Redox Reactions

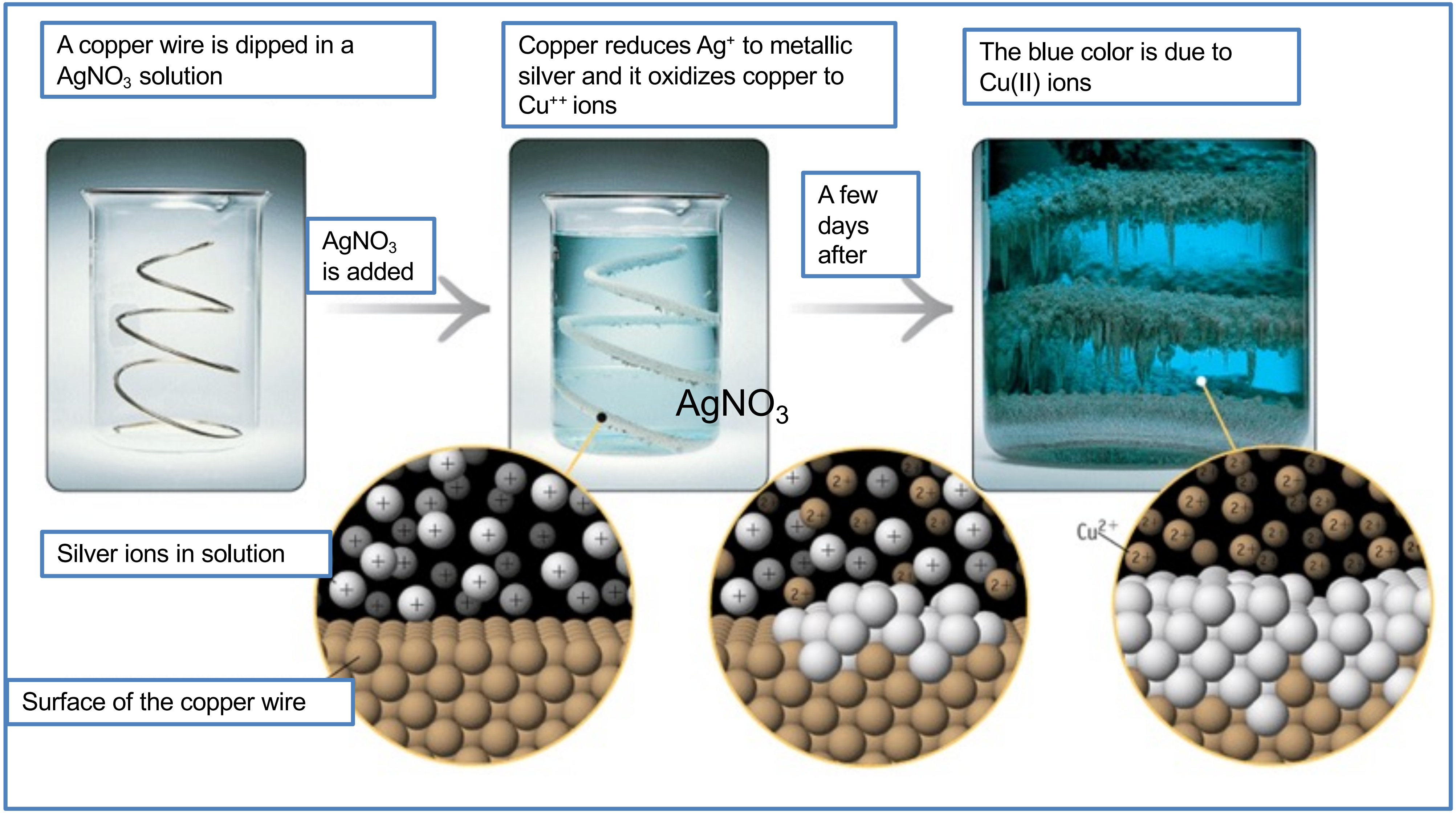
Luigi Galvani
(1737 – 1798)

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

RedOx Reactions



A copper wire is dipped in a $AgNO_3$ solution

$AgNO_3$ is added

Copper reduces Ag^+ to metallic silver and it oxidizes copper to Cu^{++} ions

A few days after

The blue color is due to Cu(II) ions

Silver ions in solution

Surface of the copper wire

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

Redox Reactions

In a redox reaction there is an electron transfer between a reducing agent and an oxidizing agent. The essential characteristics of all redox reactions are as follows:

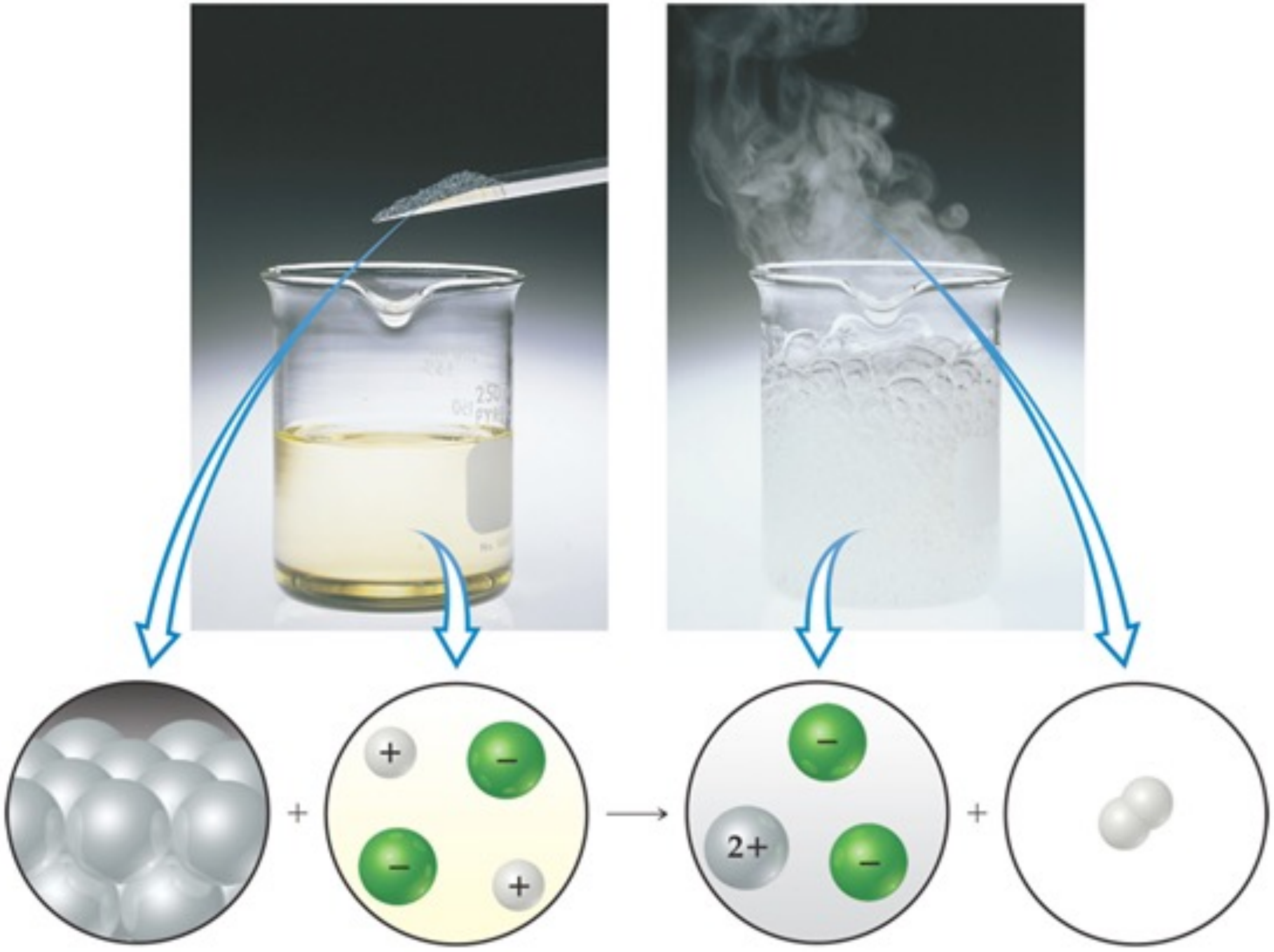
- A reactant is oxidized and the other is reduced
- The oxidation and reduction reactions have to be balanced
- The oxidizing agent (the chemical species that causes oxidation) **is reduced**
- The reducing agent (the chemical causing the reduction) **is oxidized**
- To determine if a substance is oxidized or reduced, oxidation numbers are used
  oxidation: an element is oxidized if its oxidation number increases,
  and it is reduced if its oxidation number decreases

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

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

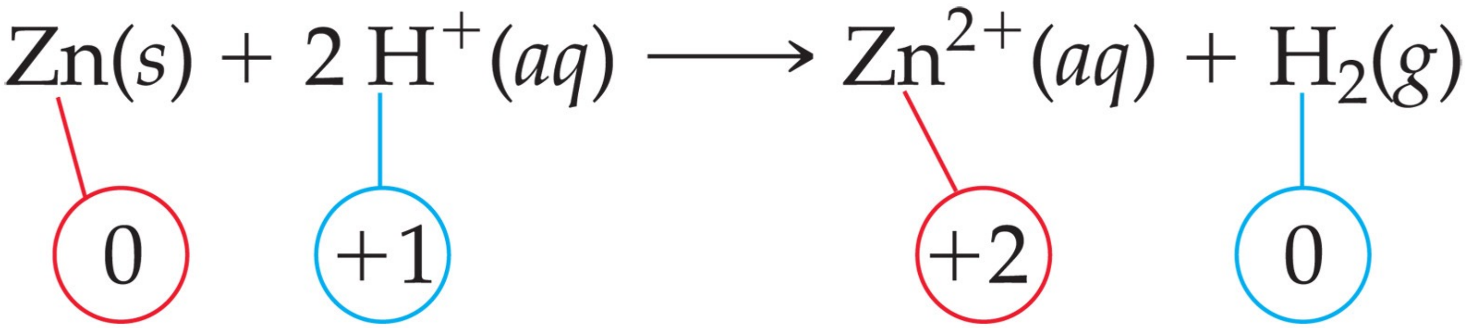
Ag^{+} is reduced, its oxidation number decreses. Ag^{+} is the oxidizing agent

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



Zn (s) HCl (aq) $ZnCl_2$ (aq) H_2 (g)

Oxidation and reduction



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

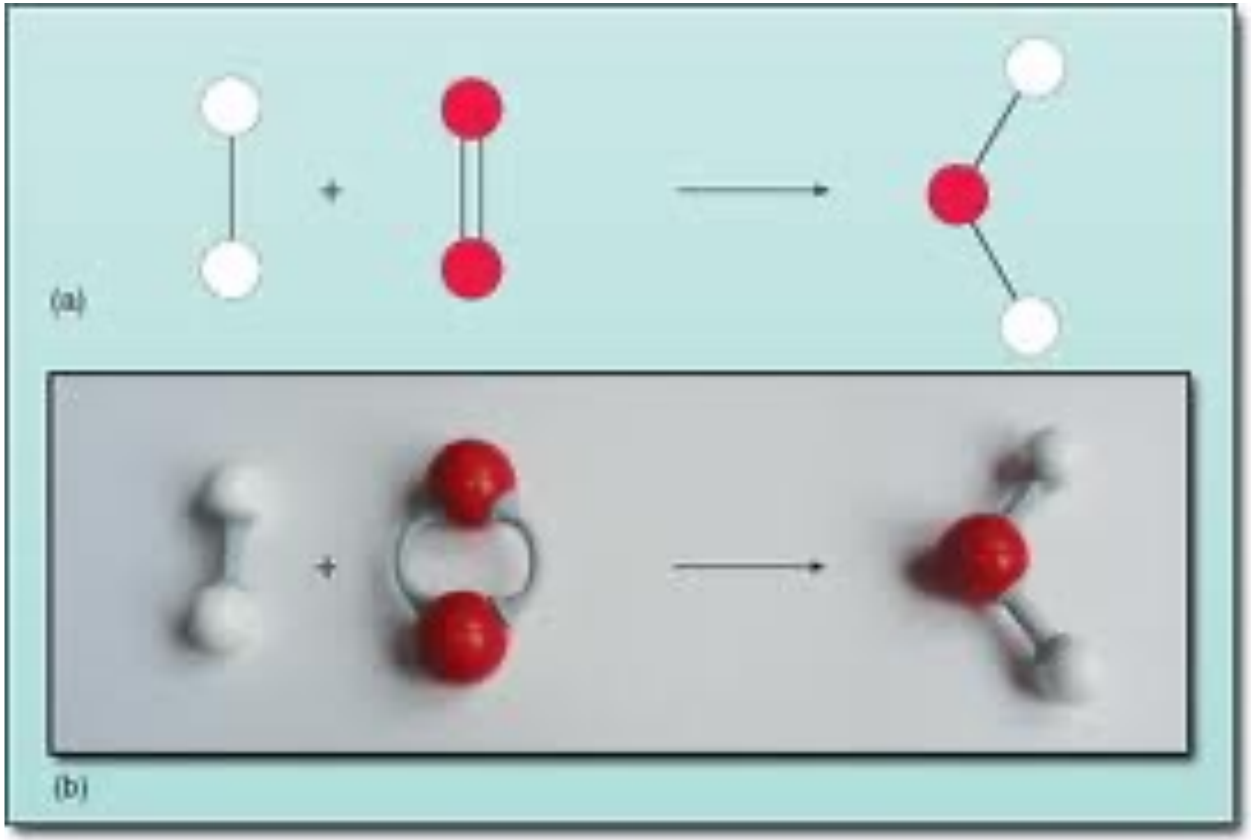
- The species is oxidized when it loses electrons
  - Zinc loses 2 electrond $Zn \longrightarrow Zn^{2+} + 2\,e^{-}$

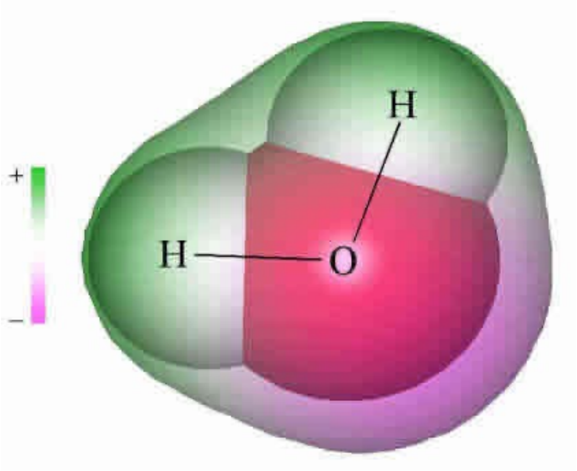
- A species is reduced when it acquires electrons
  - Each of the H^{+} gains one electron and they combine to yield H_2

$$2\,H^{+} + 2\,e^{-} \longrightarrow H_2$$

- the species that is reduced is called oxidizing agent
  - H^{+} oxidizes Zn by acquiring is electrons
- the species that is oxidised is called reducing agent
  - Zn reduces H^{+} by donating electrons

Even though if no ions are formed, moving the e^- toward one of the atoms, makes the process a redox reaction





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 are the same as those consumed in the reduction.

Semireactions method

The reduction and oxidation processes "the semireactions", are written separately and are balanced (mass + charge). Eg. In 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:

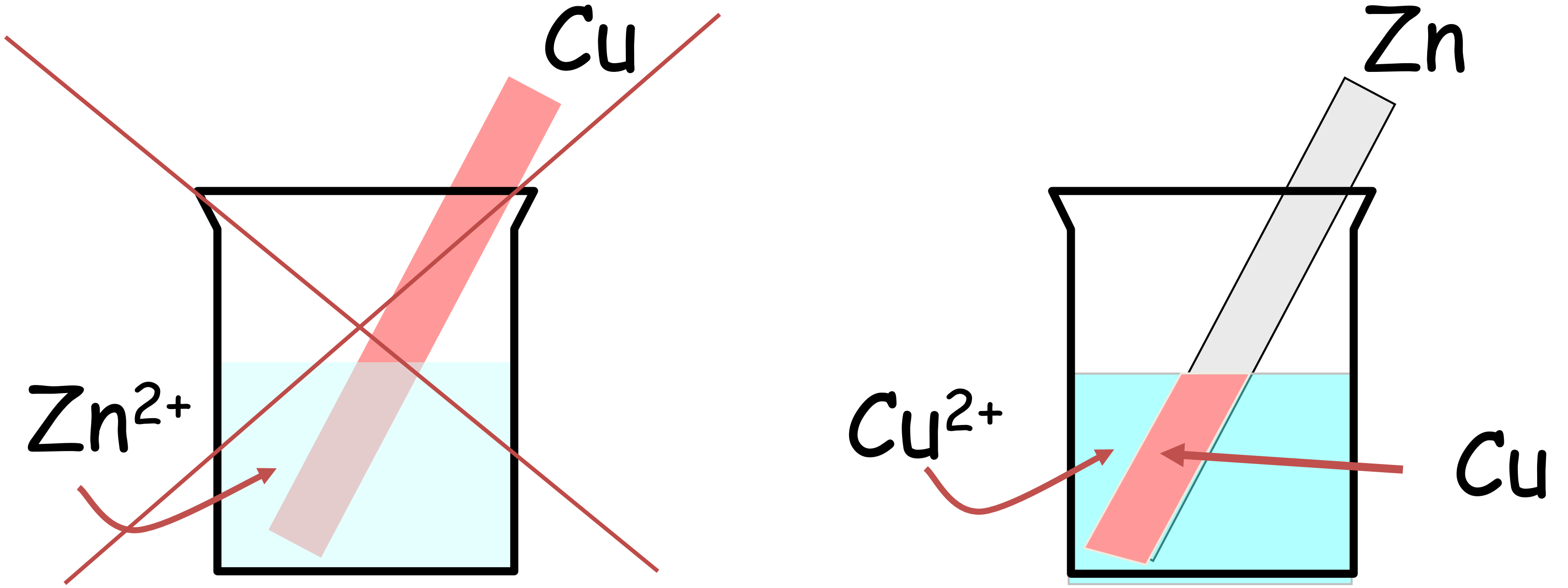
$$\begin{array}{r}
2\ Ag^+ (aq) + \cancel{2}\ e^- \rightarrow 2\ Ag (s) \\
Cu (s) \rightarrow Cu^{2+} (aq) + \cancel{2}\ e^- \\
\hdashline
Cu (s) + 2\ Ag^+ (aq) \rightarrow Cu^{2+} (aq) + 2\ Ag (s)
\end{array}$$

Lets consider the two possible reactions:

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

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

Electronegativity
Zn = 1.6
Cu = 1.9



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.

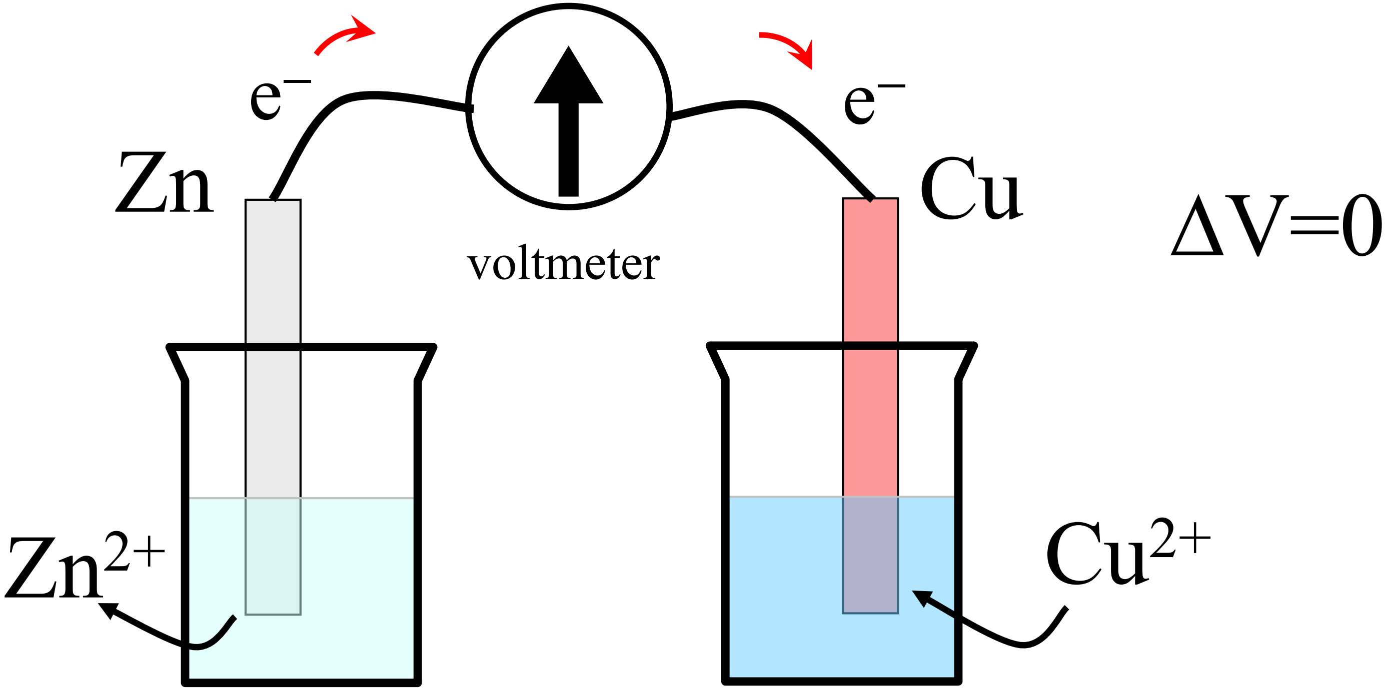
How can we build a battery?

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

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.

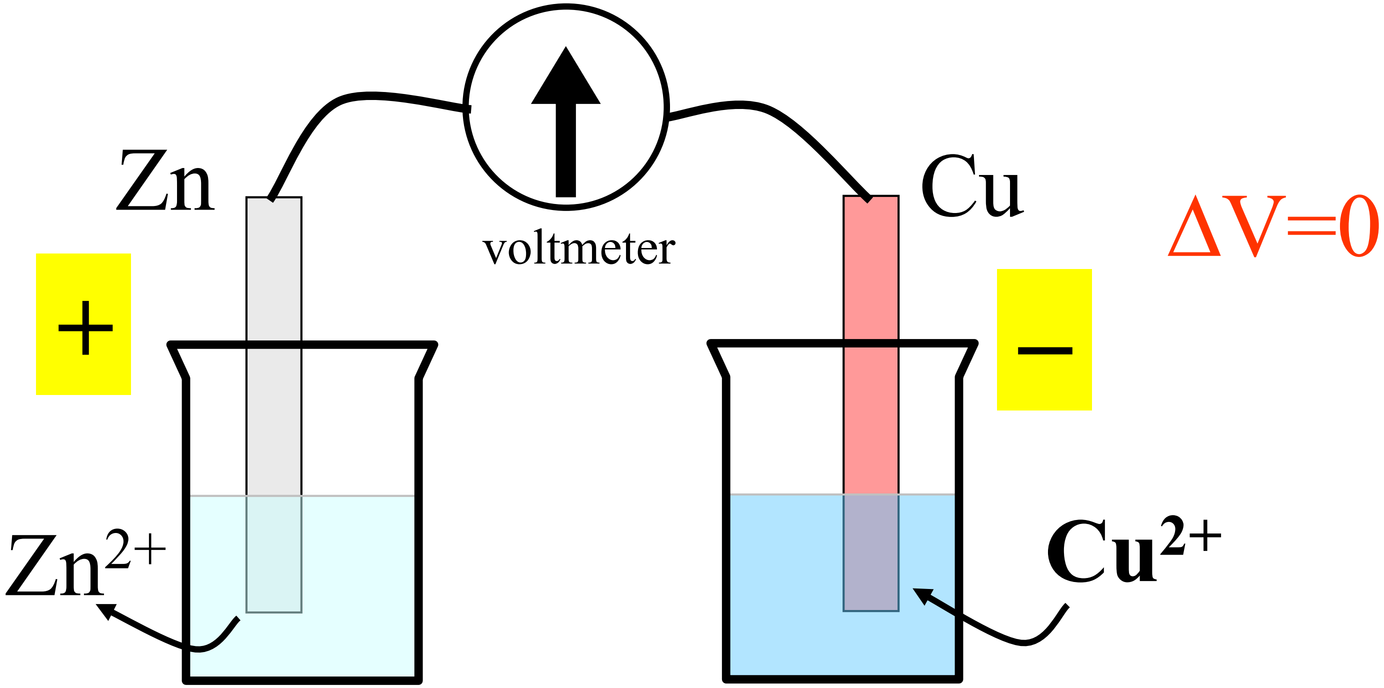


$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

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 reestablished, a + charge is built to the left and a - charge is built to the left
This blocks further transfer of elecrons

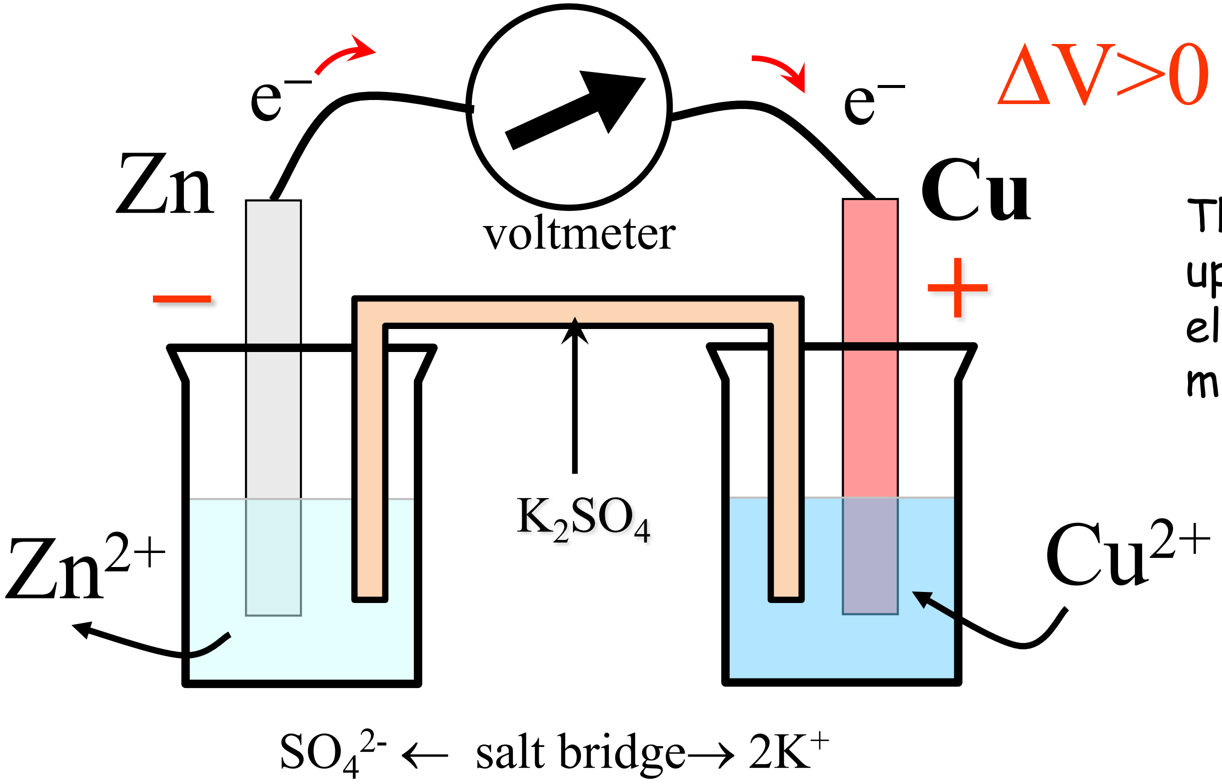


$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

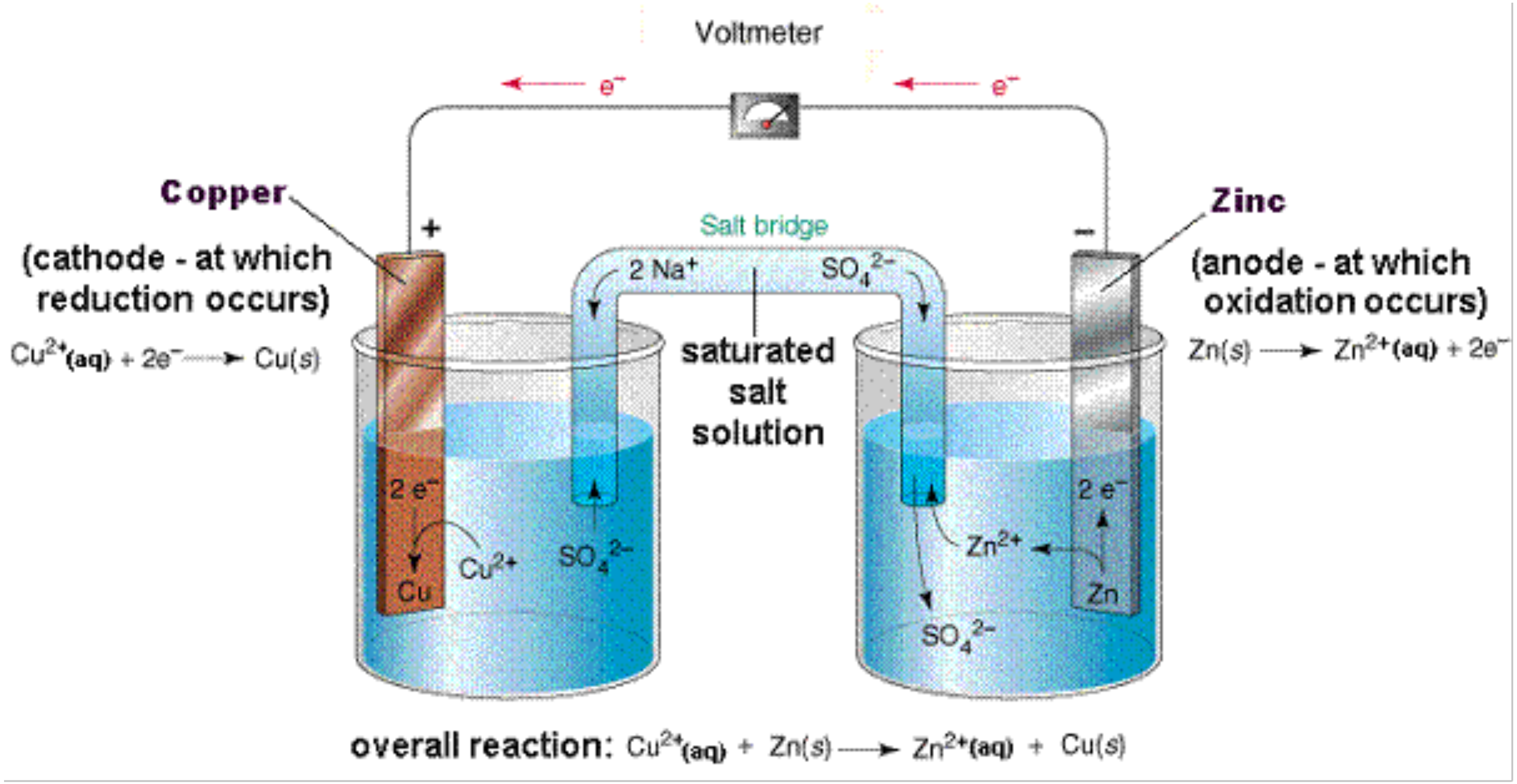
Oxidation $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$

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 generally made up by a tube containing an electrolyte in a gel to prevent mixing of the two solutions.

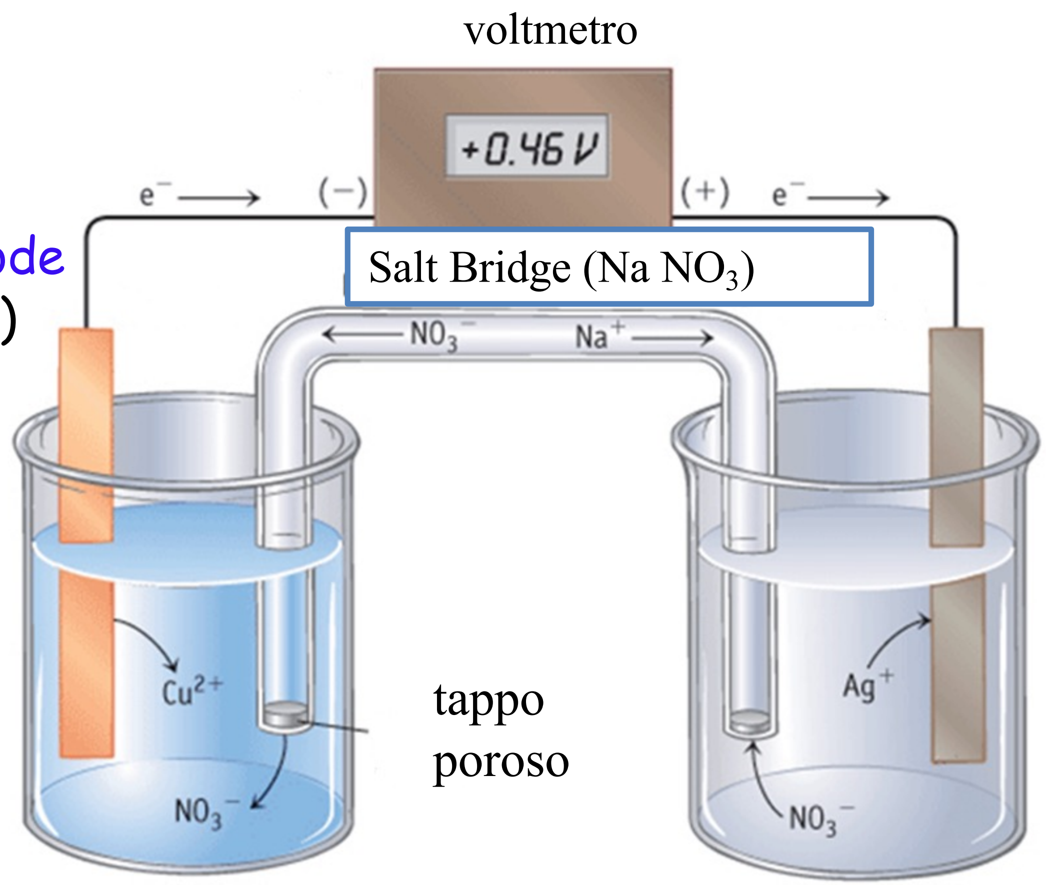

Voltmeter
e^-
e^-
Copper
(cathode - at which reduction occurs)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
+
Salt bridge
2 Na^+
SO_4^{2-}
saturated salt solution
–
Zinc
(anode - at which oxidation occurs)
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
2 e^-
Cu
Cu^{2+}
SO_4^{2-}
Zn^{2+}
2 e^-
Zn
SO_4^{2-}
overall reaction: $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$

A voltaic cell consists of two containers where the semireactions take place: (1) Zn rod in a Zn^{2+} solution; (2) Cu rod in a solution of Cu^{2+}.

To allow the redox reaction we need two connections
- Electric connection for electrons
- Ionic connection by means of the salt bridge

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^+).

Definition: anode the electrode where oxidation takes place and catode the electrode where reduction takes place. In a voltaic cell eletrons move from anode to catode, the anode is negative and the catode is positive.



voltmetro

anode
(-)

Salt Bridge (Na NO_3)

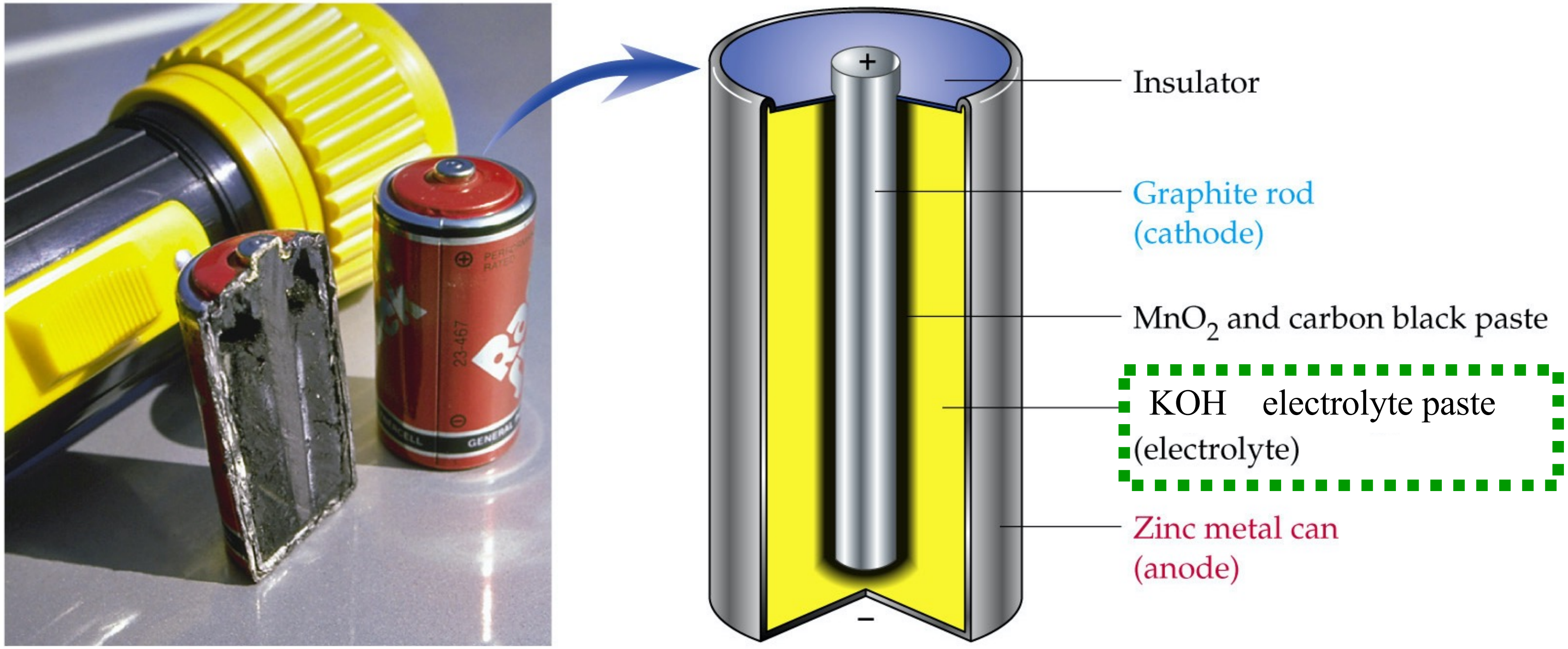
catode
(+)

tappo
poroso

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

Reaction in the cell: Cu (s) + 2 Ag^+ (aq) $\rightarrow$ Cu^{2+} (aq) + 2 Ag (s)

Alcaline battery (common, manganese-zinc)



anode cathode

$$\mathrm{Zn} \;\Big|\; \mathrm{Zn}^{++} \;\Big\|\; \mathrm{Mn}^{++}, \mathrm{Mn} \;\Big|\; \text{graphite}$$

$E'_0 = -\ 0.76\ \mathrm{V}$ $E'_0 = +\ 1.51\ \mathrm{V}$

$\Delta E = 1.51 - (-\ 0.76) = 2.27\ \mathrm{V}$

The two half-reactions are:

•Anode (oxidation reaction), negatively charged electrode because accepting e^- from the reductant in the cell:

$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$ (E° ox = +1.28 V)

•Cathode (reduction reaction), positively charged electrode because giving e^- to the oxidizer in the cell:

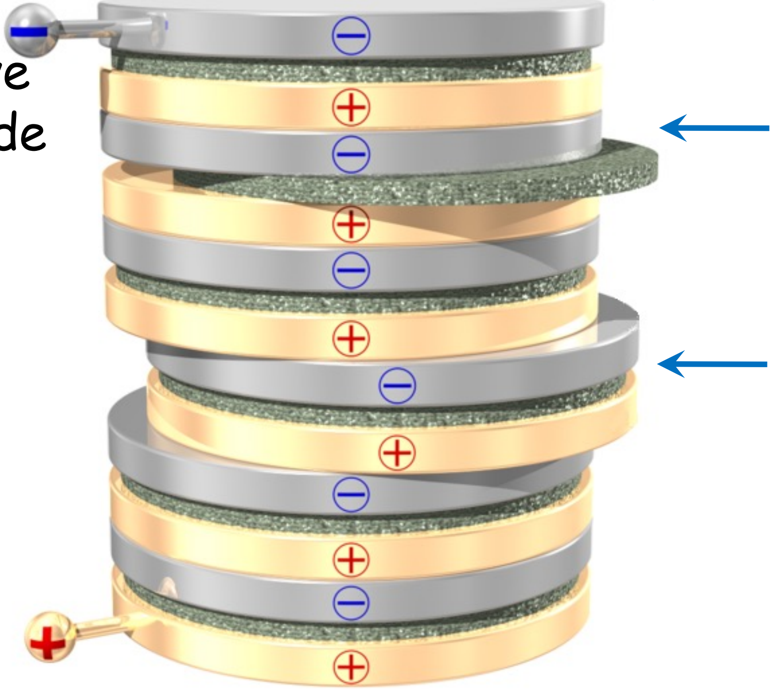
$2MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow 2MnO(OH)(s) + 2OH^-(aq)$

•The overall reaction (sum of anodic and cathodic reactions) is:

Zn(s) + 2MnO2(s) <-> ZnO(s) + Mn2O3(s)

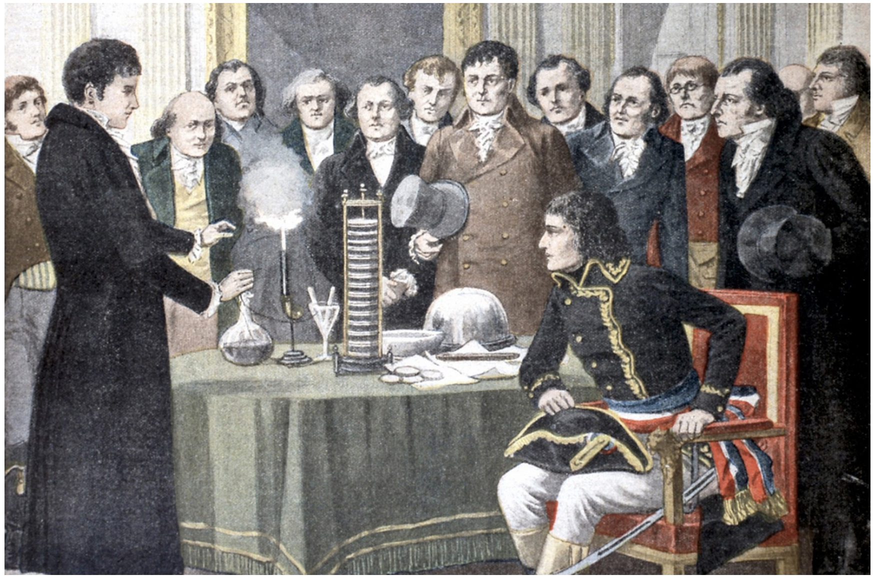
($E°_{cell} = E°_{ox} + E°_{red}$ = nominally +1.5 V)

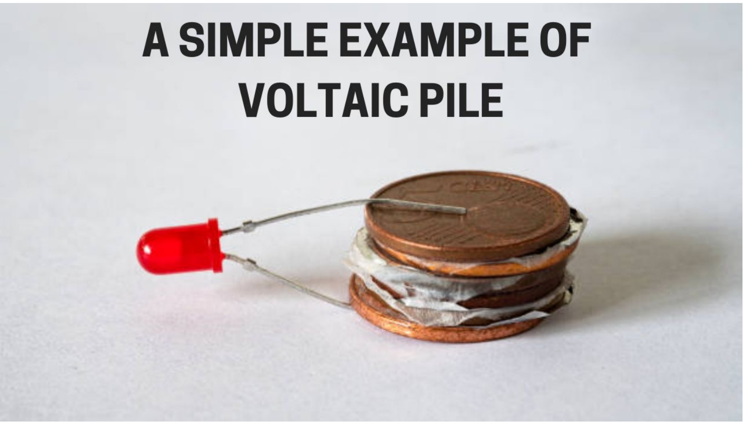
The Volta battery (pila=stack) consists basically of multiple superimposed elements, called voltaic elements, each of which is made of a Zn (or Sn) disk superimposed on one of Cu (or Ag), joined by a layer of felt or cardboard, soaked in salt or acidified H_2O.
By connecting the upper and lower ends of the battery by means of an electric conductor, a circuit is generated in which a current passes.



Volta' battery
(1799)

Between the two metal electrodes of each cell there is a difference of potential that is maintained by chemical forces. In fact, each electrode tends to release positive metal ions in the solution with which it is in contact, assuming a negative potential.




A SIMPLE EXAMPLE OF VOLTAIC PILE

When the cell is providing an electrical current through an external circuit, the metallic zinc at the surface of the zinc anode is oxidized and dissolves into the electrolyte as electrically charged ions (Zn^{2+}), leaving two negatively charged electrons (e^-) behind in the metal:

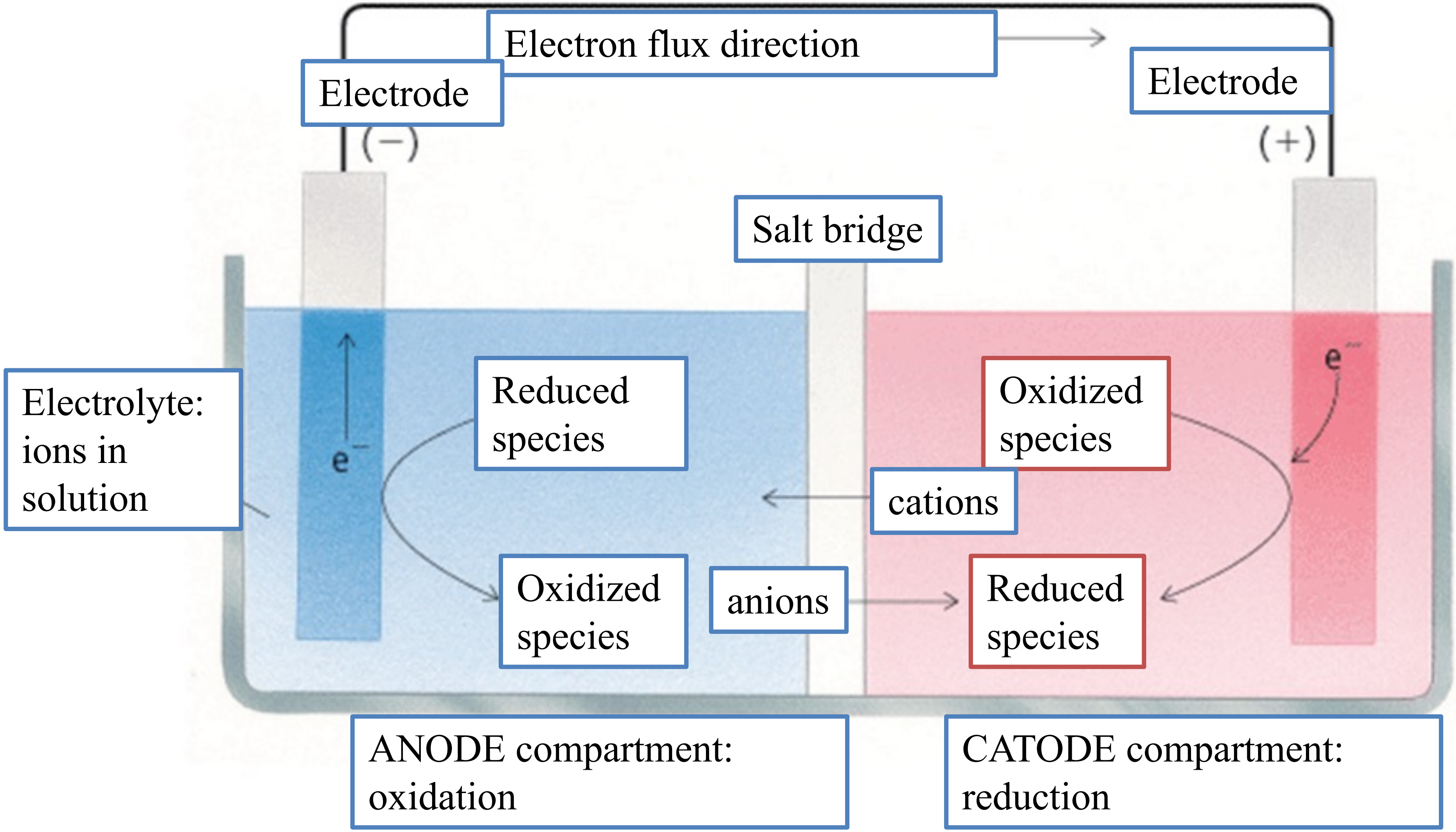
anode (oxidation): $Zn \rightarrow Zn^{2+} + 2\ e^-$

While zinc is entering the electrolyte, two positively charged hydrogen ions (H^+) from the electrolyte accept two electrons at the copper cathode surface, become reduced and form an uncharged hydrogen molecule (H_2):

cathode (reduction): $2\ H^+ + 2\ e^- \rightarrow H_2$

The electrons used from the copper to form the molecules of hydrogen are made up by an external wire or circuit that connects it to the zinc. The hydrogen molecules formed on the surface of the copper by the reduction reaction ultimately bubble away as hydrogen gas.

In general:



Electron flux direction

Electrode

Electrode

Salt bridge

Electrolyte: ions in solution

Reduced species

Oxidized species

Oxidized species

cations

anions

Reduced species

ANODE compartment: oxidation

CATODE compartment: reduction

Voltaic cells with inert electrodes

In order to carry any redox reaction in a voltage cell, other types of electrodes must be used.

In cases where reagents and products can not be used as electrodes (non-metals generally do not transfer electricity), inert electrodes are used.

These electrodes are made up of materials that transfer electrons, but which are neither oxidized nor reduced in the electrochemical cell.

- Graphite electrode
- Pt electrode
- Hydrogen electrode

Hydrogen electrode

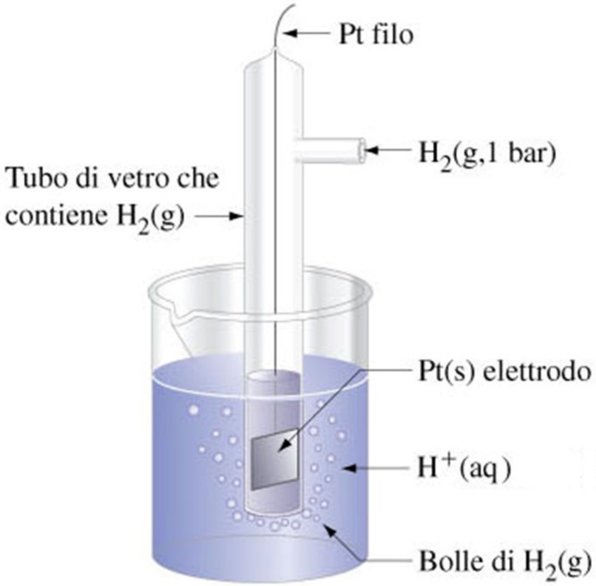
This electrode is particularly important in electrochemistry as it is used as a reference electrode to assign the voltage to the cells.

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 porous surface of the latter. The electrode is dipped in an aqueous solution containing 1 M H + (aq).

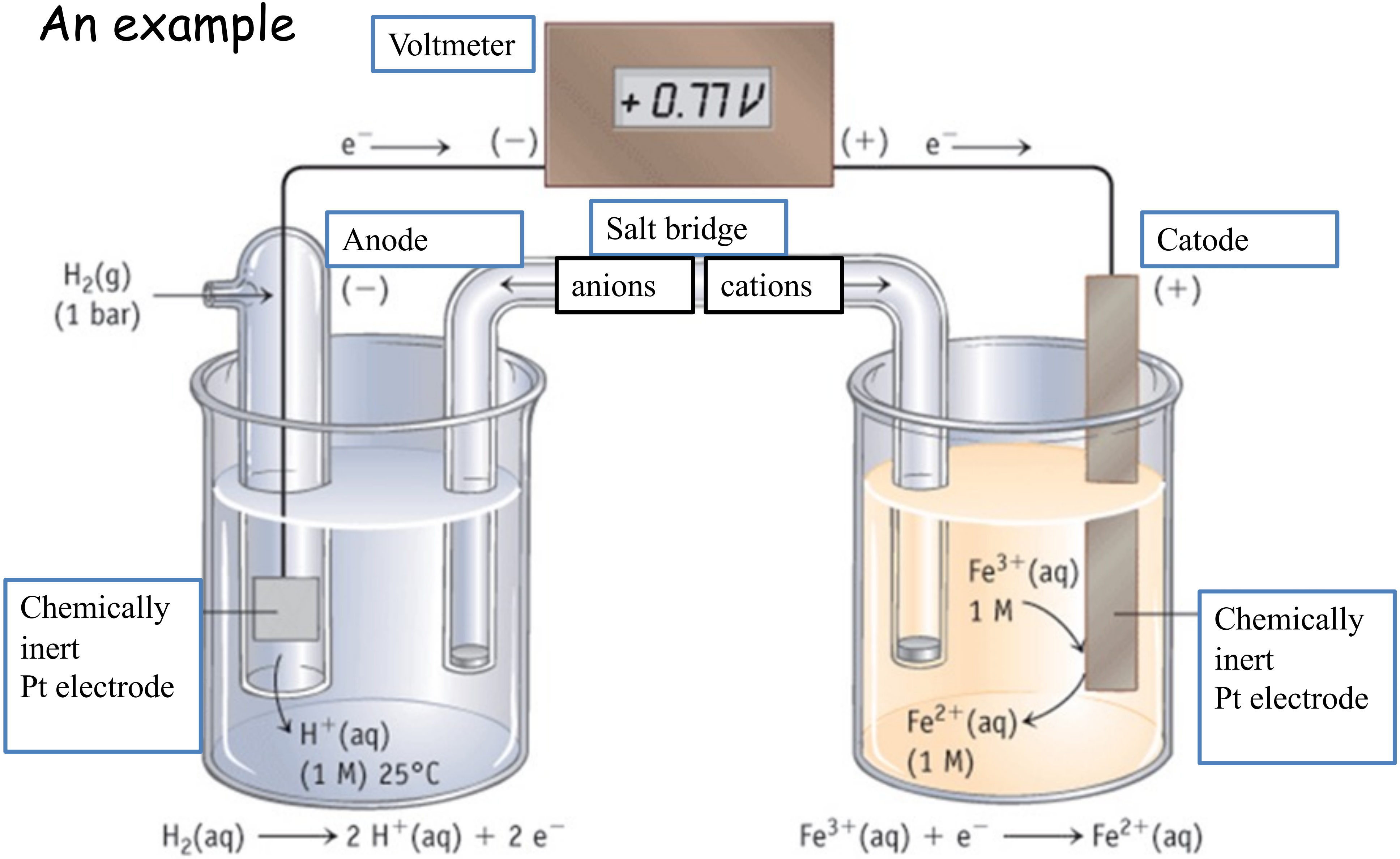
The oxidizing oxidation is:

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

The reaction takes place on the surface of the electrode, and the electrons involved in the reaction are tranferred through the electrode of Pt



An example



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

Voltaic cells notation

A voltage cell is usually represented indicating the species involved, and the inert electrodes, written in a certain order and separated by vertical lines.

For example, the Daniell battery: $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

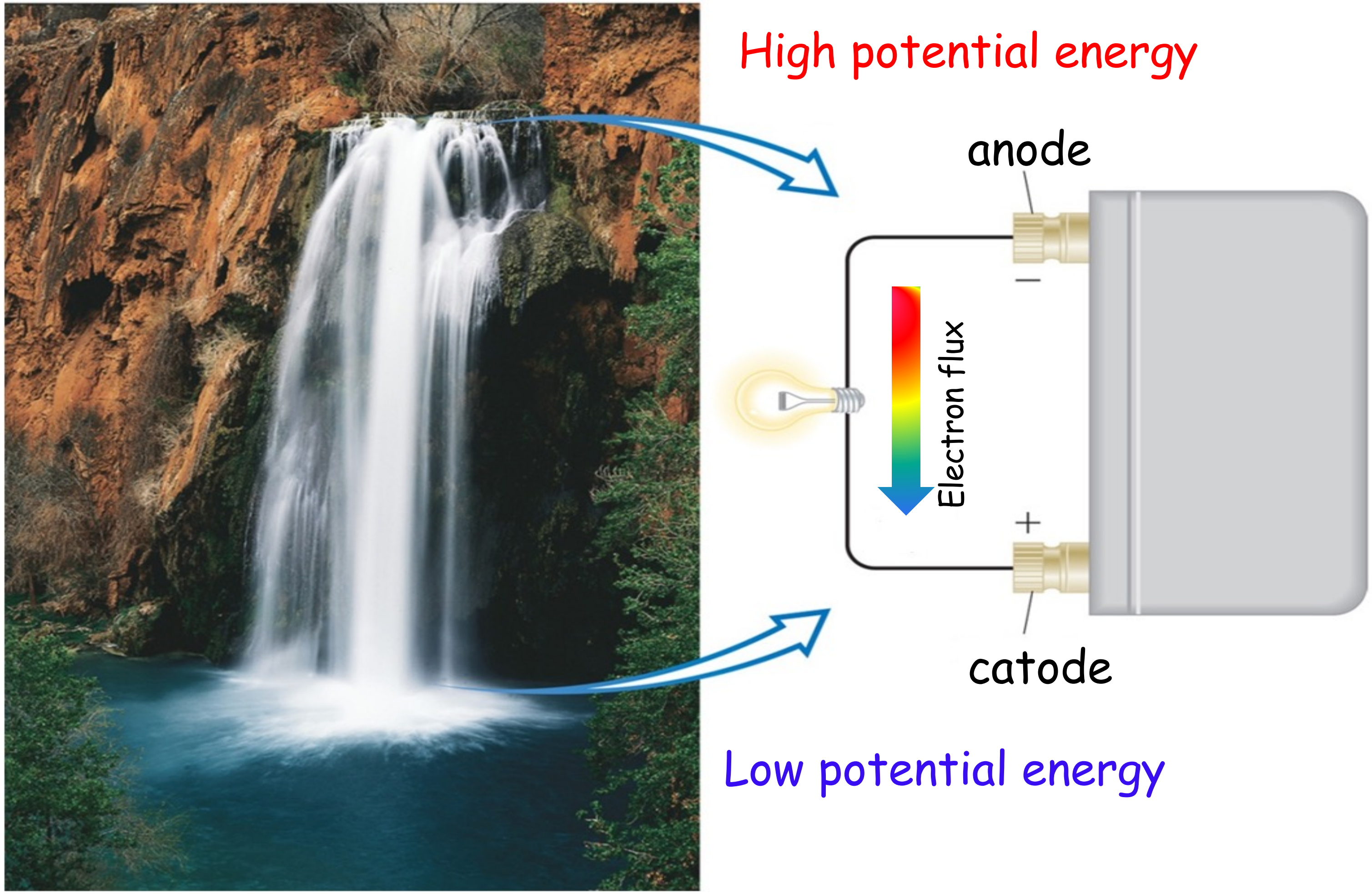
$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^-$	ossidazione	anodo
$Cu^{2+}\ (aq) + 2\ e^- \rightarrow Cu\ (s)$	riduzione	catodo

Is written as:

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

The anode is on the left and the catode is on the right, the species are written in the same order as in the half-reactions.

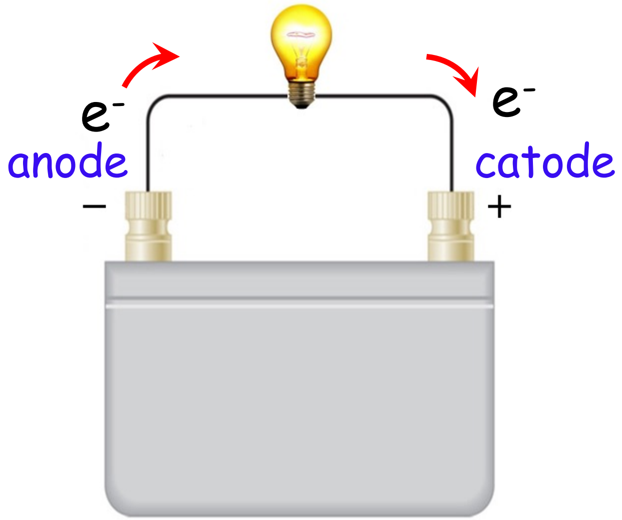
The electromotive force (emf)



- 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 volt (V)

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 two cells at standard conditions :

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

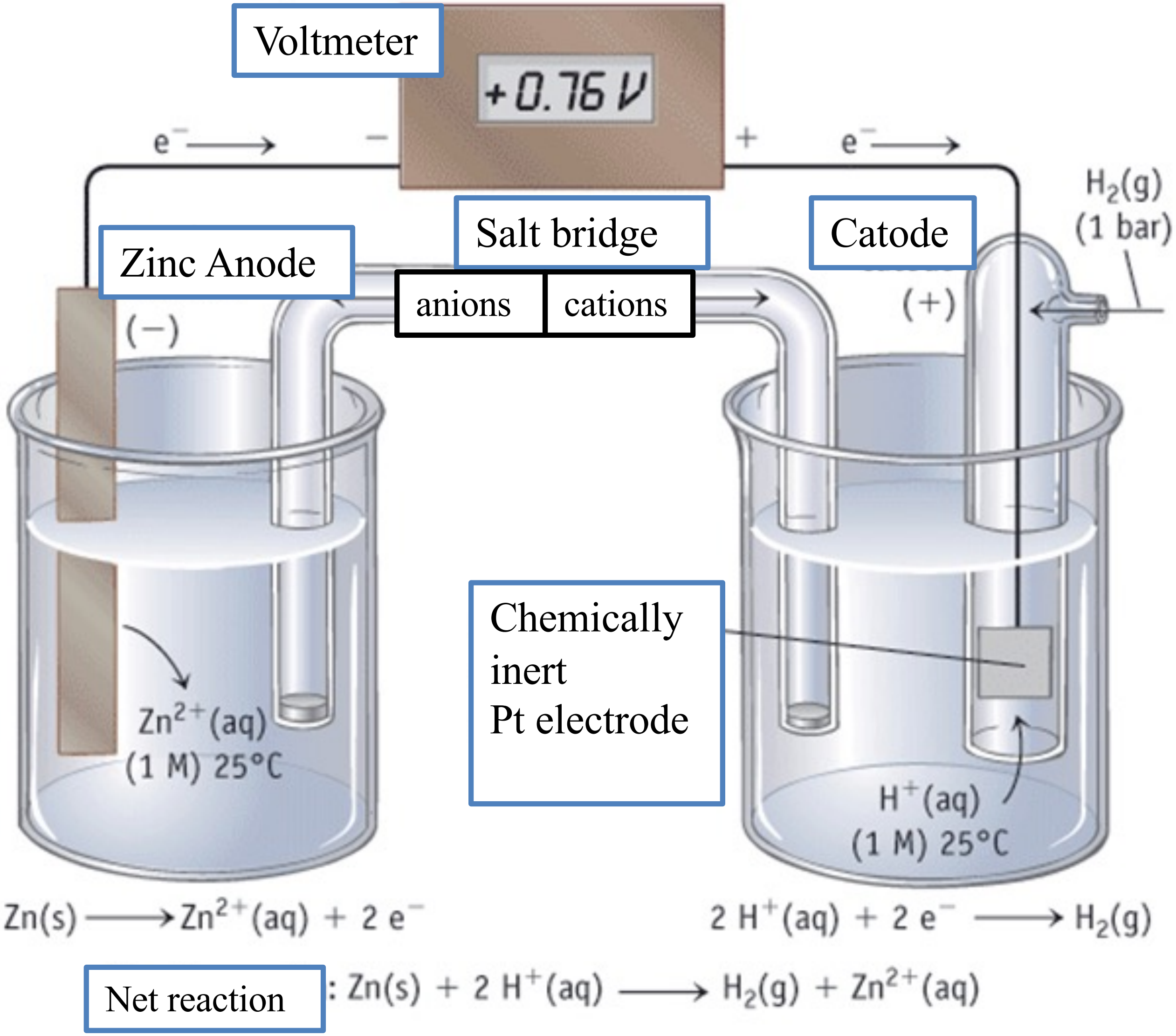
A potential mesured at standard conditions is called «standard potential» E°_{cell}

In thermochemistry and thermodynamics standard conditions are: (STP acronym of Standard Temperature Pressure) 25° C - 298,15 K- and 1 atm.

These refer to reactions in which gases are formed and consumed. In these cases, normally, one considers gas volumes and not moles.
If unspecified one intends normal conditions 273,15 K (20° C) e 1 atm.

At these conditions, 1 mole of any gas occupies 22,414 litres.

A battery at standard conditions

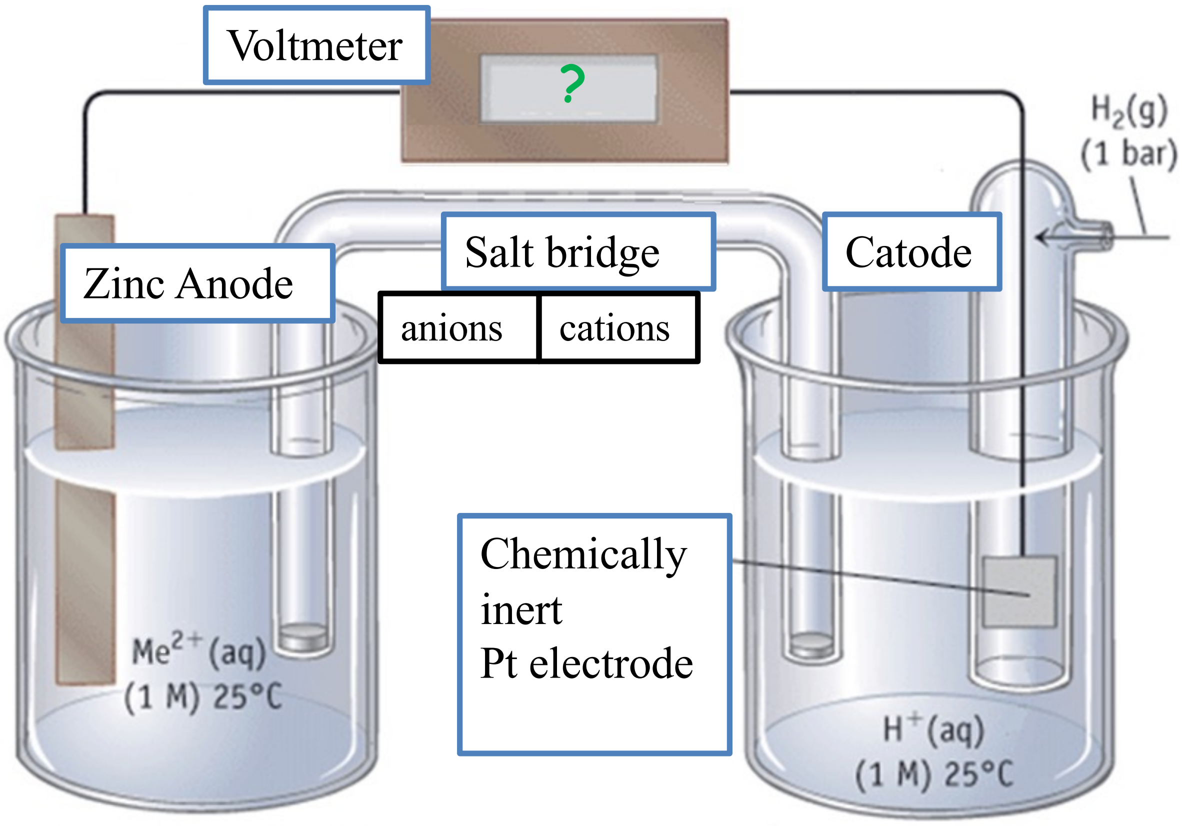


$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

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

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

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



Reference
Electrode
0 Volt

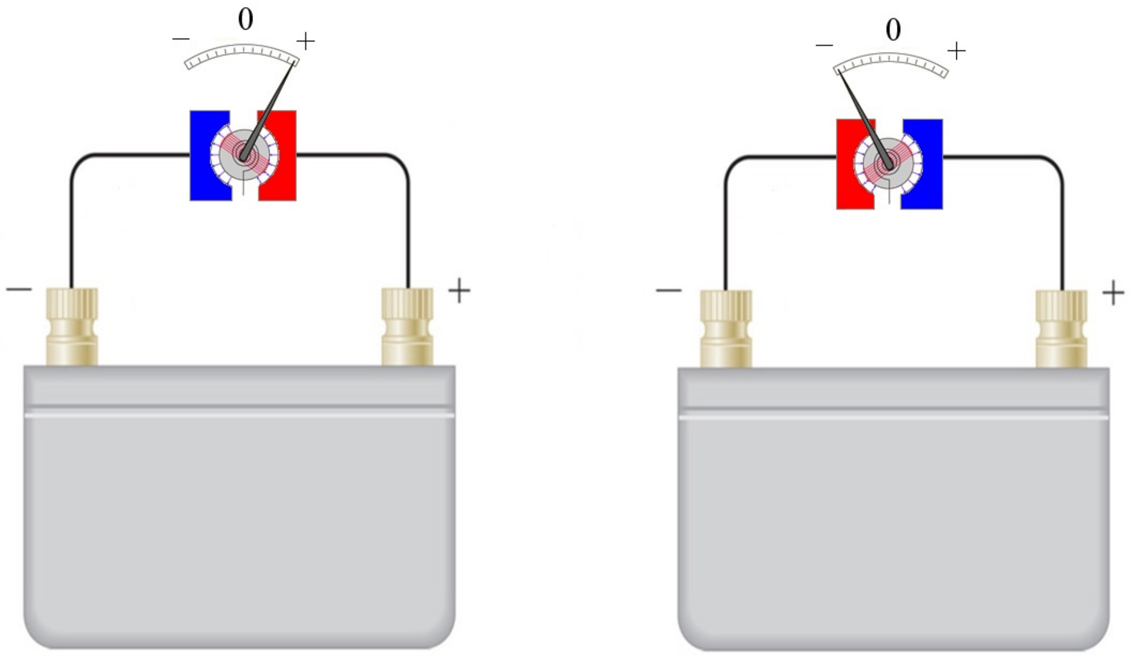
$Me \rightleftarrows Me^{2+} + 2\ e^-$

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

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

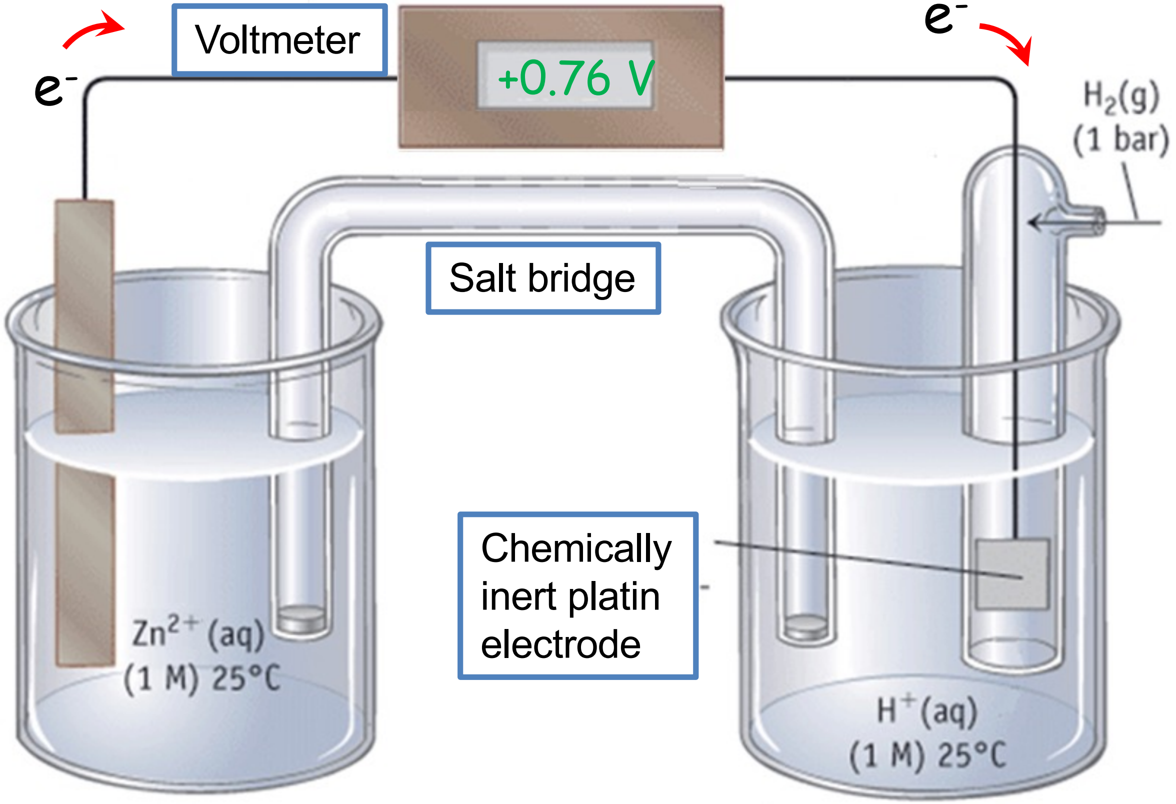
What will be the reaction's direction? Which one is the catode and which one is the anode?
In a voltaic cell, electrons go from positive to negative, moving from anode to catode.

A voltmeter allows one to measure direction of the flow.



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

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



e^-

Voltmeter

e^-

Salt bridge

anode
(-)

catode
(+)

Chemically
inert platin
electrode

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

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

Standard redox potentials

Since $\Delta E°_{\text{cell}}$ indicates the difference of potential between half cells:

$$\Delta E°_{\text{cell}} = E°_{\text{catode}} - E°_{\text{anode}}$$

$E°_{\text{catode}}$ and $E°_{\text{anode}}$ are the standard redox potentials for he half reactions taking place at catode and anode

- knowing $E°_{\text{catode}}$ an $E°_{\text{anode}}$ one can calculate the stadard redox potential $\Delta E°_{\text{cell}}$ of a voltaic cell

- when $\Delta E°_{\text{cell}}$ is positive the raction is spontaneous

TABLE 18.1 Standard Reduction Potentials at 25°C

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

Nernst equation

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

$$\underset{\text{reduced species}}{C\,(s)} \rightleftarrows \underset{\text{oxidized species}}{C^{z+}\,(aq)} + z\,e^{-} \qquad \underset{\text{reduced species}}{A^{z-}\,(aq)} \rightleftarrows \underset{\text{oxidized species}}{A\,(s)} + z\,e^{-}$$

One can demonstrate that the half cell potential is:

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

- 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 C$\times$$mol^{-1}$), charge of 1 mole of electrons

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 at 25 ° C

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

reduced species

oxidized species

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

The electrode potential (compared to the hydrogen reference one)

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

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

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 hydrogen reference one)

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

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

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

$$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s) \quad E° = -0.25\ V \quad e$$
$$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s) \quad E° = -1.66\ V$$

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:

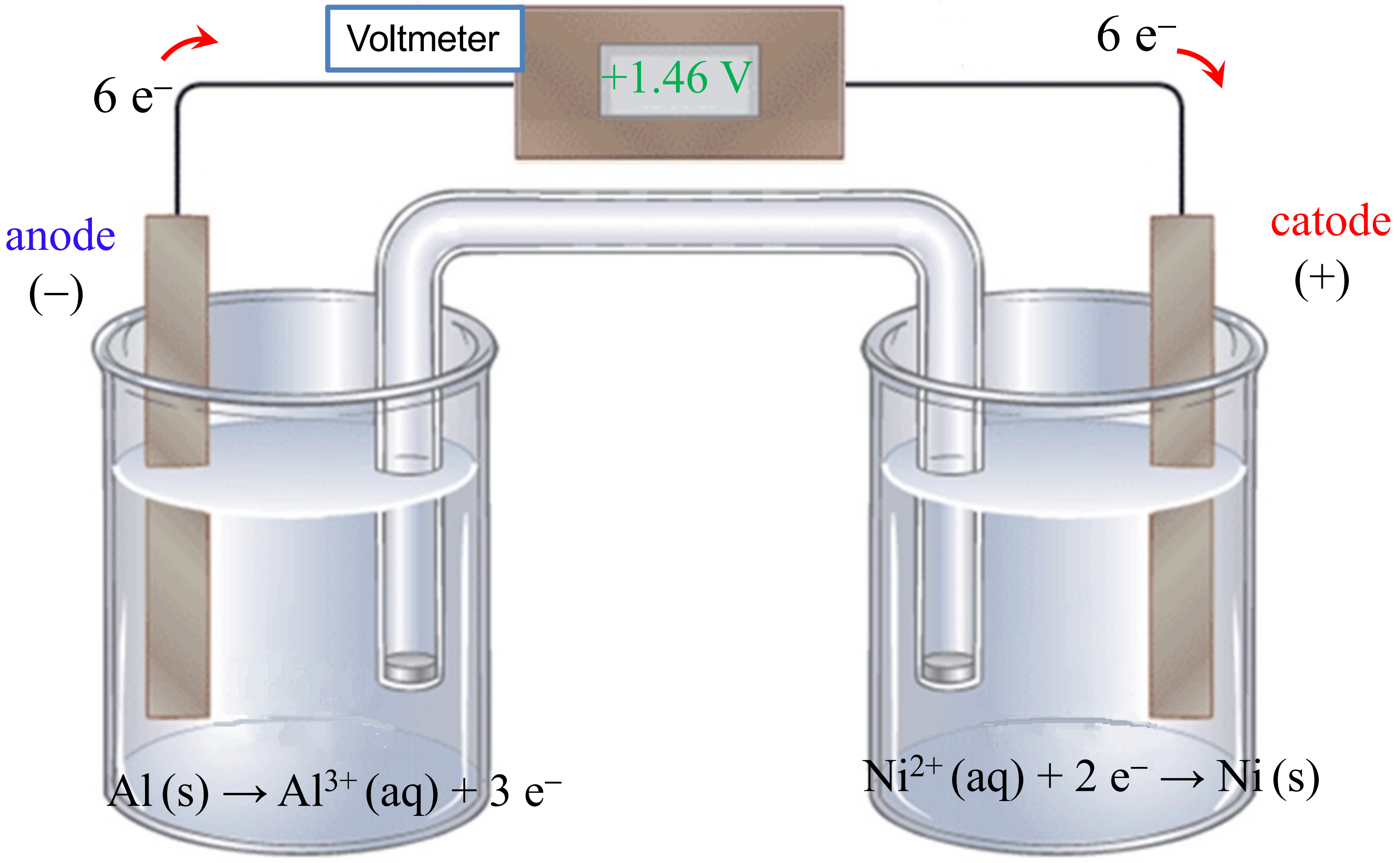
$$\Delta E°_{cell} = E°_{catode} - E°_{anode} = (-0.25) - (1.66) = 1.41\ V$$

TABLE 18.1 Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2\,F\,(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	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	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

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

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



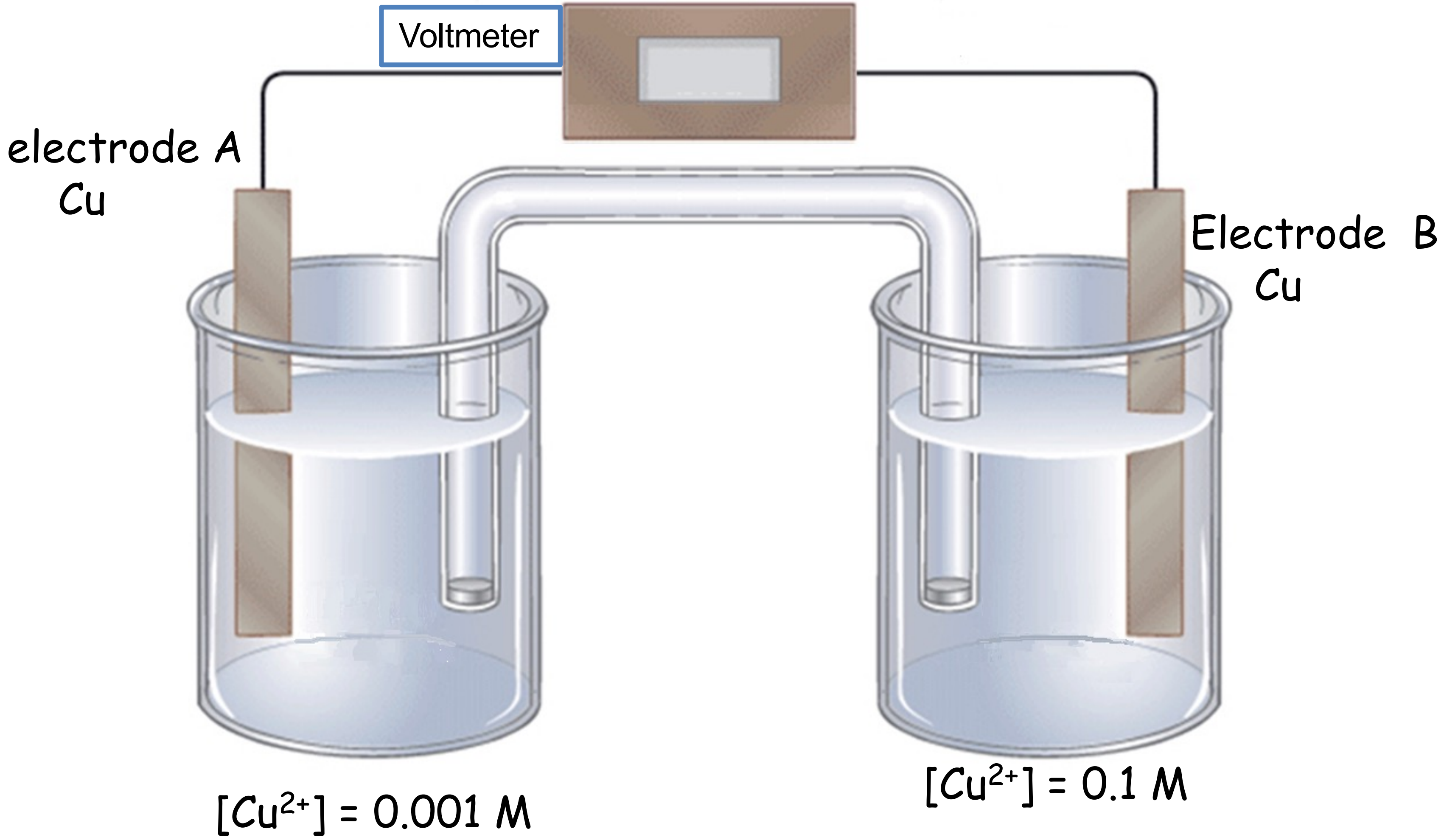
$Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$

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

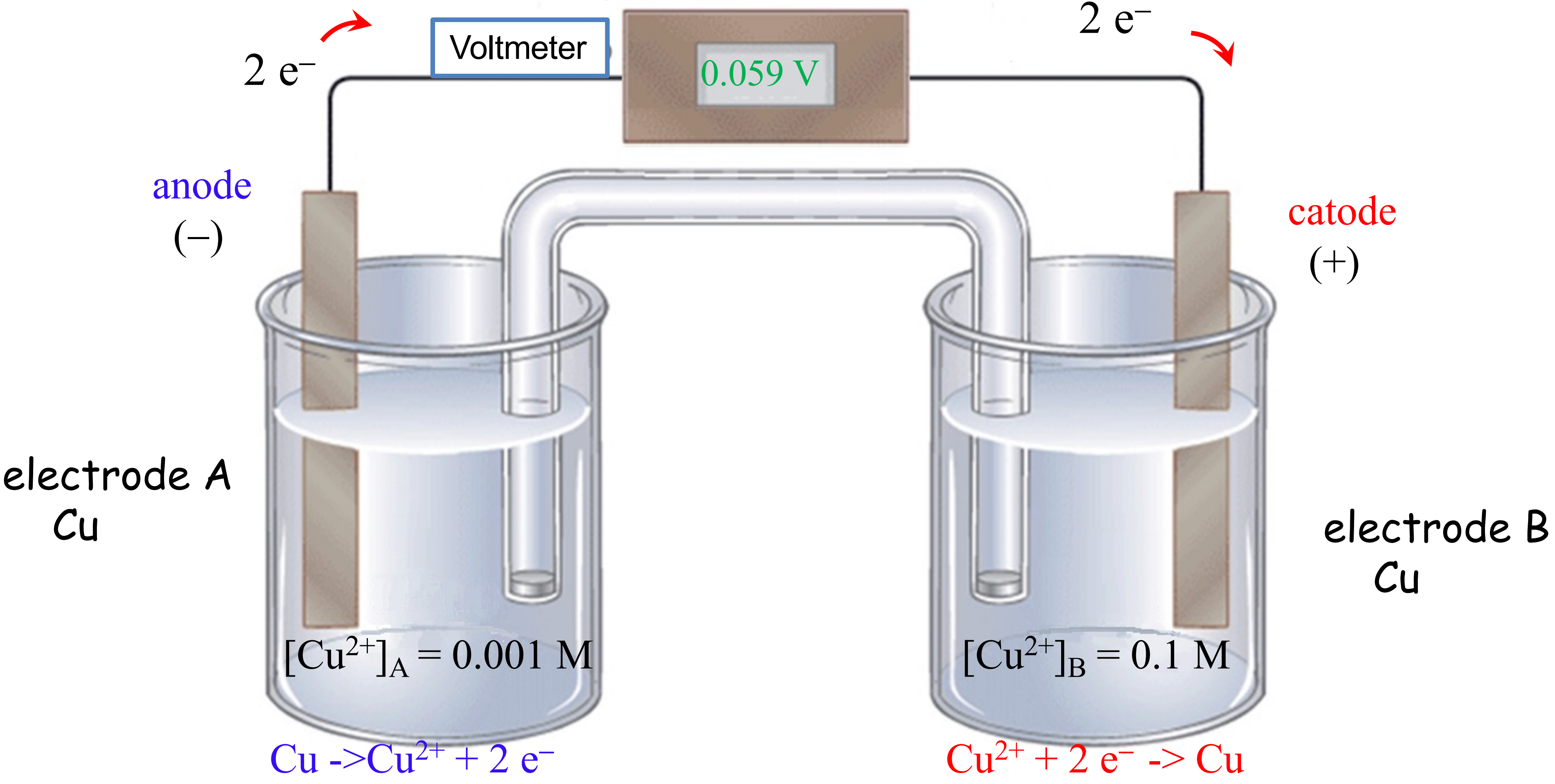
$2\ Al(s) + 3\ Ni^{2+}(aq) \rightleftarrows 2\ Al^{3+}(aq) + 3\ Ni(s)$

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 celles



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

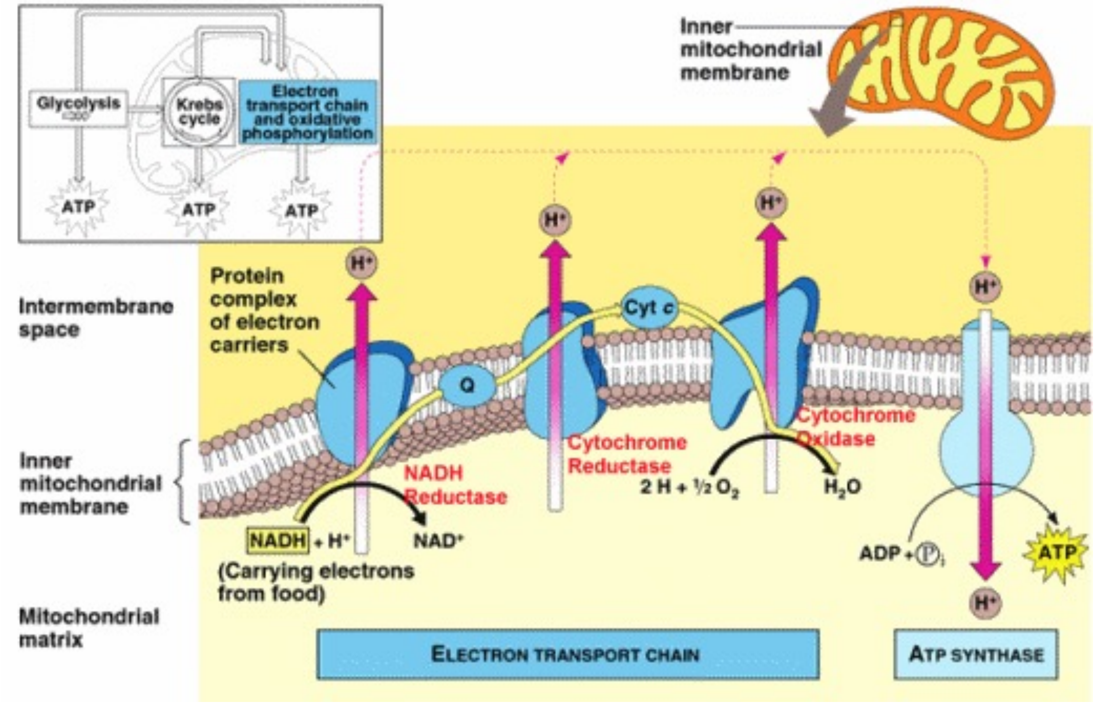


$Cu \rightarrow Cu^{2+} + 2\ e^-$ $Cu^{2+} + 2\ e^- \rightarrow Cu$

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

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

A relevant application of the concentration electrode: the pHmeter



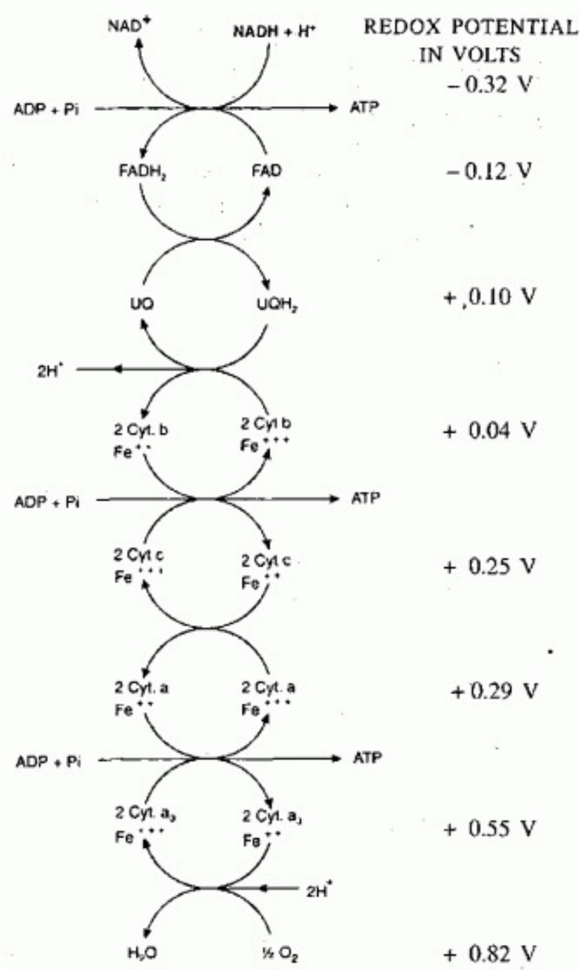
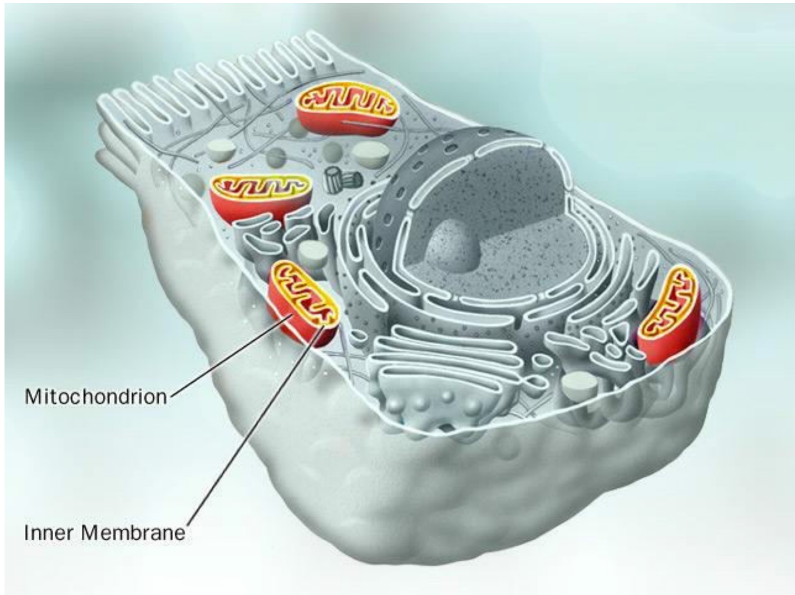
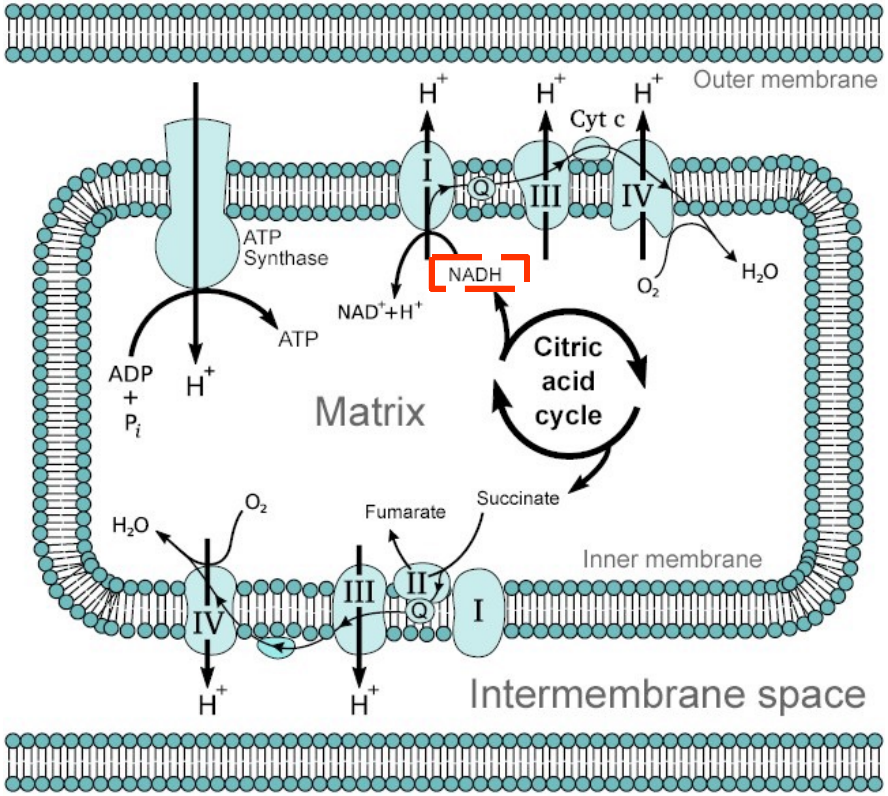
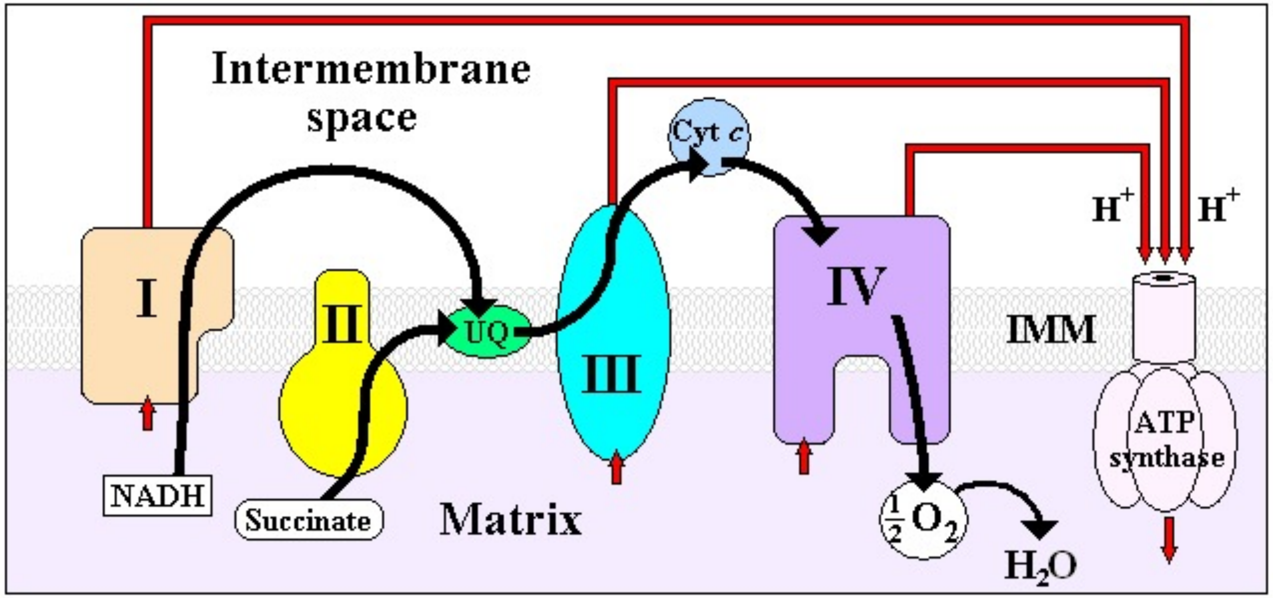


Fig. 5.3.3.3 : Electron transport system and oxidative phosphorylation

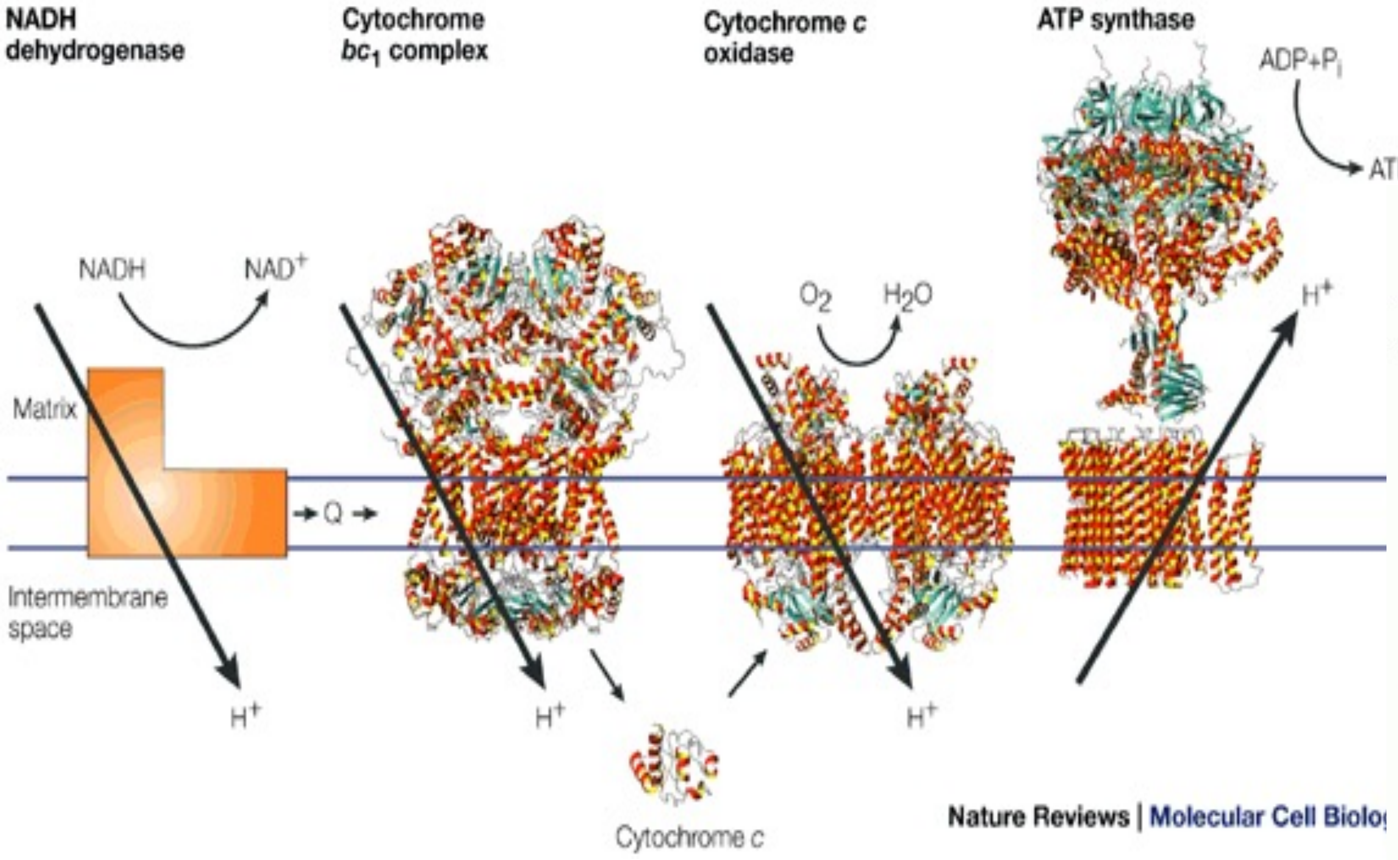
Redox reactions are exploited to provide energy for all cellular processes.


Mitochondrion
Inner Membrane


Outer membrane
H+
H+
H+
Cyt c
I
Q
III
IV
ATP Synthase
NADH
NAD+ + H+
ATP
ADP + Pi
H+
O2
H2O
Citric acid cycle
Matrix
Succinate
Fumarate
H2O
O2
Inner membrane
IV
III
II
Q
I
H+
H+
Intermembrane space


Intermembrane space
Cyt c
H+
H+
I
II
UQ
III
IV
IMM
ATP synthase
NADH
Succinate
Matrix
½ O2
H2O

The Respiratory Chain



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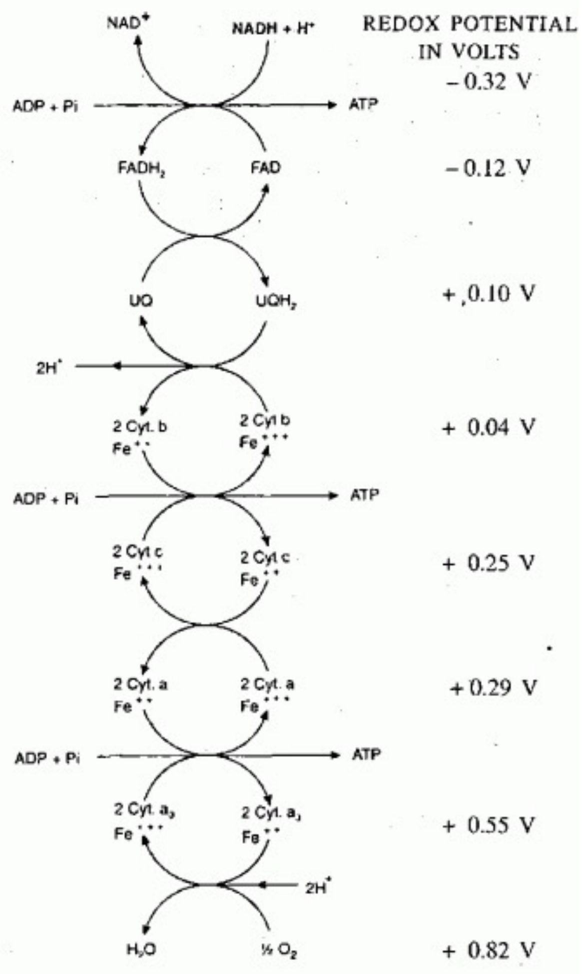

Fig. 5.3.3.3 : Electron transport system and oxidative phosphorylation

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 to 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.

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