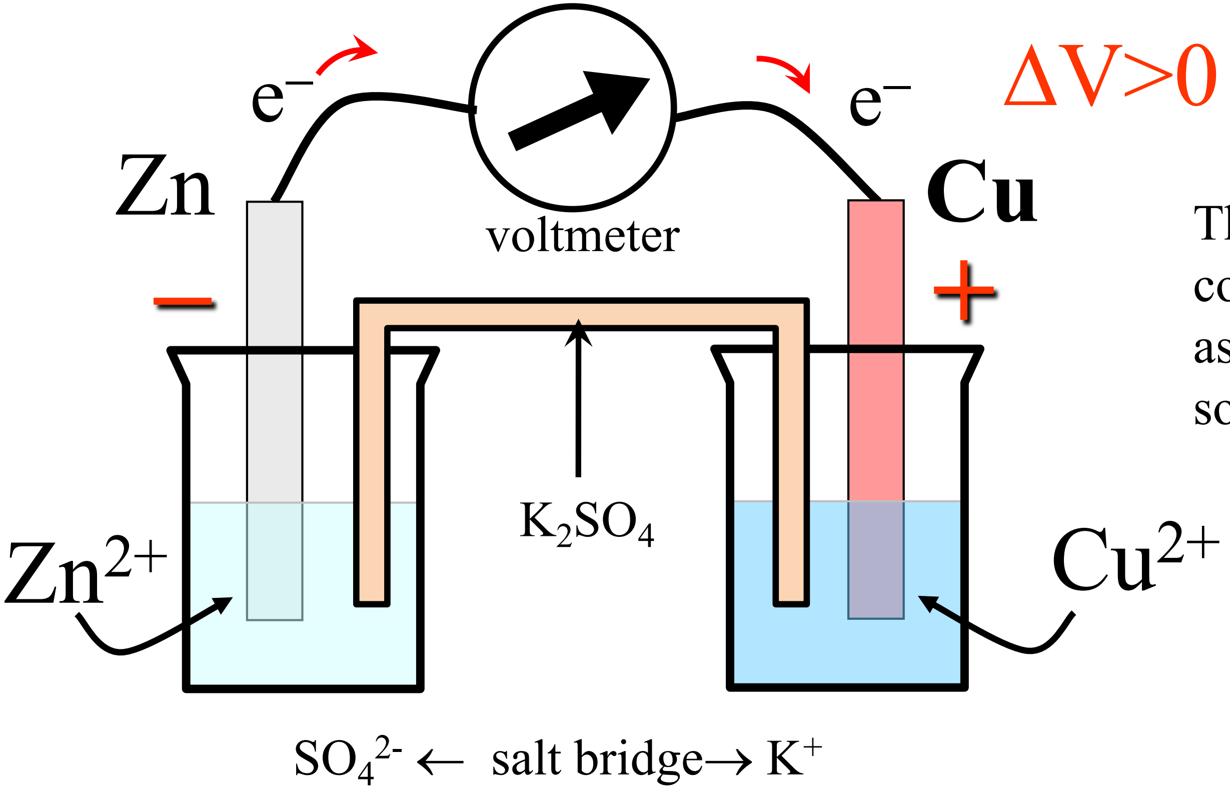


$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

oxidation $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}$

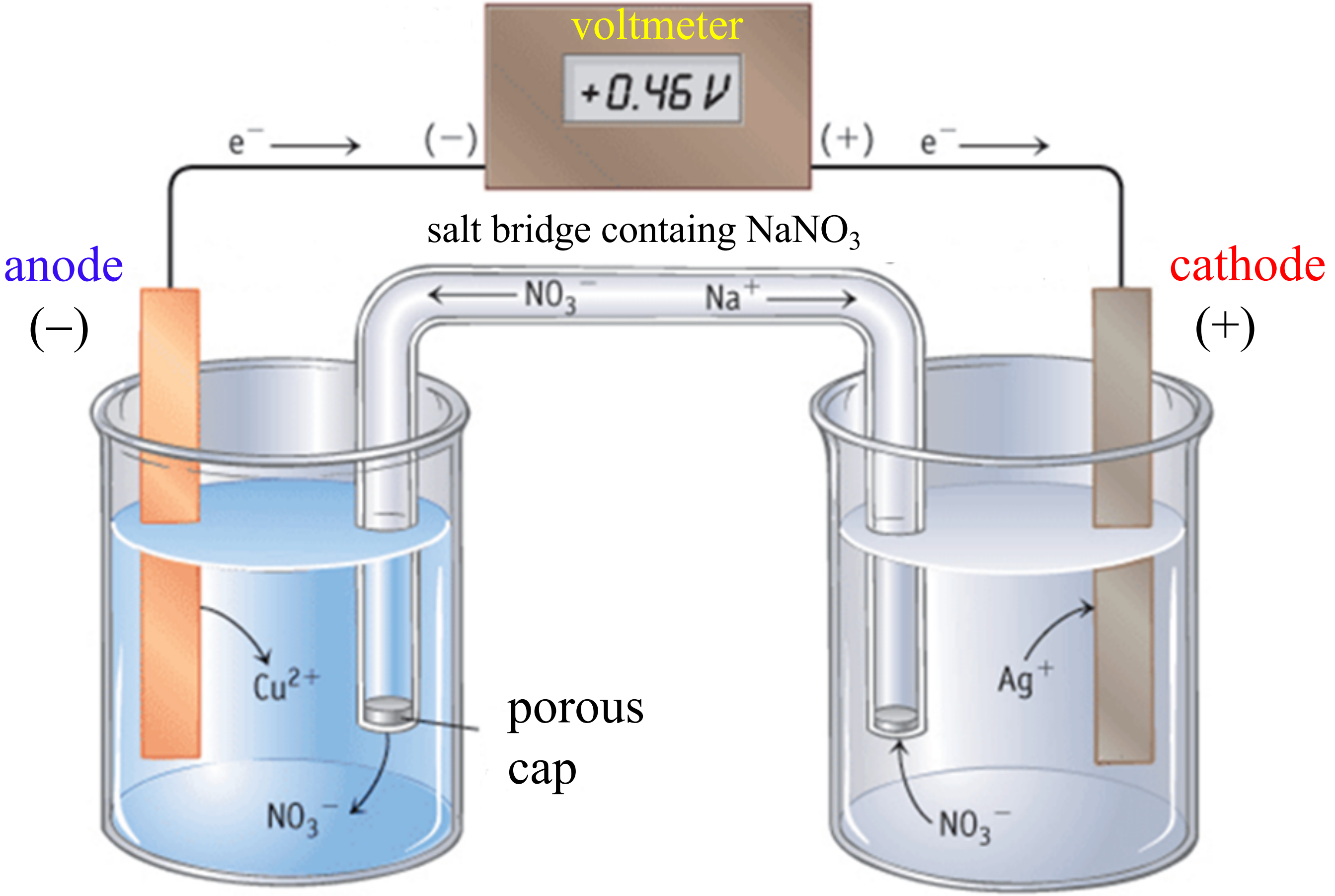
reduction $Cu^{2+}(aq) + 2\,e^{-} \rightarrow Cu(s)$

The salt bridge is necessary, due to the production of positive ions Zn^{2+} on the left and consumption of positive ions Cu^{2+} in the right half-cell: if negative ions (SO_4^{2-}) could not diffuse from right to left the reaction would not proceed (and vv for K^+).



The salt bridge is usually a tube containing an electrolyte in a gel so as to prevent the mixing of the two solutions.

Anode is defined as the electrode where oxidation takes place and the electrode where reduction takes place is called the cathode. In a cell the electrons flow from the anode to the cathode so that the anode has a negative sign and the cathode has a positive sign

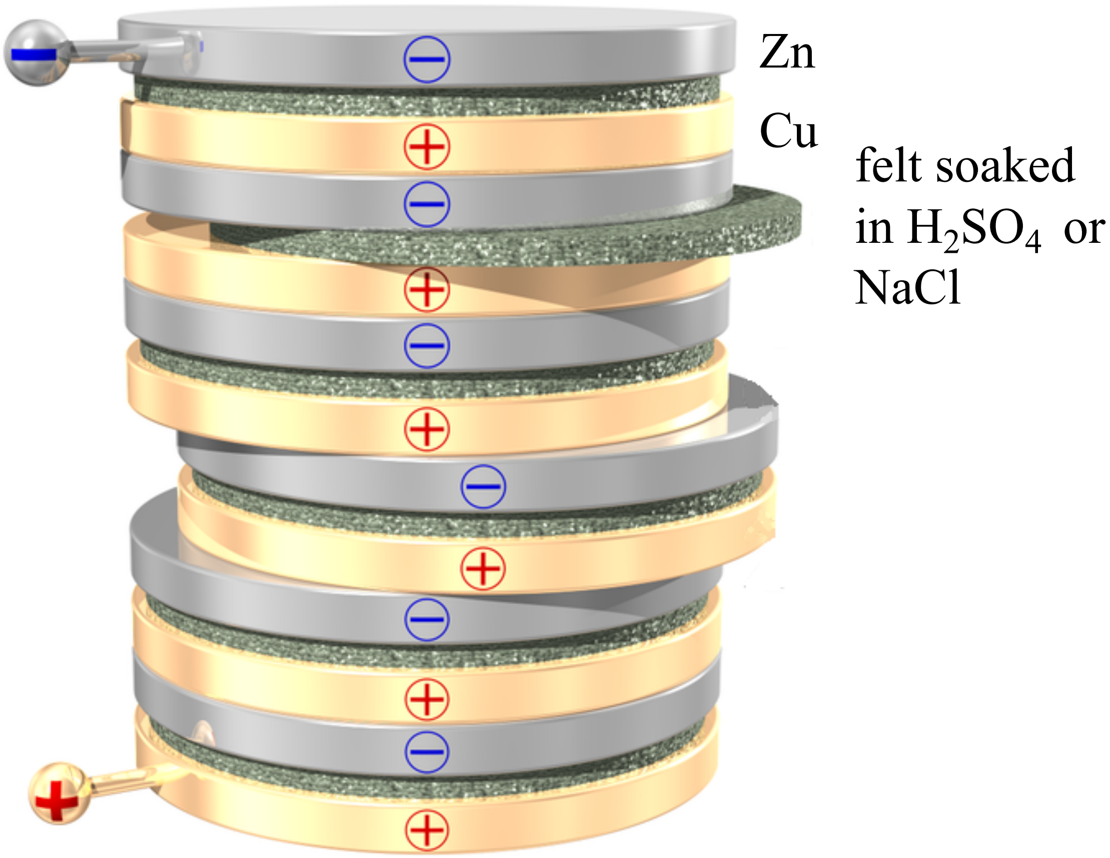


anode (negative): $Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2\ e^-$ oxidation

cathode (positive): $Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$ reduction

Overall: $Cu\ (s) + 2\ Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$

How do you build a battery?



Volta's battery on display in Treviglio

Voltaic cells with inert electrodes

In order to study any redox reaction in a voltaic cell it is necessary to use other types of electrodes.

In cases where reagents and products cannot be used as electrodes (non-metals generally do not conduct electric current) inert electrodes are used.

These electrodes are made of materials that conduct electric current, but which are neither oxidized nor reduced in the electrochemical cell.

- graphite electrode
- Pt electrode
- hydrogen electrode

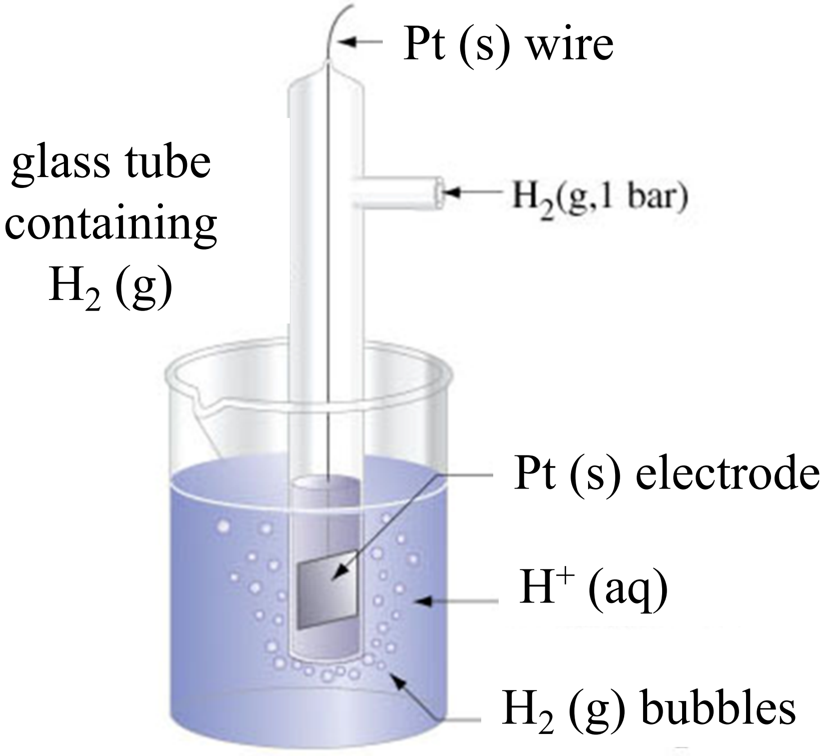
The hydrogen electrode

This electrode is particularly important in electrochemistry as it is used as a reference electrode to assign the voltage to all cells.

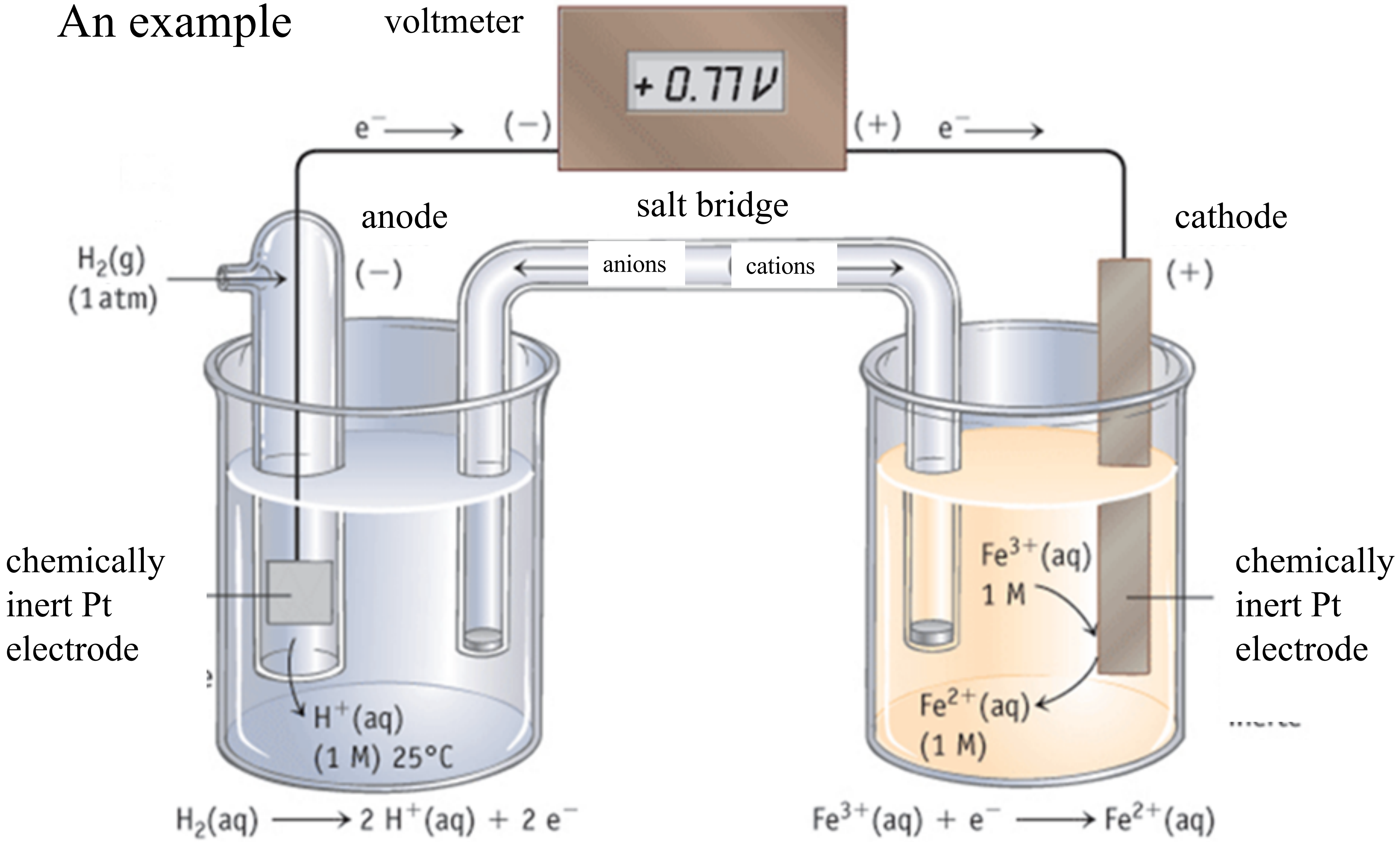
In this half-cell, H_2 (g) is bubbled onto a platinum electrode (Pt). The contact between the gas and the electrode is optimized by the large surface area of the latter. The electrode is immersed in an aqueous solution containing 1 M H_3O^+ (aq).
The half-redox reaction is:

$$2\ H^+(aq) + 2\ e^- = H_2\ \ (g)$$

The reaction takes place on the surface of the electrode, and the electrons involved in the reaction reach or leave the reaction environment through the Pt electrode



An example



Net reaction: $2\,Fe^{3+}\,(aq) + H_2\,(aq) \rightarrow 2\,Fe^{2+}\,(aq) + 2\,H^+\,(aq)$

Notation for voltaic cells

A voltaic cell is usually schematized by a conventional notation in which the species involved in the cell reaction, plus any inert electrodes, are written in a certain order and separated by vertical lines. For example, Daniel’s battery:

$$\mathrm{Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)}$$

$\mathrm{Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^{-}}$ oxidation → anode

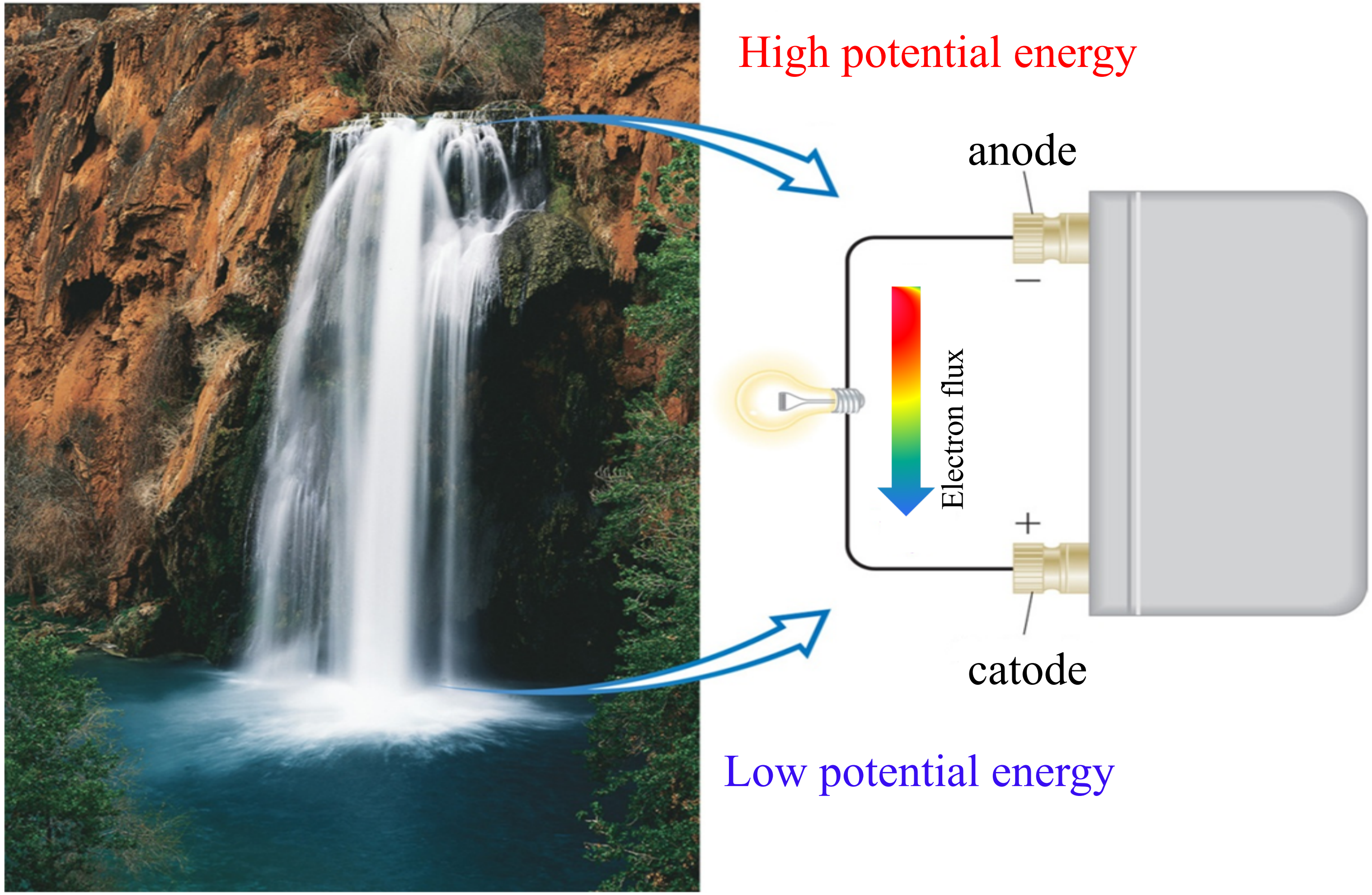
$\mathrm{Cu^{2+}\ (aq) + 2\ e^{-} \rightarrow Cu\ (s)}$ reduction → cathode

is outlined as:

$$\boxed{\mathrm{Zn\ (s)\ |\ Zn^{2+}\ (aq)\ ||\ Cu^{2+}\ (aq)\ |\ Cu\ (s)}}$$

In this notation the anode is written to the left and the cathode to the right with the species written in the same order as they appear in the respective semi-reactions.

The electromotive force (emf)

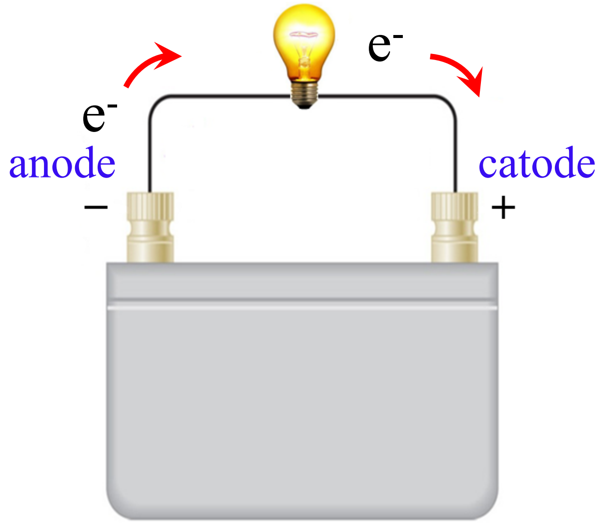

High potential energy

Low potential energy

- H_2O flows in one direction in a waterfall
- Electrons flow spontaneously from high to low potential energy.

Standard electrochemical potentials

The electrons generated at the anode of an electrochemical cell move through the outer circuit to the cathode, and the force required to move them derives from the potential energy difference between the two electrodes.



This difference in potential energy is called electromotive force (emf), literally "force that moves electrons".

- The emf is measured in volts (V)
- 1 volt is the potential difference necssary to transfer 1 joule of energy to an electrical charge of 1 coulomb (1 V = 1 J x 1 C)
- 1 coulomb is the amount of electric charge that passes trhrough a circuit when a current of 1 ampere flows for 1 second (1 C = 1 A x 1 s)

Measurement of standard electrochemical potentials

We want to study the voltage of a cell aiming at:
1) understanding the factors that determine the potential
2) predict the potential of a voltaic cell

The voltage of a cell depends on:

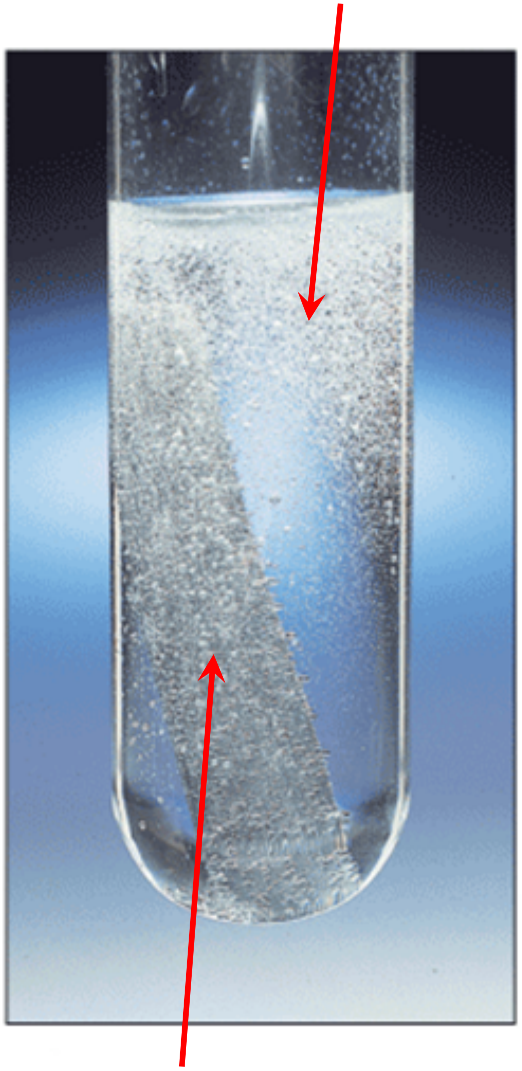
- the half-cell (i.e., the chemical reaction)
- the concentrations of reactant and products
- the pressure, for gaseous reactant/products
- the temperature

One can compare the voltage of a cell with different one at standard conditions :

- T= 298 K
- Solutes at 1 M and gases at 1 bar

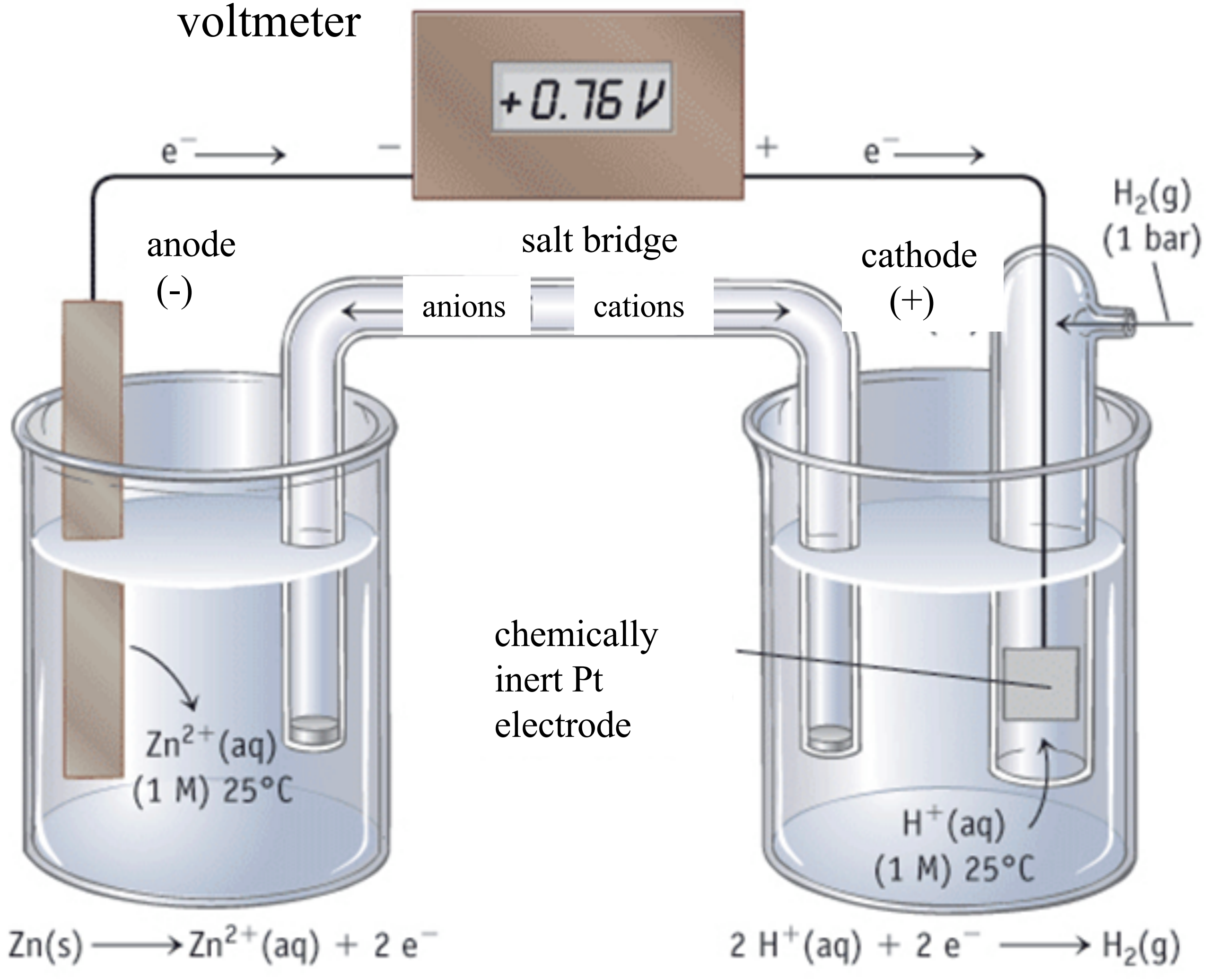
A potential mesured at standard conditions is called standard potential ΔE^0_{cell}

A battery under standard conditions



nascent H_2

Zn bar



voltmeter

anode

(-)

salt bridge

anions

cations

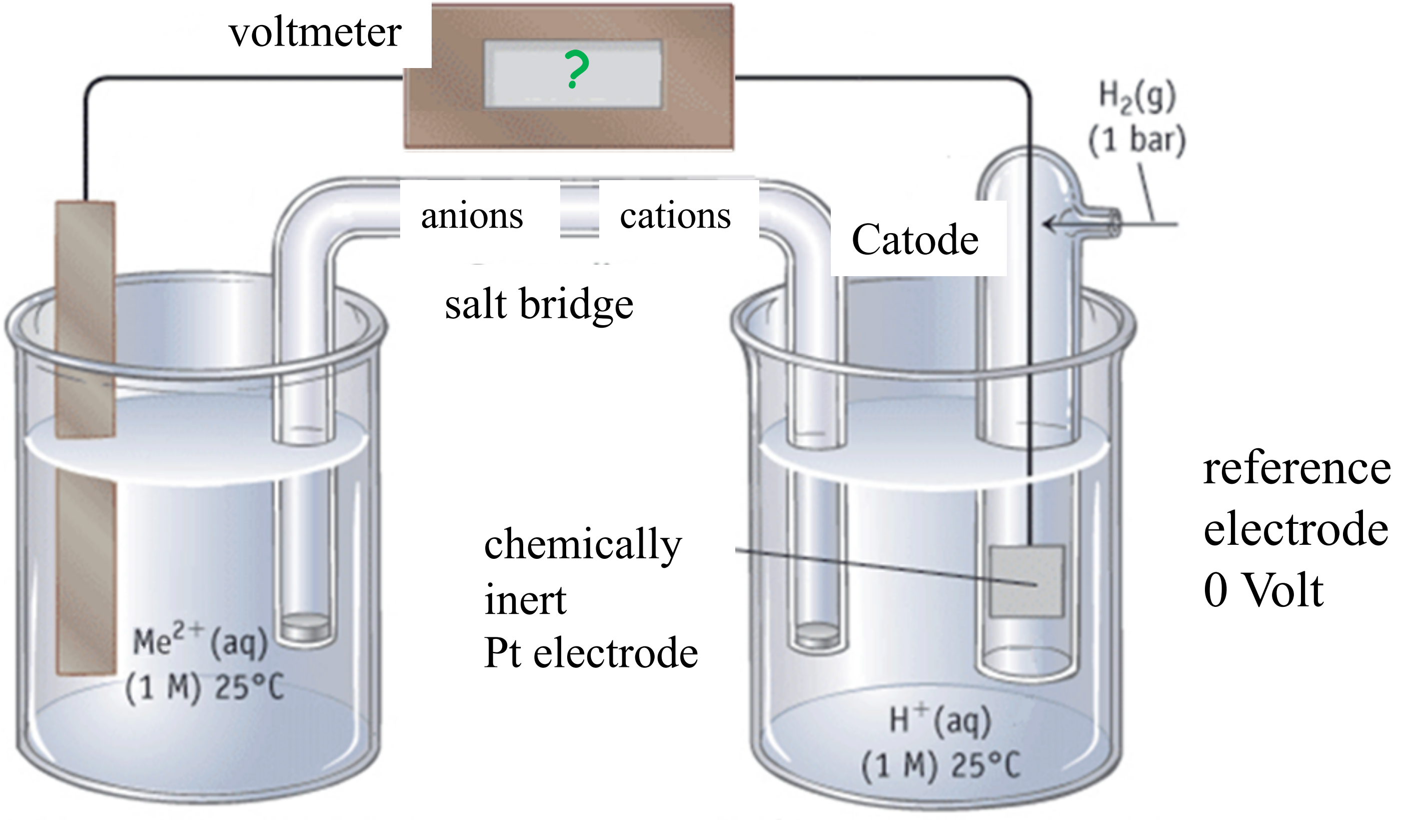
cathode

(+)

chemically inert Pt electrode

net reaction: $Zn(s) + 2\,H^+(aq) \longrightarrow H_2(g) + Zn^{2+}(aq)$

Let’s build a series of voltaic cells made with a hydrogen electrode and a metal (Me) electrode, both at standard conditions.



$Me \rightleftarrows Me^{2+} + 2\,e^-$

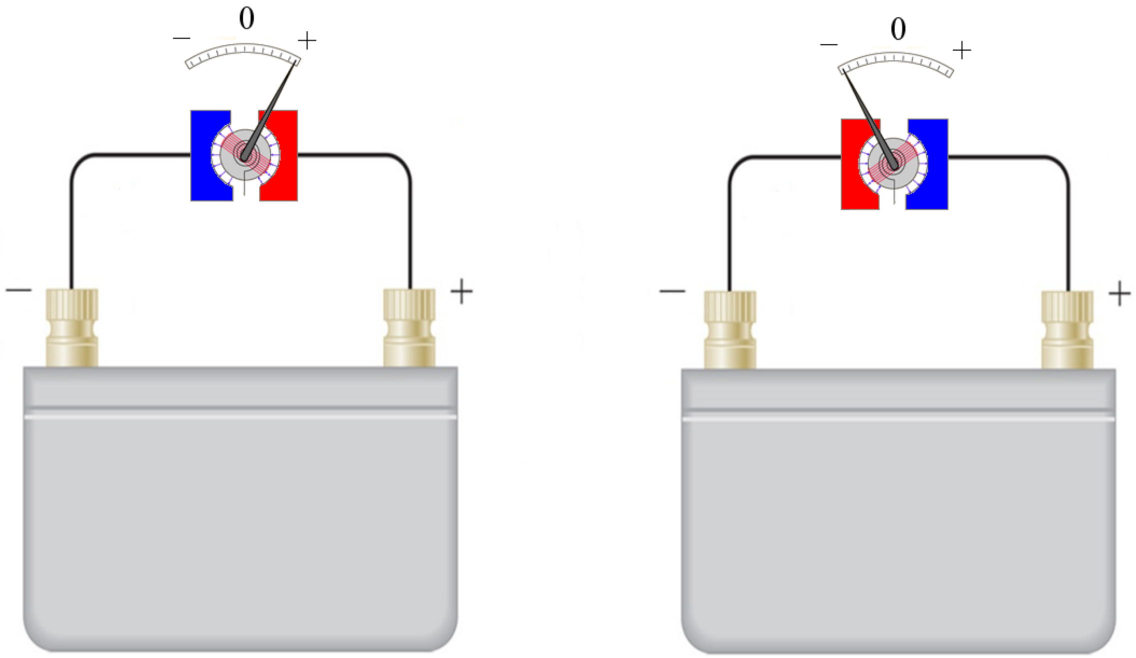
$H_2 \rightleftarrows 2\,H^+ + 2\,e^-$

What will be the reaction’s direction? Which electrode is the catode and which one is the anode?

What will be the reaction’s direction? Which one is the catode and which one is the anode?

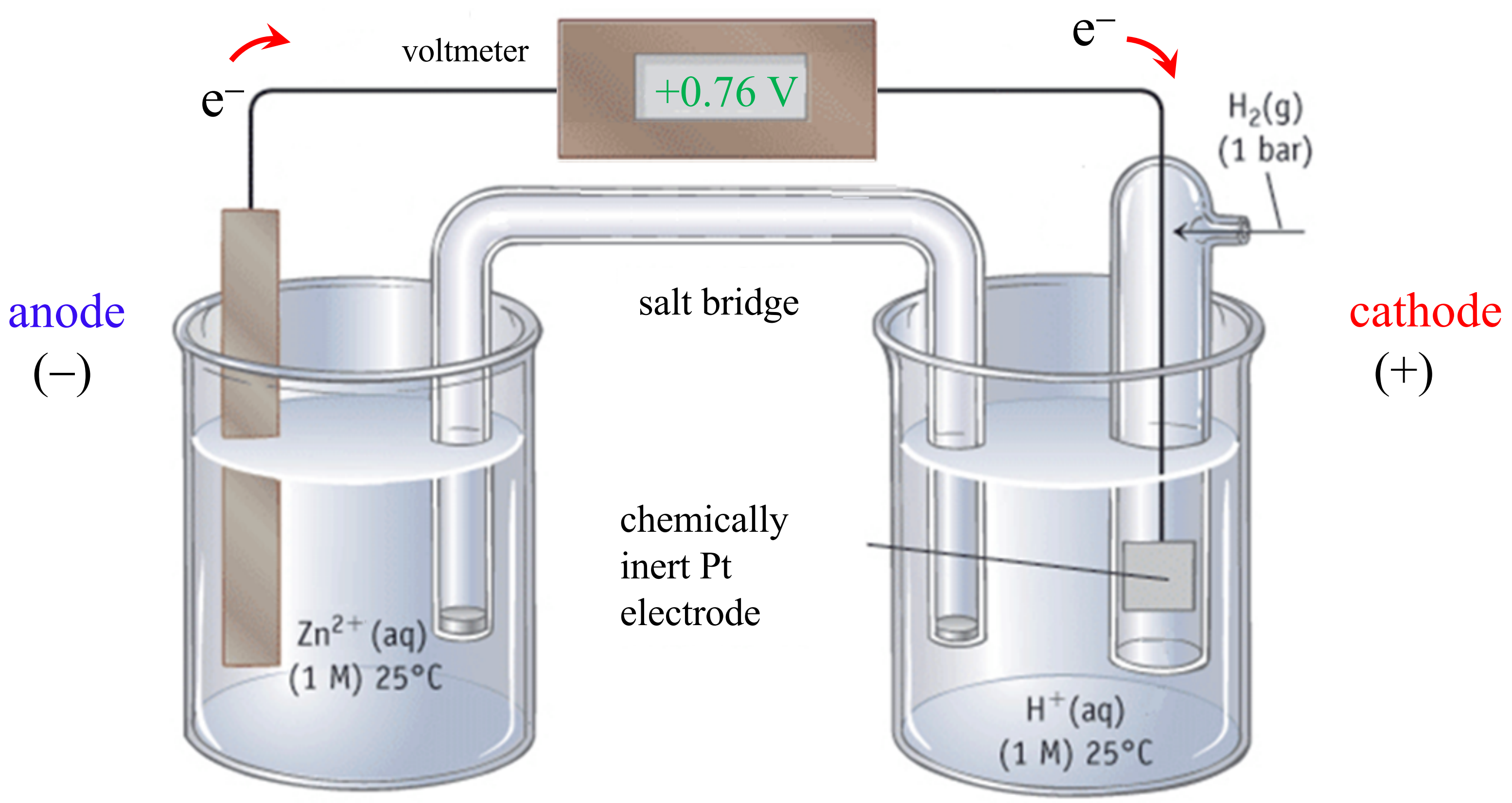
In a voltaic cell, electrons go from positive to negative, moving from anode to catode.

A voltmeter allows one to establish the flow direction.



We measure a positive potential if the positive terminal of the voltmeter is connected to the catode (and vice versa).

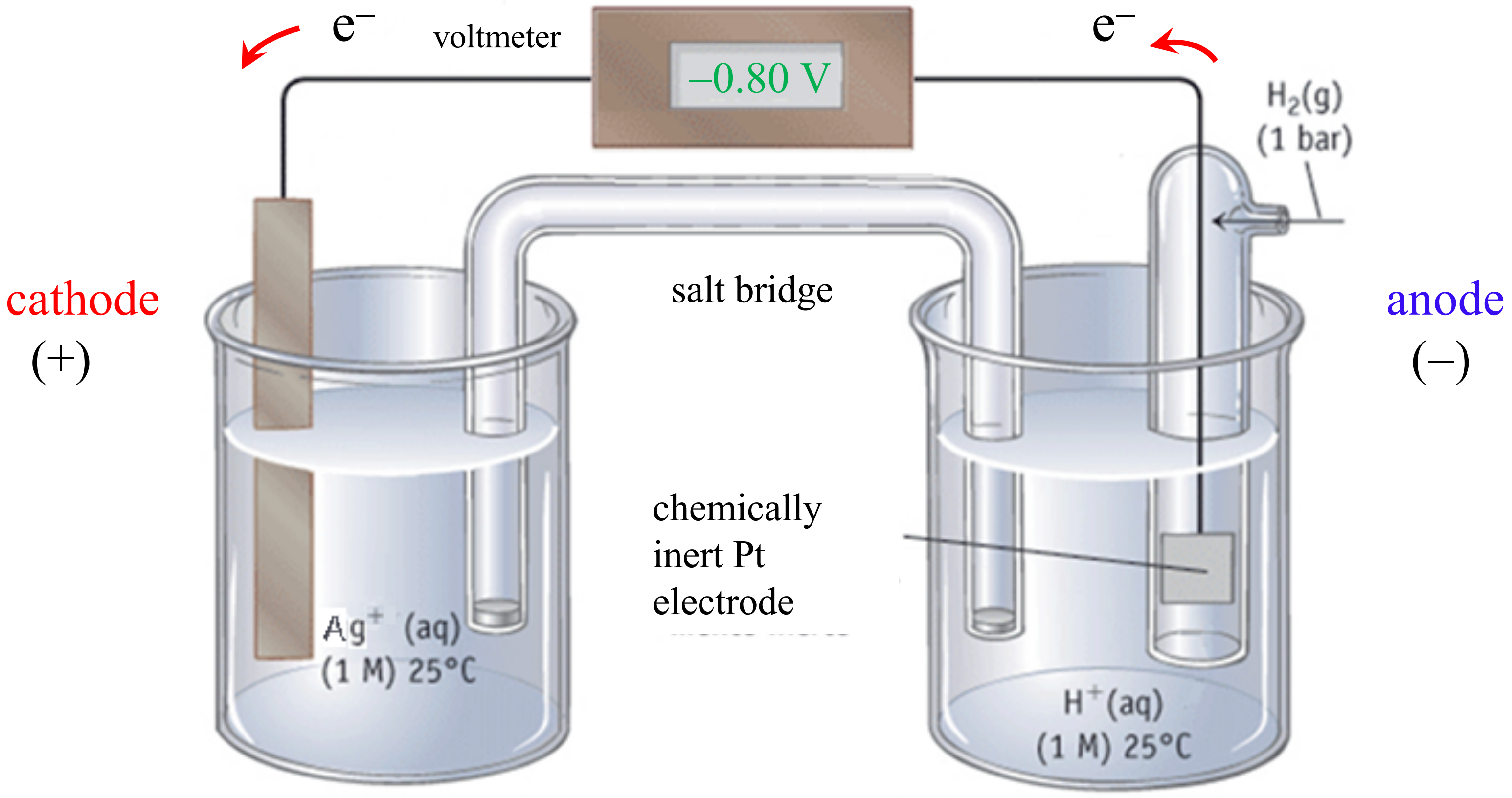
$$Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$$



left half-cell
$Zn \rightarrow Zn^{2+} + 2\,e^-$

right half-cell
$2\,H^+ + 2\,e^- \rightarrow H_2$

$$H_2 + 2\,Ag^+ \rightarrow 2\,H^+ + \;Ag$$



e^- voltmeter -0.80 V e^-

cathode

(+)

salt bridge

anode

(–)

chemically
inert Pt
electrode

left half-cell

$Ag \leftarrow Ag^+ + \; e^-$

right half-cell

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

Standard redox potentials

The efm ΔE^0_{cell} is defined as the difference of potential between half cells:

$$\Delta E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$E^0_{cathode}$ and E^0_{anode} are the standard redox potentials for the half reactions taking place at catode and anode

- knowing $E^0_{cathode}$ an E^0_{anode} one can calculate the standard redox potential ΔE^0_{cell} of a voltaic cell

- when ΔE^0_{cell} is positive the raction is spontaneous

Standard Reduction Potentials at 25°C

Stronger oxidizing agent

Weaker reducing agent

Reduction Half-Reaction		**E° (V)**
$F_2(g) + 2e^-$	$\longrightarrow 2\,F\,(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent

Stronger reducing agent

Standard redox potentials in aqueous solution at 25 °C

Growing oxidizing power

Reduction half-reaction	E^0 (V)
F_2 (g) + 2 e^- → F^- (aq)	2.87
O_3 (g) + 2 H^+ (aq) + 2 e^- → O_2 (g) + H_2O	2.07
H_2O_2 (aq) + 2 H^+ (aq) + 2 e^- → 2 H_2O	1.77
Cl_2 (g) + 2 e^- → 2 Cl^- (aq)	1.36
O_2 (g) + 4 H^+ (aq) + 4 e^- → 2 H_2O	1.23
Br_2 (l) + 2 e^- → 2 Br^- (aq)	1.07
NO_3^- (aq) + 4 H^+ (aq) + 3 e^- → NO (g) + 2 H_2O	0.96
Ag^+ (aq) + e^- → Ag (s)	0.8
Fe^{3+} (aq) + e^- → Fe^{2+} (aq)	0.77
O_2 (g) + 2 H^+ (aq) + 2 e^- → H_2O_2 (aq)	0.68
I_2(s) + 2 e^- → 2 I^- (aq)	0.53
Cu^{2+} (aq) + 2 e^- → Cu (s)	0.34
Cu^{2+} (aq) + e^- → Cu^+ (aq)	0.13
2 H^+ (aq) + 2 e^- → H_2 (g)	0
Pb^{2+} (aq) + 2 e^- → Pb (s)	–0.13
Ni^{2+} (aq) + 2 e^- → Ni (s)	–0.25
Co^{2+} (aq) + 2 e^- → Co (s)	–0.28
Cd^{2+} (aq) + 2 e^- → Cd (s)	–0.4
Fe^{2+} (aq) + 2 e^- → Fe (s)	–0.44
Zn^{2+} (aq) + 2 e^- → Zn (s)	–0.76
Mn^{2+} (aq) + 2 e^- → Mn (s)	–1.18
Al^{3+} (aq) + 3 e^- → Al (s)	–1.66
Mg^{2+} (aq) + 2 e^- → Mg (s)	–2.37
Na^+ (aq) + e^- → Na (s)	–2.71
Ca^{2+} (aq) + 2 e^- → Ca (s)	–2.87
Li^+ (aq) + e^- → Li (s)	–3.05

Growing reducing power

The Nernst equation

For all generic reversible electrodes, with a cation C^{z+} or an anion A^{z-}, in in a redox rection:

reduced species

$C\ (s) \rightleftarrows C^{z+}\ (aq) + z\ e^{-}$

oxidized species

reduced species

$A^{z-}\ (aq) \rightleftarrows A\ (s) + z\ e^{-}$

oxidized species

One can demonstrate that the half-cell potential is:

$$E = E^{0} + \frac{RT}{zF} ln \frac{[oxidized\ species]}{[reduced\ species]}$$

- R = universal gas constant (8.314 J $K^{-1}mol^{-1}$) (careful w/ units R)
- T = absolute temperature
- z = number of electrons transferred
- F = Faraday constant (96486 $Cxmol^{-1}$), charge of 1 mole of electrons

The Nernst law

Example 1: we prepare a Cu electrode in equilibrium with Cu(II) ions $[Cu^{2+}] = 0.1$ M, knowing that E° = 0.34 V a 25 ° C

$$Cu\,(s) \rightleftarrows Cu^{2+}\,(aq) + 2\,e^{-}$$

reduced species

oxidized species

$$E = E^0 + \frac{RT}{zF} ln \frac{[oxidized\ species]}{[reduced\ species]}$$

The electrode potential (compared to the reference hydrogen electrode)

$$E_{Cu/Cu^{2+}} = E^{o}_{Cu/Cu^{2+}} + \frac{RT}{2F}\ln[Cu^{2+}]$$

$$= 0.34 + \frac{8.314 \cdot 298}{2 \cdot 96487}\ln(0.1) = 0.31\ V$$

Now we build a Zn electrode in equilibrium with zinc at $[Zn^{2+}] = 0.1$ M, e knowing that E° = –0.76 V a 25 ° C

$$Zn\,(s) \rightleftarrows Zn^{2+}\,(aq) + 2\,e^-$$

The electrode potential (compared to the reference hydrogen electrode)

$$E_{Zn/Zn^{2+}} = E^{o}_{Zn/Zn^{2+}} + \frac{RT}{2F}\ln[Zn^{2+}]$$

$$= -0.76 + \frac{8.314 \cdot 298}{2 \cdot 96487}\ln(0.1) = -0.79\ \mathrm{V}$$

In the cell: $Zn\,(s)\,|\,Zn^{2+}\,(aq)\,||\,Cu^{2+}\,(aq)\,|\,Cu\,(s)$ the emf is :

$$\Delta E_{cell} = E_{Cu/Cu^{2+}} - E_{Zn/Zn^{2+}} = 0.31 - (-0.79) = 1.1\ \mathrm{V}$$

Example 2: a voltaic cell is:

Half cell a: $Al\,(s)\,|\,Al^{3+}\,(aq)$ (0.001 M)
Half cell b: $Ni\,(s)\,|\,Ni^{2+}\,(aq)$ (0.5 M)

Calculate the cell potential.

First of all, determine which metal is oxidized (Al o Ni). From the standard potential table 25 ° C one can see that:

$$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni\,(s) \quad E° = -0.26\ V \quad e$$
$$Al^{3+}(aq) + 3\,e^- \rightarrow Al\,(s) \quad E° = -1.66\ V$$

Al is a stronger reducing agent than Ni (Ni^{2+} is a better oxidizing agent than Ni^{2+}). Therefore:

anode (oxidation): $Al\,(s) \rightarrow Al^{3+}(aq) + 3\,e^-$
catode (reduction): $Ni^{2+}(aq) + 2\,e^- \rightarrow Ni\,(s)$

Net ionic equation: $2\,Al\,(s) + 3\,Ni^{2+}(aq) \rightleftarrows 2\,Al^{3+}(aq) + 3\,Ni\,(s)$

In standard conditions the emf is:

$$\Delta E°_{cell} = E°_{catode} - E°_{anode} = (-0.20) - (1.66) = 1.46\ V$$

Standard Reduction Potentials at 25°C

Stronger oxidizing agent

Weaker reducing agent

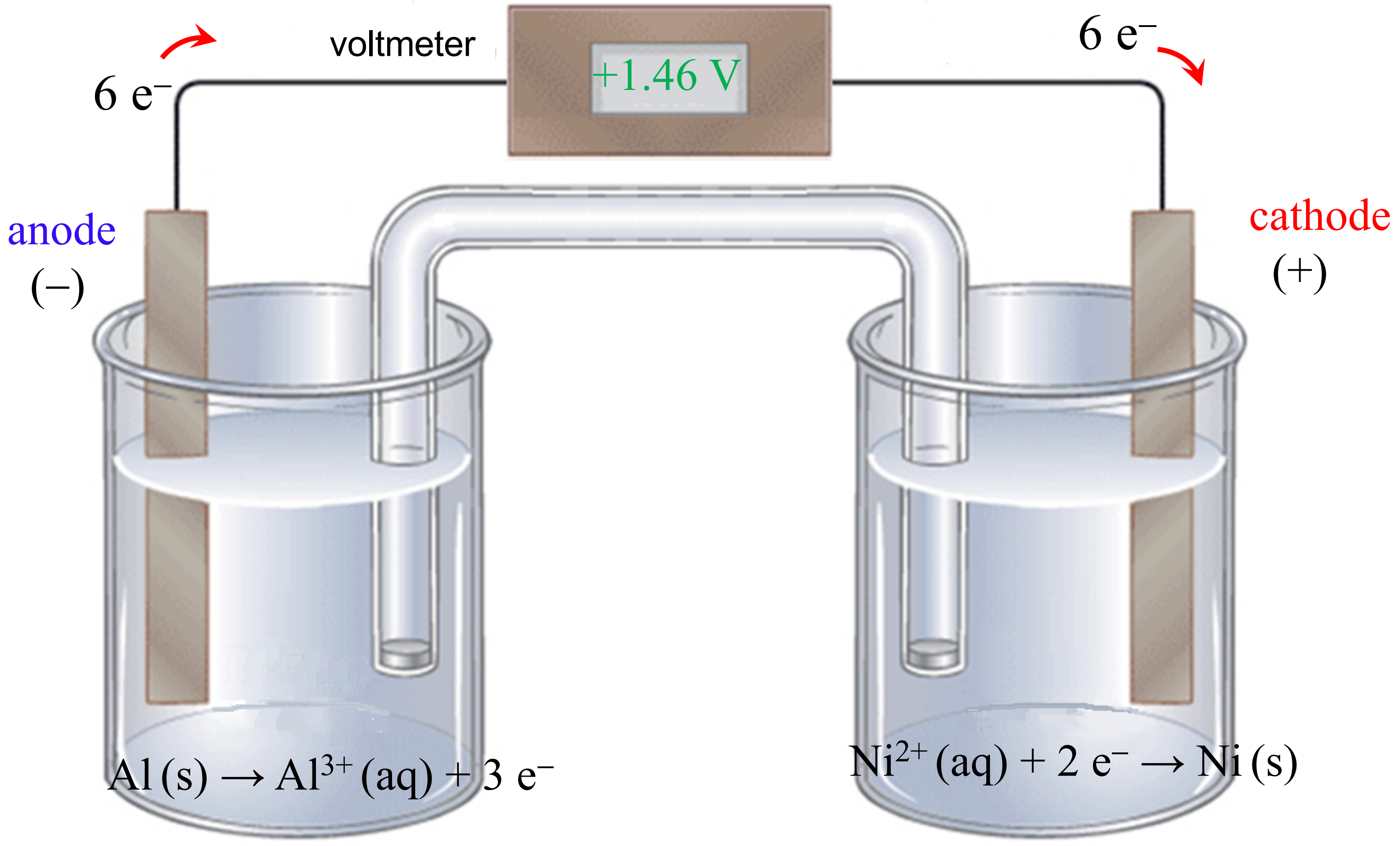
Reduction Half-Reaction		**E° (V)**
$F_2(g) + 2e^-$	$\longrightarrow 2F(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Weaker oxidizing agent

Stronger reducing agent

$Al\,(s)\,|\,Al^{3+}\,(aq)\,(0.001\ M)\,||\,Ni^{2+}\,(aq)\,(0.5\ M)\,|\,Ni\,(s)$

$$\Delta E_{cell} = \Delta E^{0}_{cell} + \frac{RT}{nF}\ln\frac{[Ni^{2+}]^{3}}{[Al^{3+}]^{2}} = 1.41 + \frac{8.314\cdot 298}{6\cdot 96487}\ln\frac{0.5^{3}}{0.001^{2}} = 1.46\ V$$



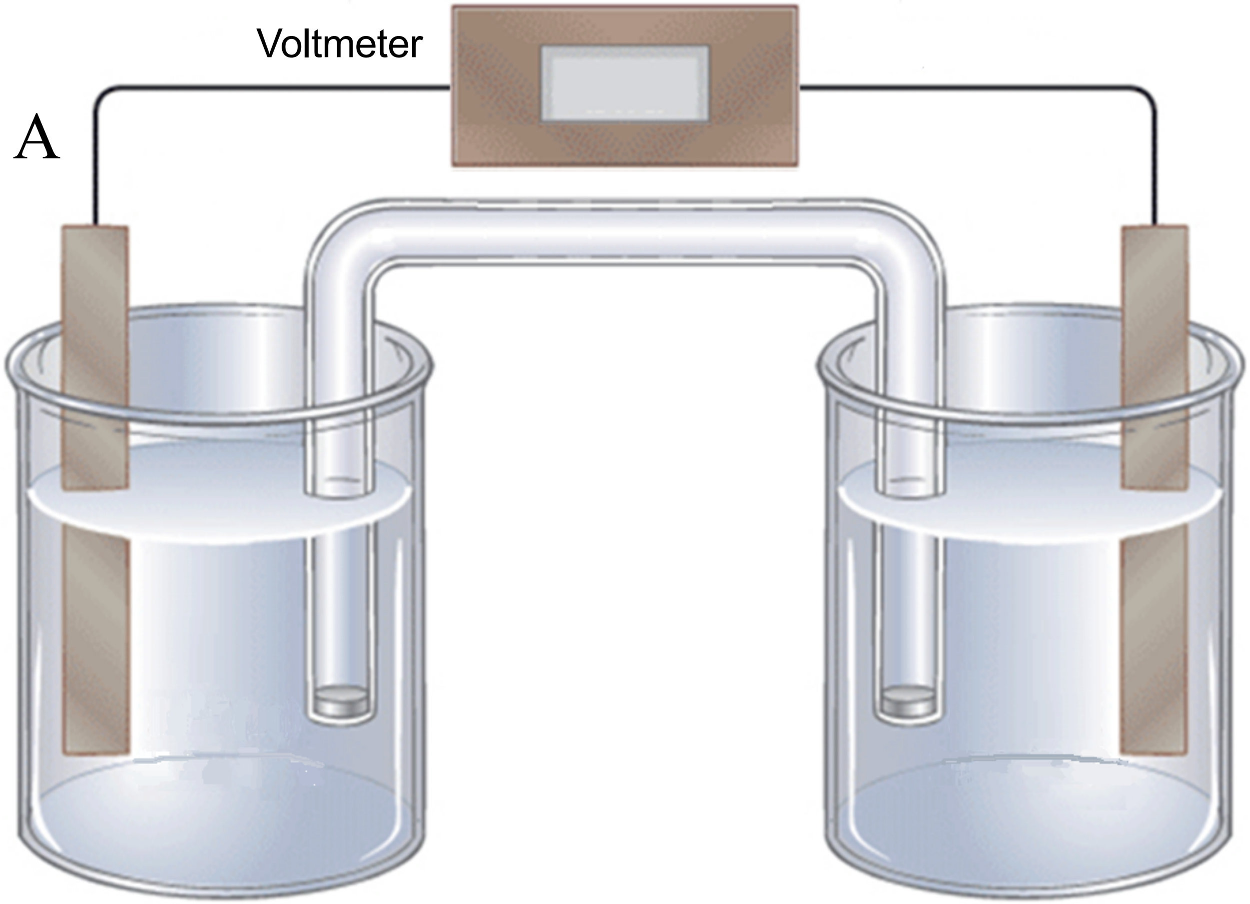
$Al\,(s) \rightarrow Al^{3+}\,(aq) + 3\ e^{-}$

$Ni^{2+}\,(aq) + 2\ e^{-} \rightarrow Ni\,(s)$

$$2\ Al\,(s) + 3\ Ni^{2+}\,(aq) \rightleftarrows 2\ Al^{3+}\,(aq) + 3\ Ni\,(s)$$

Concentration cell

In this voltaic cell, made up by two identic electrodes, the emf is due to a difference in concentration of the same ion dissolved in the half cells



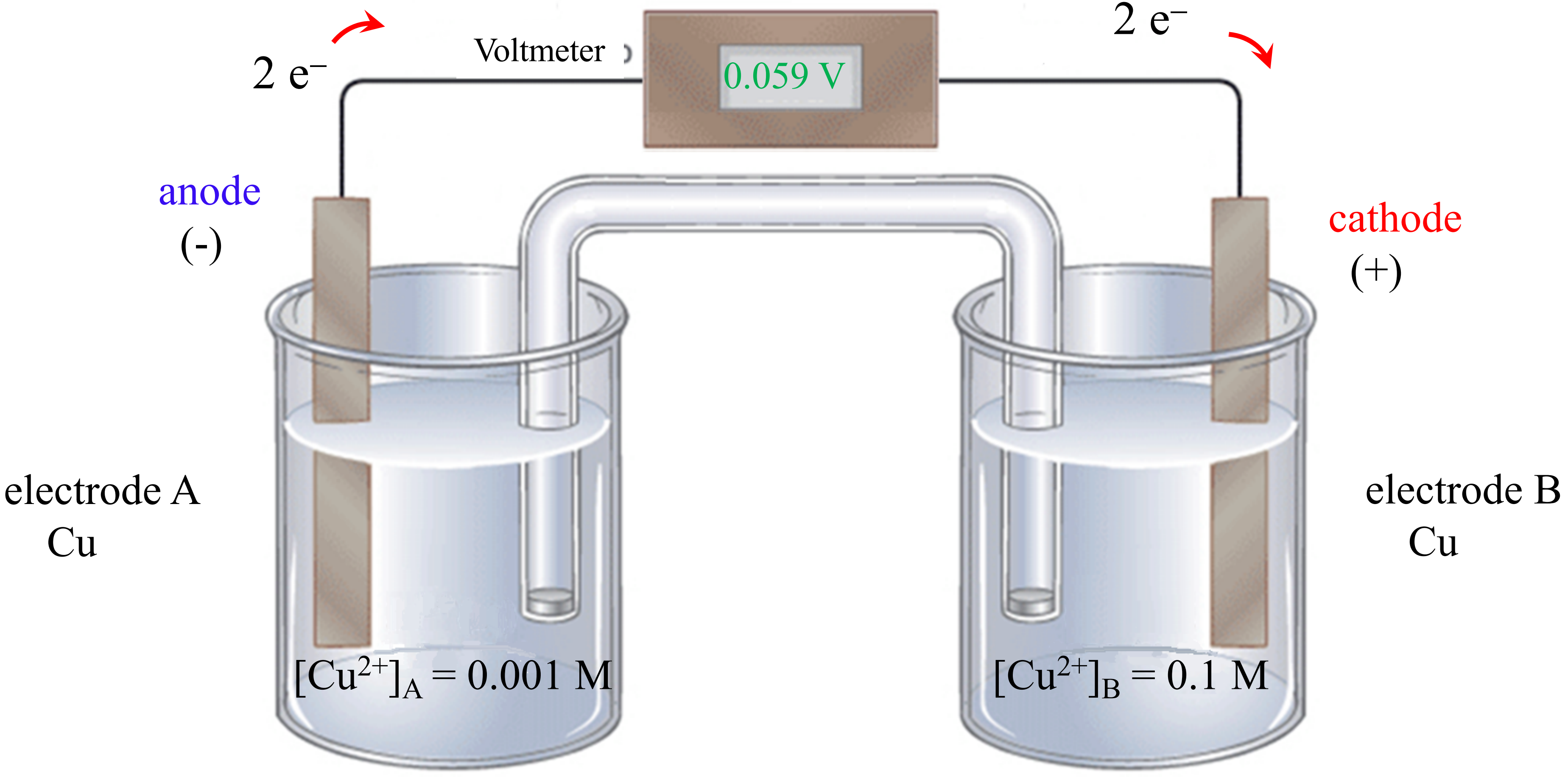
electrode A
Cu

electrode B
Cu

$[Cu^{2+}] = 0.001$ M

$[Cu^{2+}] = 0.1$ M

The current flows from the electrode with the lower concentration toward the one with the higher concentration

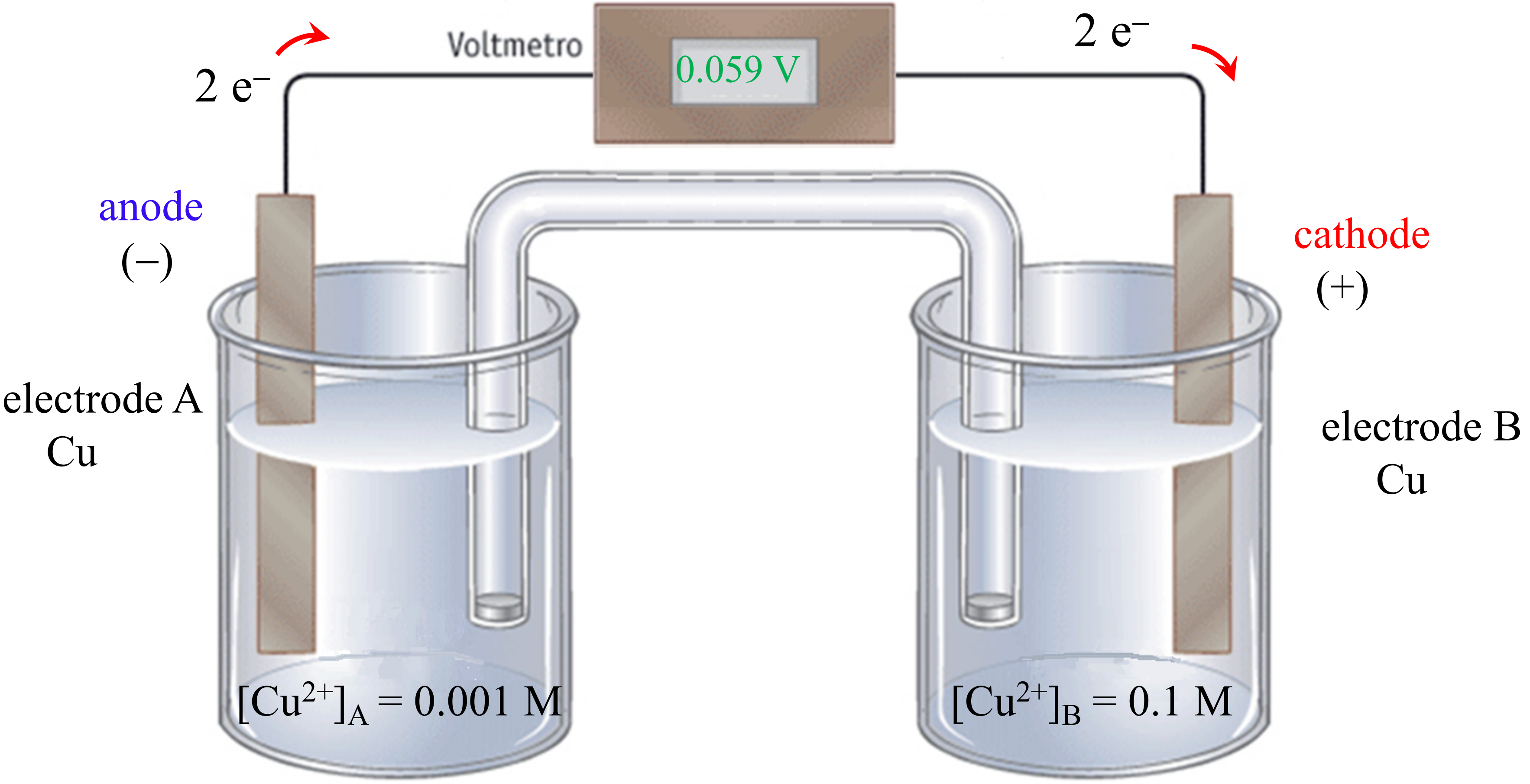


$Cu \rightarrow Cu^{2+} + 2\,e^-$ $\qquad$ $Cu^{2+} + 2\,e^- \rightarrow Cu$

$$E_A = E_A^o + \frac{RT}{2F}\ln[Cu^{2+}]_A \qquad E_B = E_B^o + \frac{RT}{2F}\ln[Cu^{2+}]_B \qquad !! \quad E_A^o = E_B^o$$

$$\Delta E_{cell} = E_B - E_A = \frac{RT}{2F}\ln\frac{[Cu^{2+}]_B}{[Cu^{2+}]_A} = \frac{8.314\cdot 298}{6\cdot 96487}\ln\frac{0.1}{0.001} = 0.059\ \text{V}$$

The current flows through the external circuit from the low concentration half-cell to the high concentration half-cell



$Cu \rightarrow Cu^{2+} + 2\ e^-$ $\quad\quad$ $Cu^{2+} + 2\ e^- \rightarrow Cu$

$$E_A = E^o_A + \frac{RT}{2F}\ln[Cu^{2+}]_A \quad E_B = E^o_B + \frac{RT}{2F}\ln[Cu^{2+}]_B \quad !! \quad E^o_A = E^o_B$$

$$\Delta E_{cell} = E_B - E_A = \frac{RT}{2F}\ln\frac{[Cu^{2+}]_B}{[Cu^{2+}]_A} = \frac{8.314\,298}{6\cdot 96487}\ln\frac{0.1}{0.001} = 0.059V$$

A relevant application of the concentration electrode: the pHmeter

Relationship between emf and the equilibrium constant K

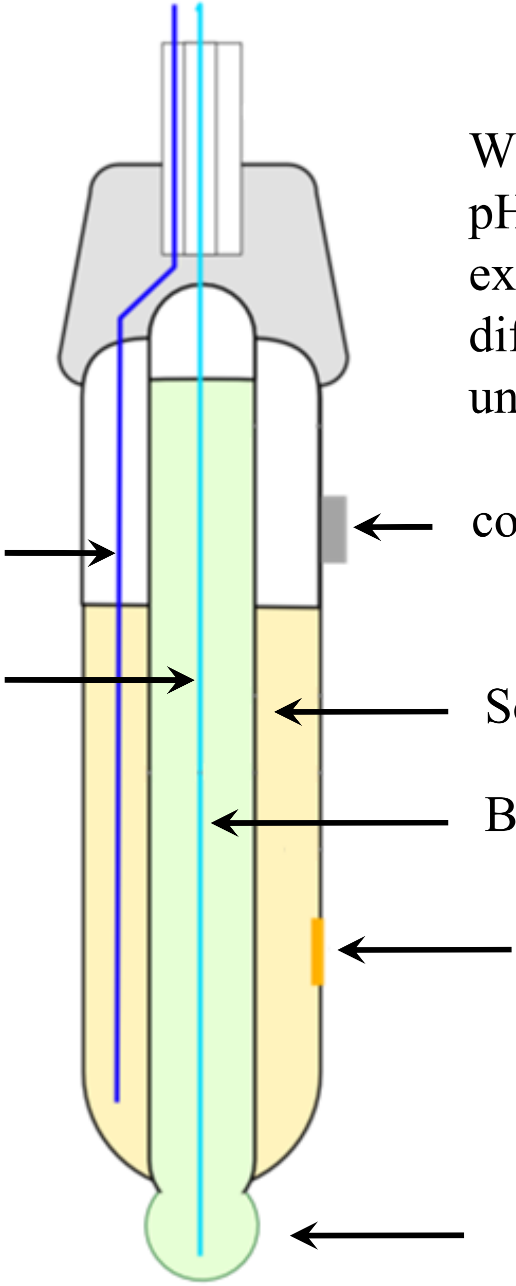
Using thermodynamics it is possible to demonstrate that the free energy change of a reaction is equal to the maximum useful work that that reaction can produce at T and P constants. This corresponds the the electric work produced by a cell, and referring to reagents and products in standard conditions:

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o}$$

If we know the standard potential we can determine the equilibrium constant of the redox reaction.

$$\Delta G^{o} = -z \cdot F \cdot \Delta E^{o} = -RT \ln K_{EQ}$$

The glass electrode consists of a glass tube covered with an outer tube containing a silver wire.



When the electrode is immersed in a solution with an unknown pH value, a potential difference is generated between the external and internal hydrogen solution. The value of this difference depends only on the concentration of H^+ ions of the unknown solution.

Ag (s)

Ag (s)

cork

Solution of KCl (aq) + AgCl (s) (reference electrode)

Buffered solution+ KCl (aq) + AgCl (s) (measuring electrode)

porous diaphragm that acts as a salt bridge

thin glass membrane(SiO_2 72%, Na_2O 22% , CaO 6%):
pH-sensitive part