

# Redox Reactions



Luigi Galvani  
(1737 – 1798)



Alessandro Volta  
(1745– 1827)



Walther H. Nernst  
(1864 – 1941)

# RedOx Reactions

A copper wire is dipped in a  $\text{AgNO}_3$  solution

Copper reduces  $\text{Ag}^+$  to metallic silver and it oxidizes copper to  $\text{Cu}^{2+}$  ions

The blue color is due to  $\text{Cu(II)}$  ions

$\text{AgNO}_3$  is added

A few days after

Silver ions in solution

Surface of the copper wire

The diagram illustrates the redox reaction between copper and silver nitrate. It is divided into three stages:

- Stage 1:** A copper wire is dipped in a solution. A box above says "A copper wire is dipped in a  $\text{AgNO}_3$  solution". A box below says "Silver ions in solution". A box at the bottom left says "Surface of the copper wire".
- Stage 2:** The wire is coated with silver. A box above says "Copper reduces  $\text{Ag}^+$  to metallic silver and it oxidizes copper to  $\text{Cu}^{2+}$  ions". A box above the wire says "A few days after". A box below the wire says "Surface of the copper wire".
- Stage 3:** The wire is heavily coated with silver. A box above says "The blue color is due to  $\text{Cu(II)}$  ions". A box below the wire says "Surface of the copper wire".

Labels in the diagram include  $\text{AgNO}_3$  is added,  $\text{AgNO}_3$ , and  $\text{Cu}^{2+}$ .

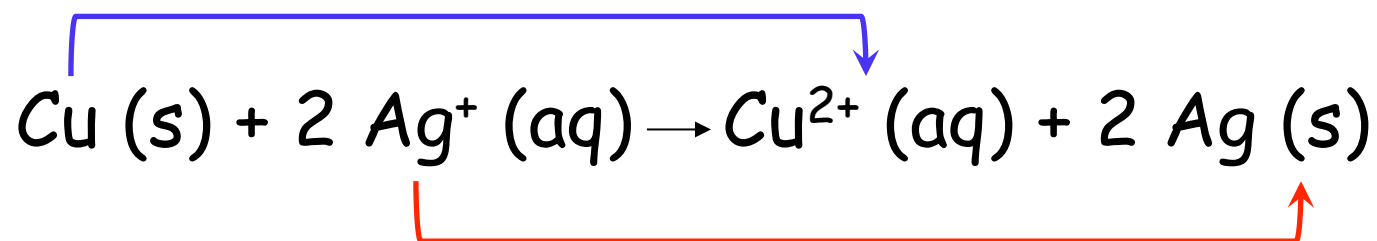


## Redox Reactions

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:

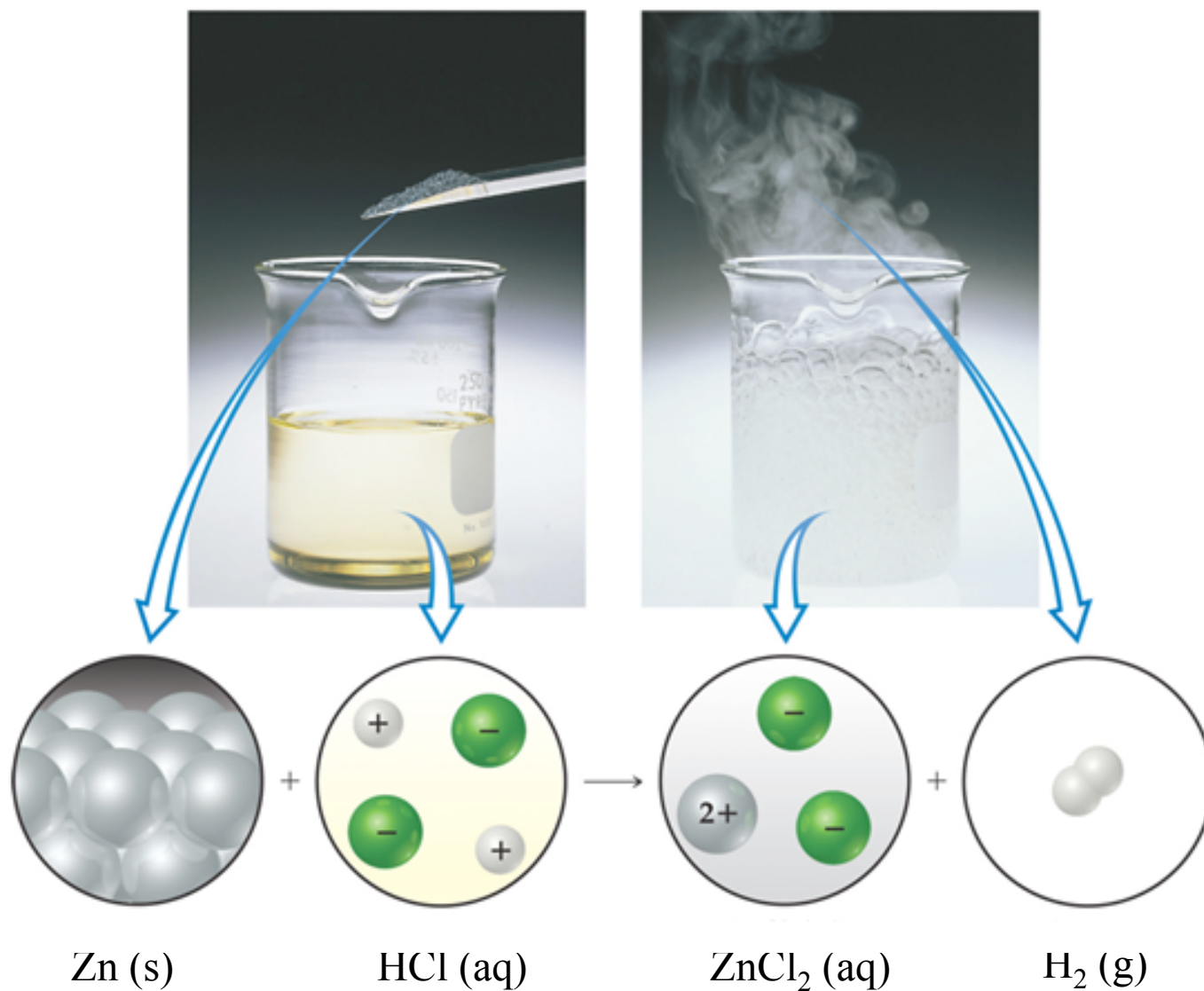
- A reactant is **oxidized** and the other is reduced
- The oxidation and reduction reactions have to be **balanced**
- The oxidizing agent (the chemical species that causes oxidation) is **reduced**
- The **reducing agent** (the chemical causing the reduction) is **oxidized**
- To determine if a substance 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

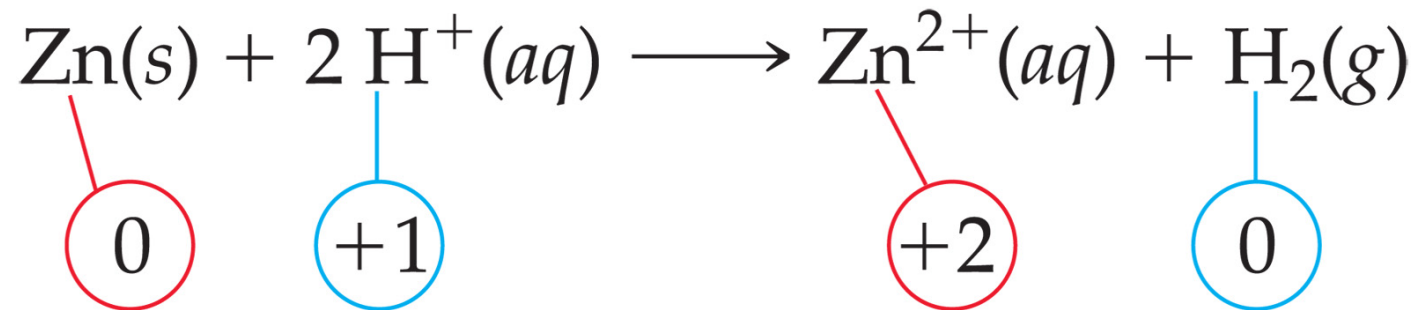


**Ag<sup>+</sup> is reduced, its oxidation number decreases. Ag<sup>+</sup> is the oxidizing agent**

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

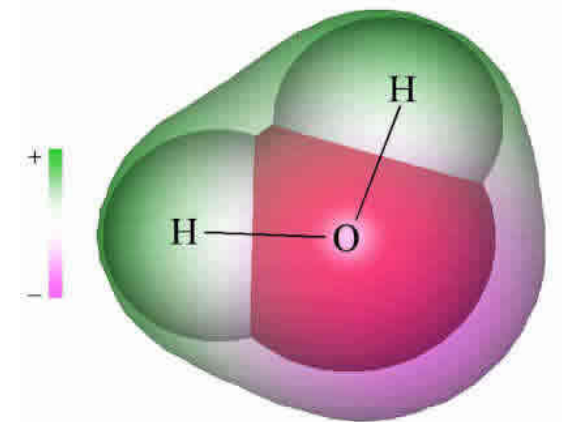
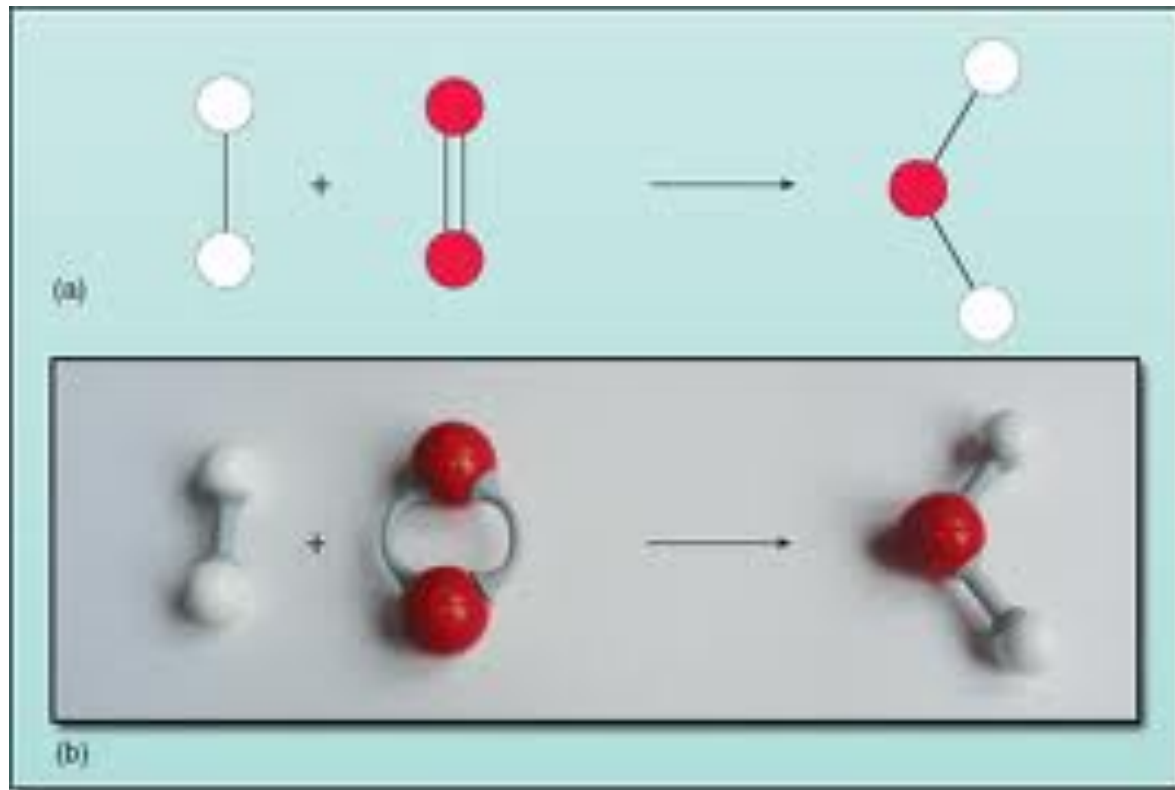


## Oxidation and reduction



- The species is **oxidized** when it **loses** electrons
  - Zinc loses 2 electrons  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 e^-$
- A species is **reduced** when it **acquires** electrons
  - Each of the  $\text{H}^+$  gains one electron and they combine to yield  $\text{H}_2$   
$$2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2$$
- the species that is **reduced** is called **oxidizing agent**
  - $\text{H}^+$  oxidizes Zn by acquiring its electrons
- the species that is **oxidised** is called **reducing agent**
  - Zn reduces  $\text{H}^+$  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

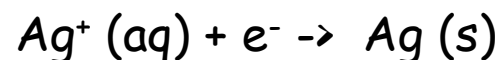
In redox reactions the mass and charge must be balanced. The same number of atoms must appear in the products and reagents of a chemical equation, and the sum of the electrical charges of all species on both sides of the arrow must be equal.

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

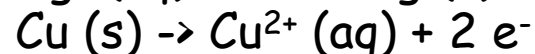
### Semireactions method

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

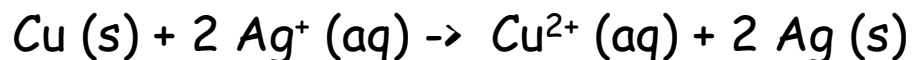
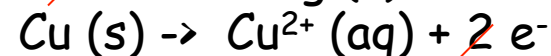
Reduction semireaction:



oxidation semireaction:



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

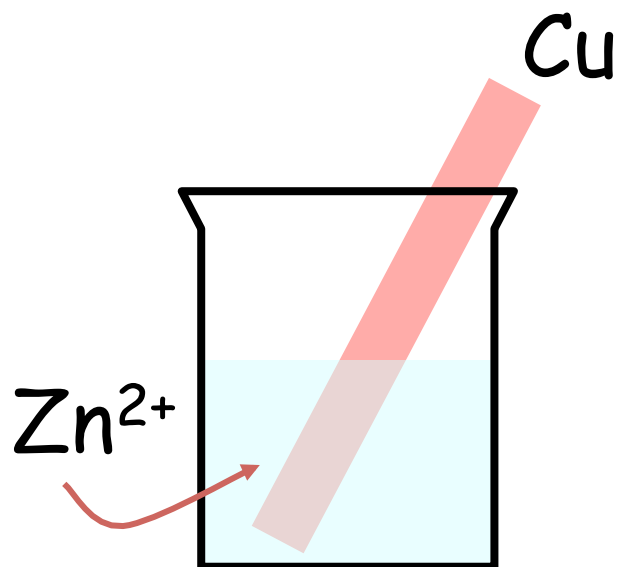




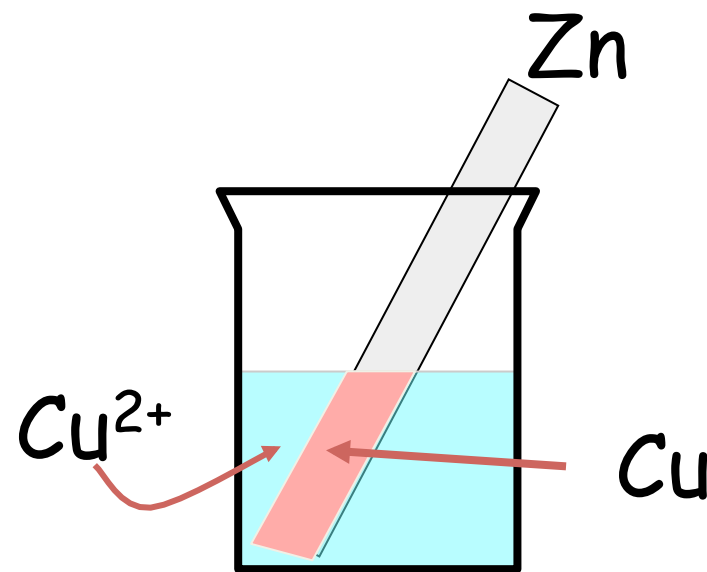
Lets consider the two possible reactions:



Electronegativity
Zn = 1.6
Cu = 1.9



Reducing power of  $\text{Cu}^{2+}/\text{Cu}$  <



Reducing power of  $\text{Zn}^{2+}/\text{Zn}$

Only the second reaction is spontaneous

## Voltaic cells

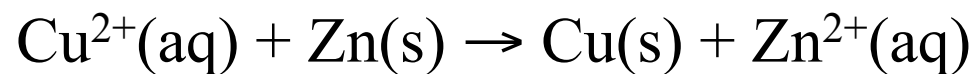
We can therefore devise a device that uses the spontaneous redox reactions to move electrons (hence electrical current) and therefore produce electricity. Such devices are known as voltaic cells or galvanic cells or batteries.

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

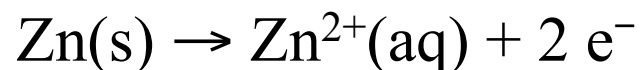
In a voltaic cell, the chemical energy is converted into electricity. In the opposite process, known as **electrolysis**, electricity is used to drive a chemical reaction in a non-spontaneous direction.

How can we build a battery?

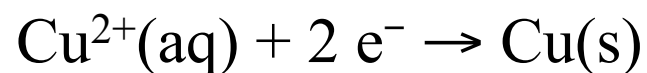




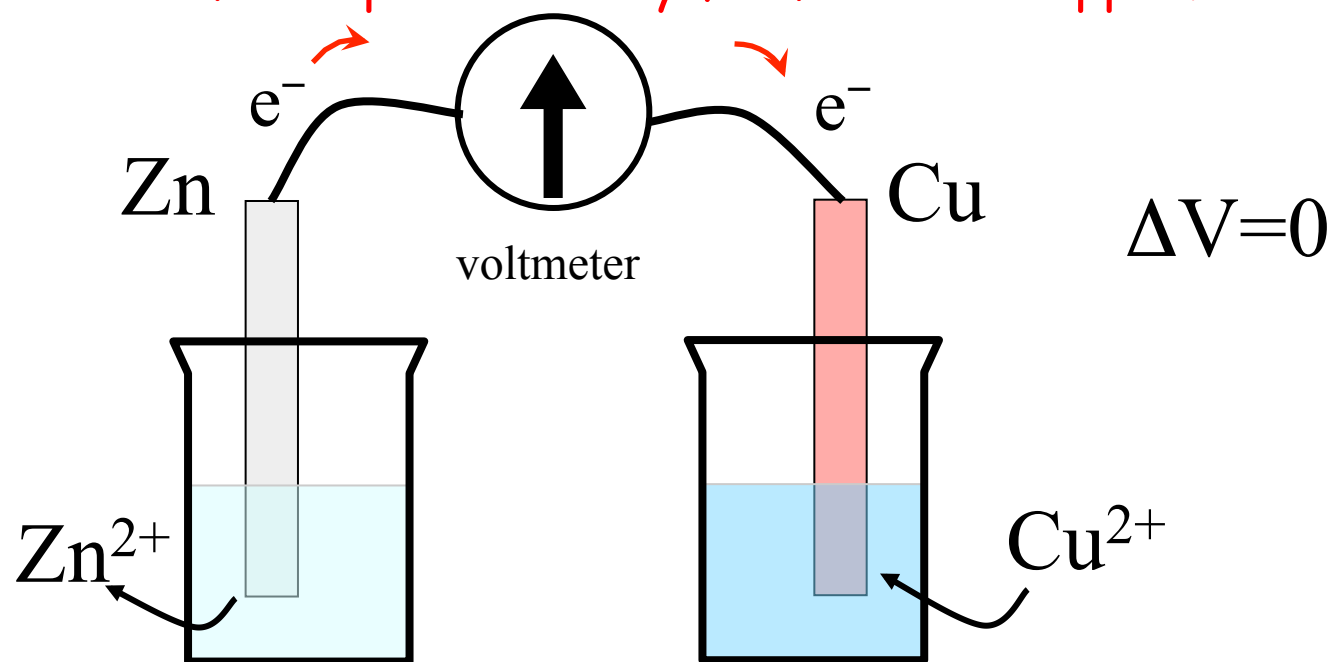
oxidation



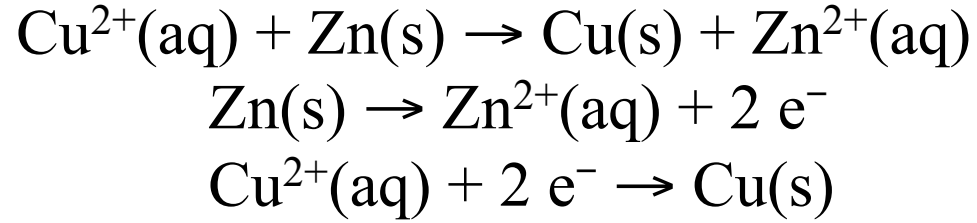
reduction



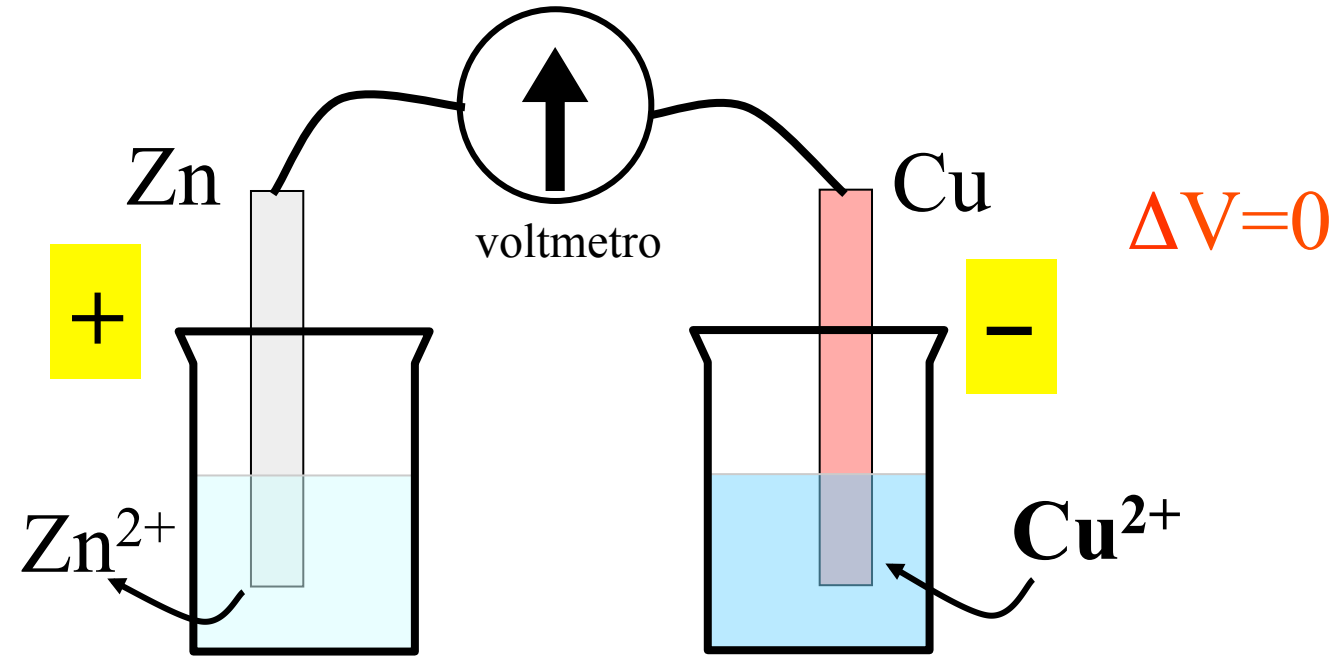
Electrons move spontaneously from zinc to copper.

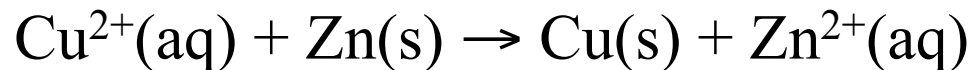


oxidation  
reduction

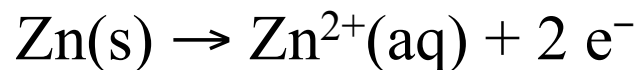


Since electrons move from left to right, if the neutrality of the solutions is not reestablished, a + charge is built to the left and a - charge is built to the left. This blocks a further transfer of electrons.

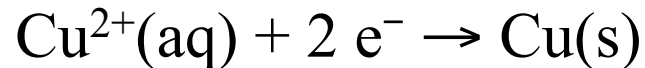




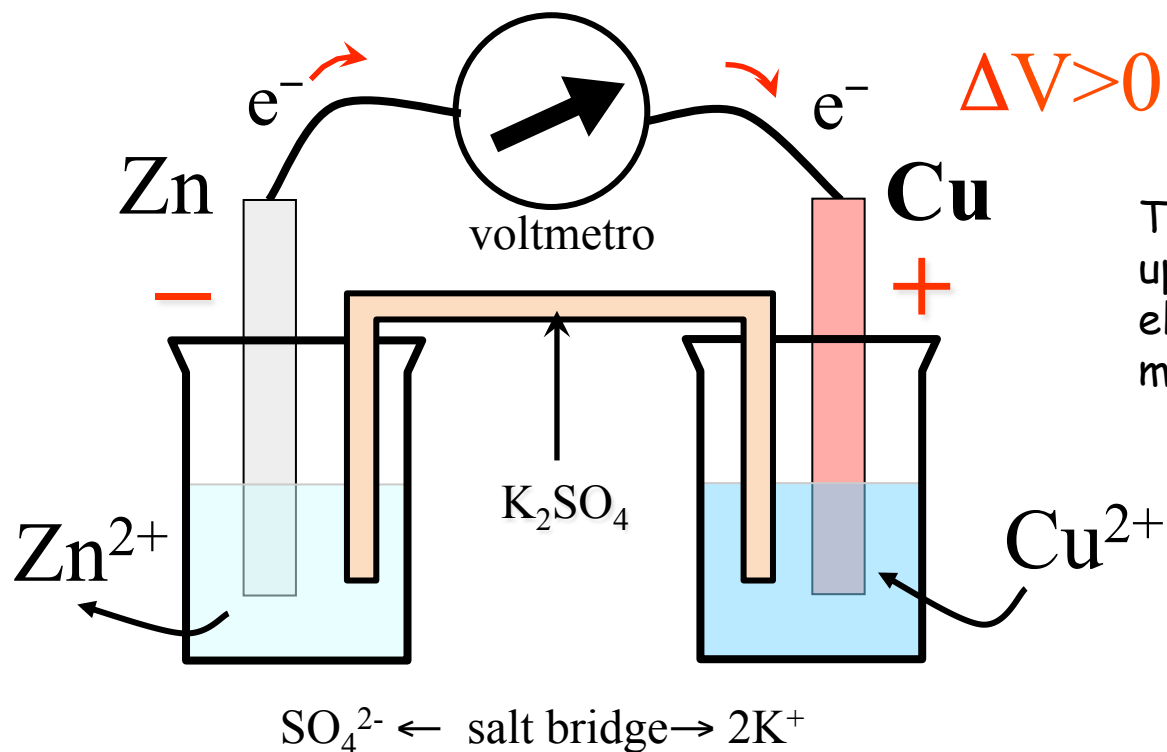
Oxidation



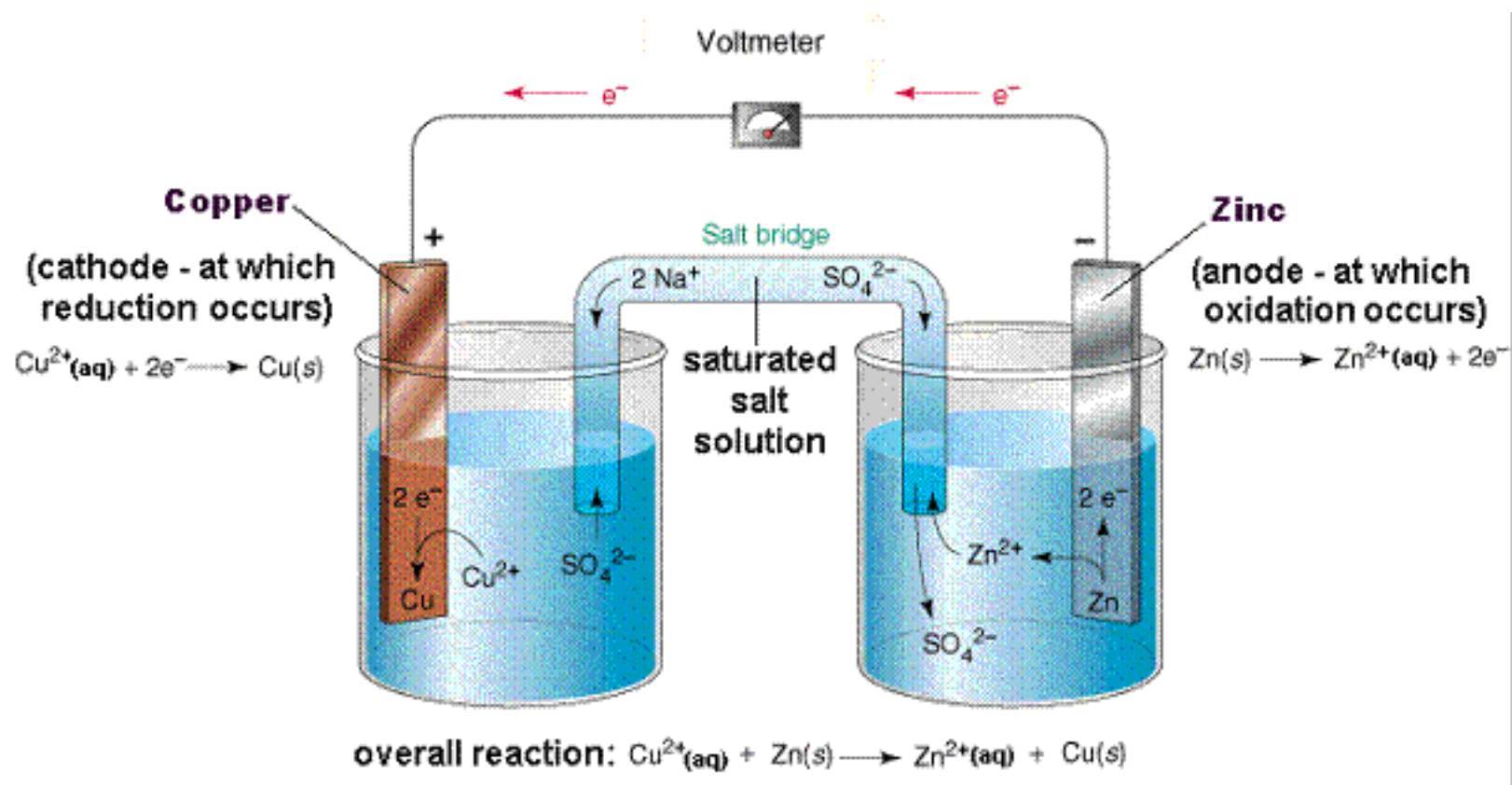
Reduction



The salt bridge is necessary, due to the production of positive ions  $\text{Zn}^{2+}$  on the left and consumption of positive ions  $\text{Cu}^{2+}$  in the right half-cell: if negative ions ( $\text{SO}_4^{2-}$ ) could not diffuse from right to left the reaction would not proceed (and vv for  $\text{K}^+$ ).



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



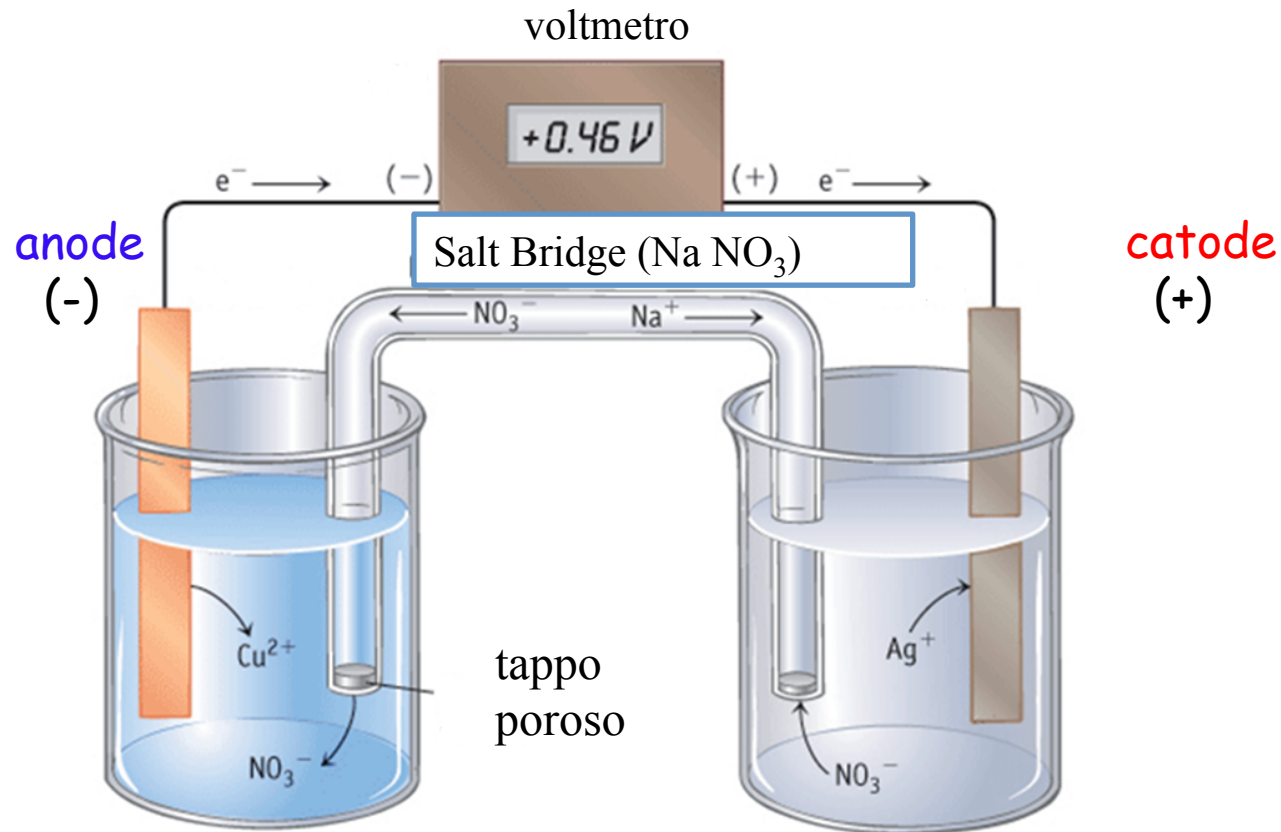
A voltaic cell consists of two containers where the semireactions take place: (1) Zn rod in a  $\text{Zn}^{2+}$  solution; (2) Cu rod in a solution of  $\text{Cu}^{2+}$ .

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  $\text{Zn}^{2+}$  on the left and consumption of positive ions  $\text{Cu}^{2+}$  in the right half-cell: if negative ions ( $\text{SO}_4^{2-}$ ) could not diffuse from right to left the reaction would not proceed (and vv for  $\text{K}^+$ ).

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



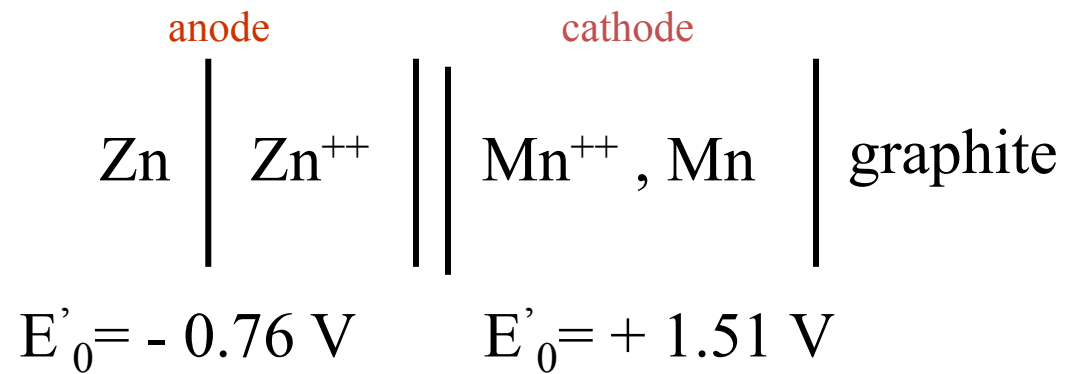
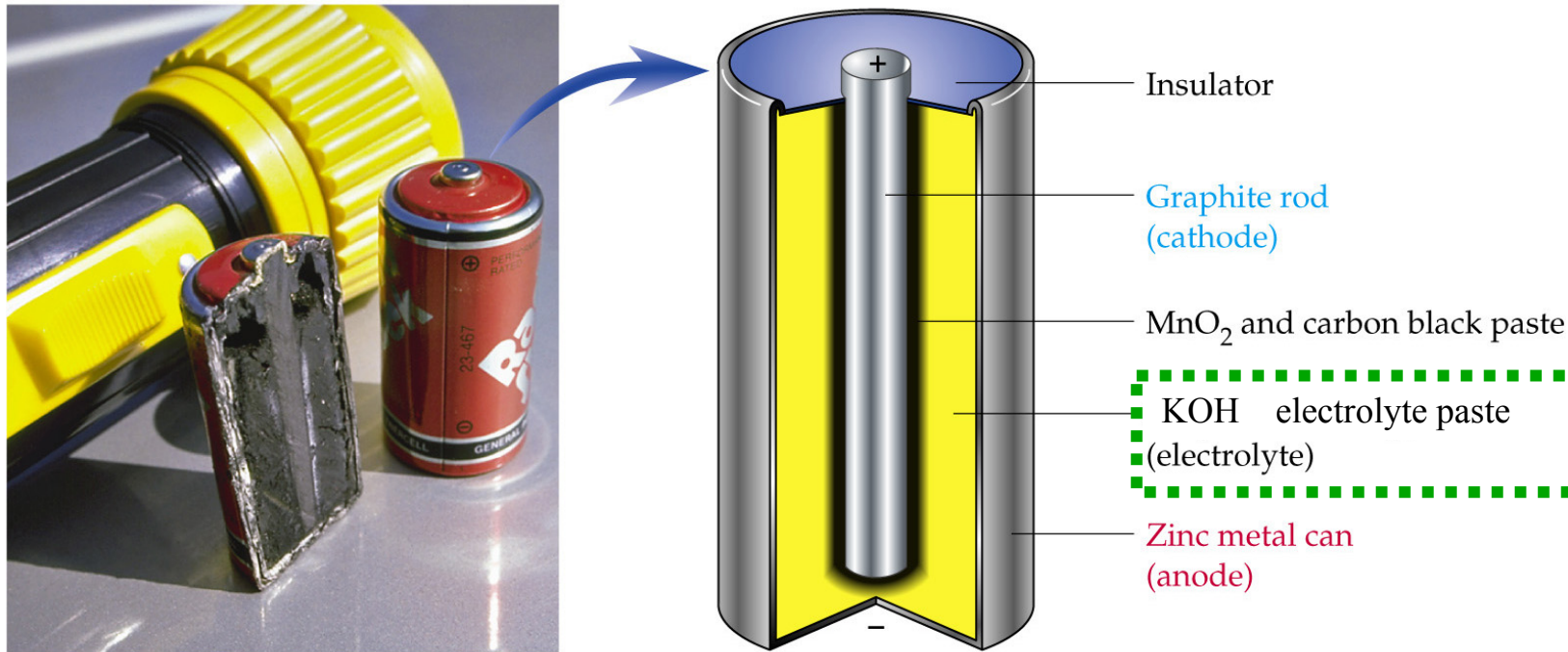
anode (negative):  $\text{Cu (s)} \rightarrow \text{Cu}^{2+} \text{(aq)} + 2 \text{e}^-$  oxidation

catode (positive):  $\text{Ag}^+ \text{(aq)} + \text{e}^- \rightarrow \text{Ag (s)}$  reduction

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

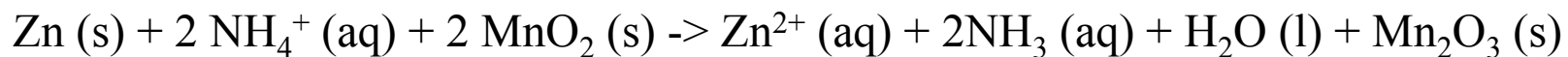
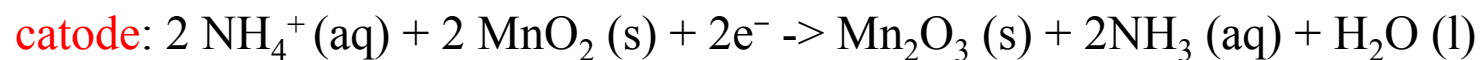
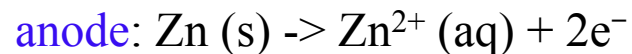
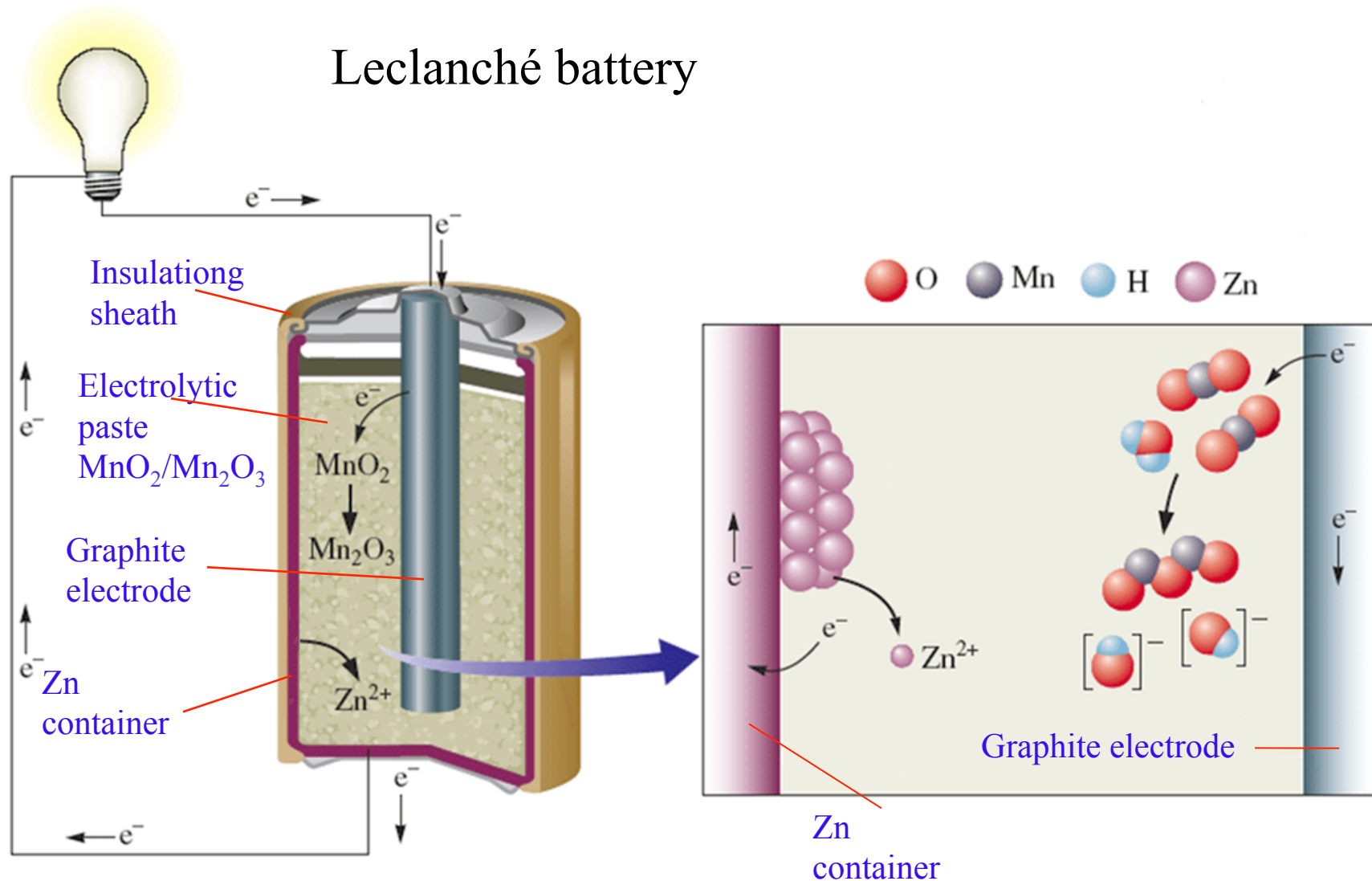


# Alcaline battery (common, manganese-zinc)



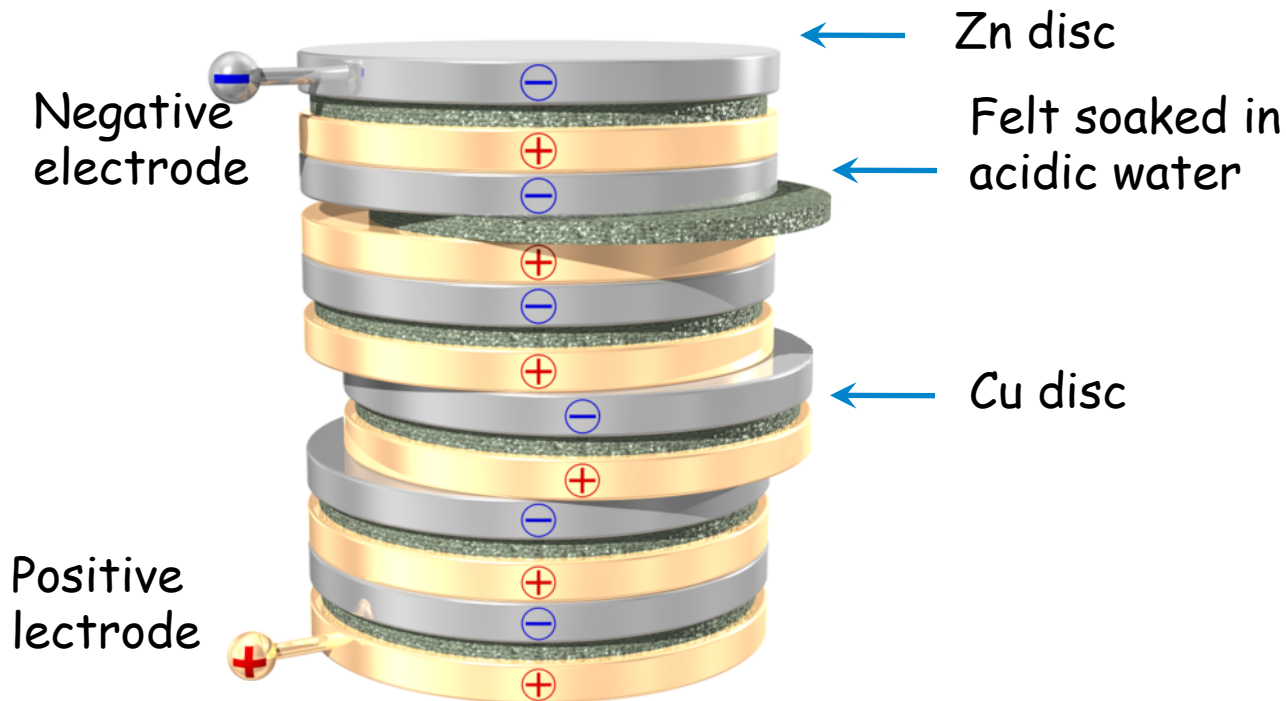
$\Delta E = 1.51 - (-0.76) = 2.27 \text{ V}$

# Leclanché battery



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 salted or acidified  $H_2O$ .

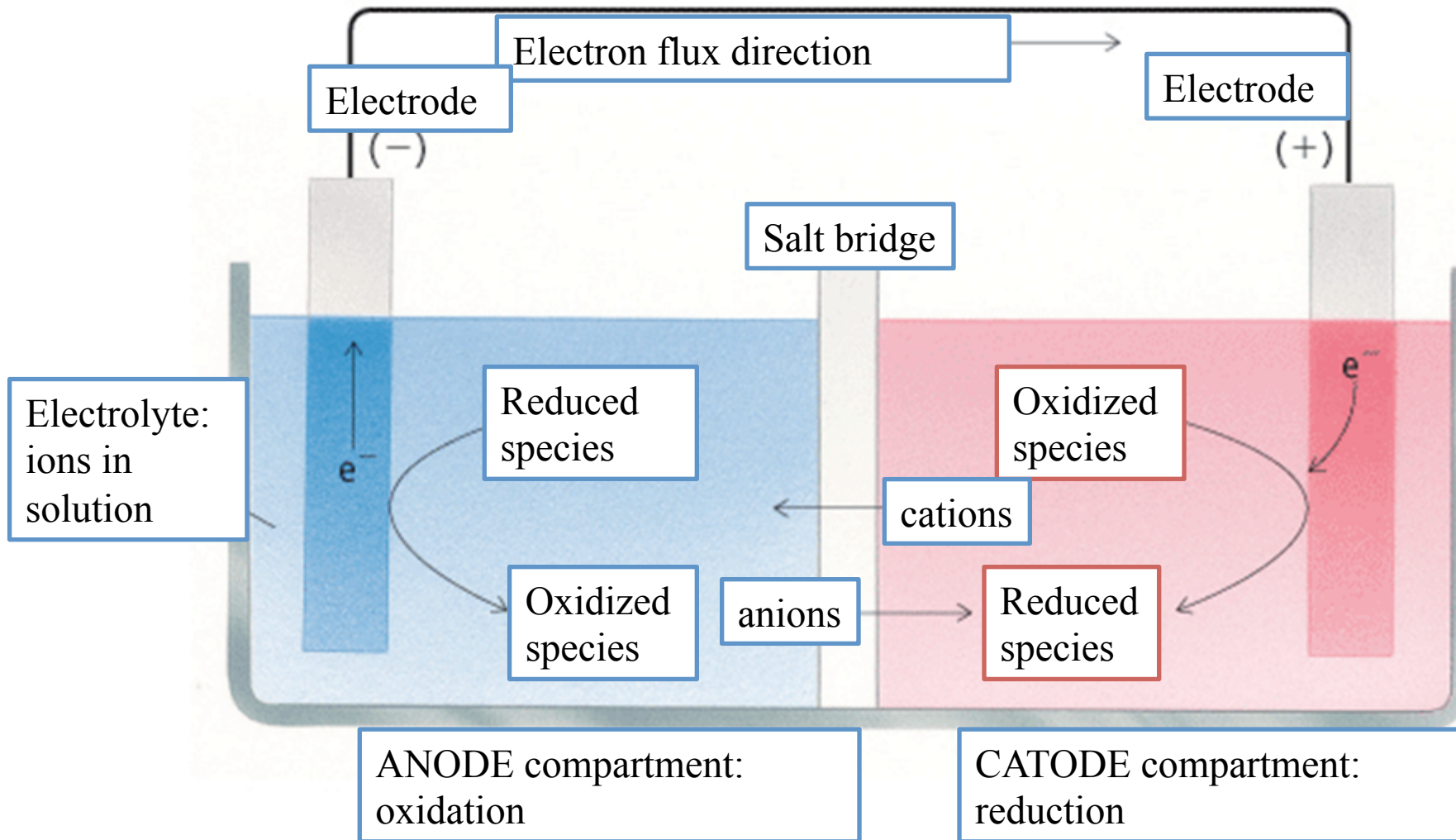
By connecting the upper and lower ends of the battery by means of an electric conductor, a circuit is generated in which a current passes.



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.

In general:



## 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  $\text{H}_2$  (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  $1 \text{ M H}^+$  (aq).

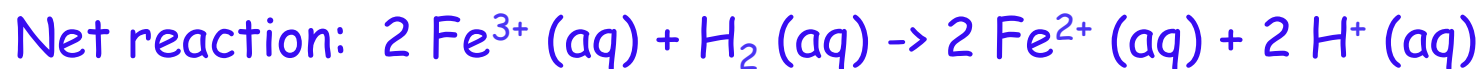
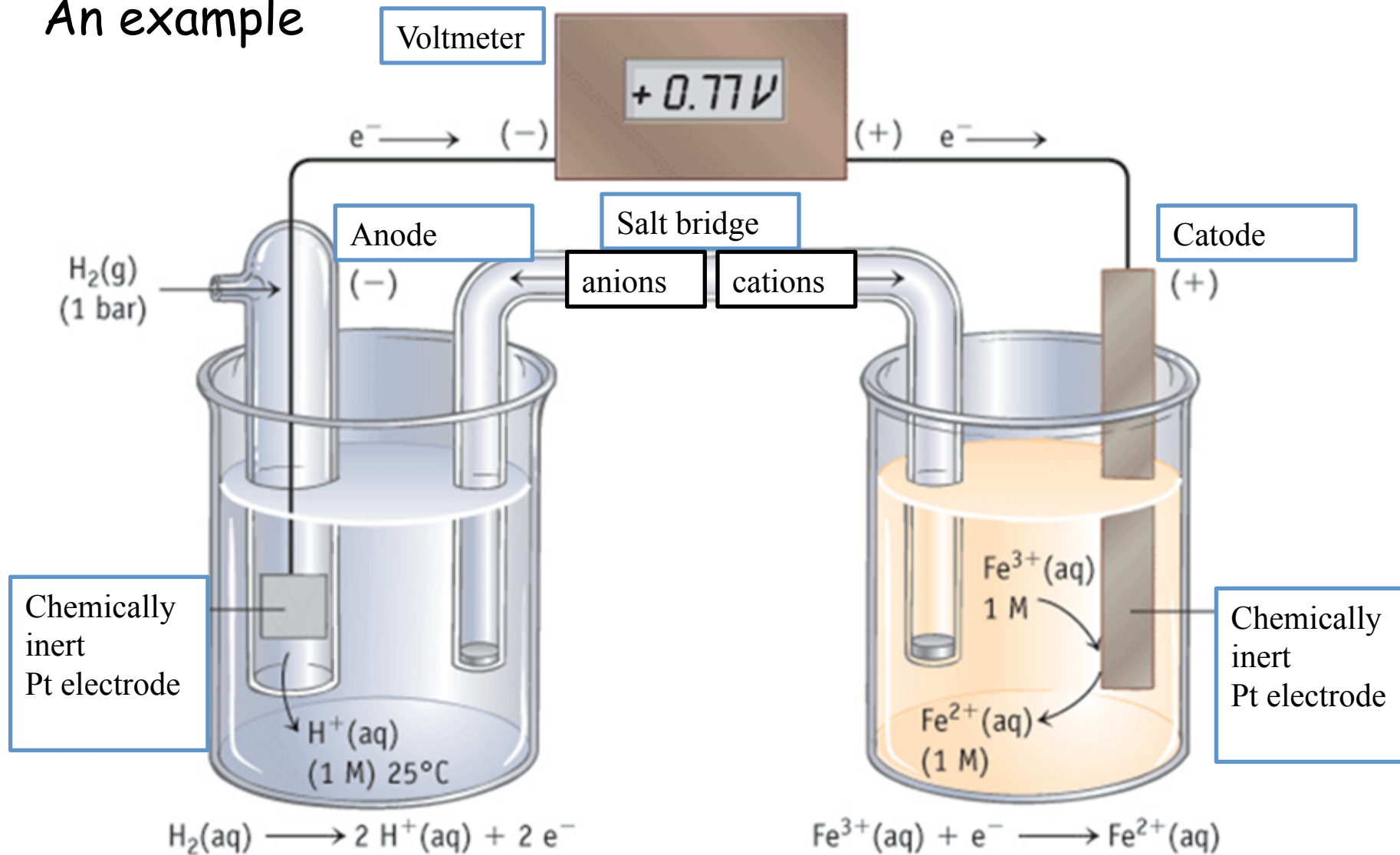
The oxidizing oxidation is:



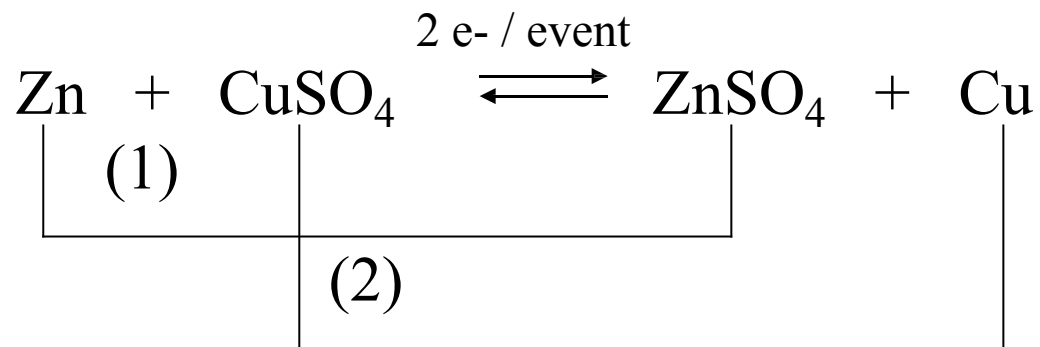
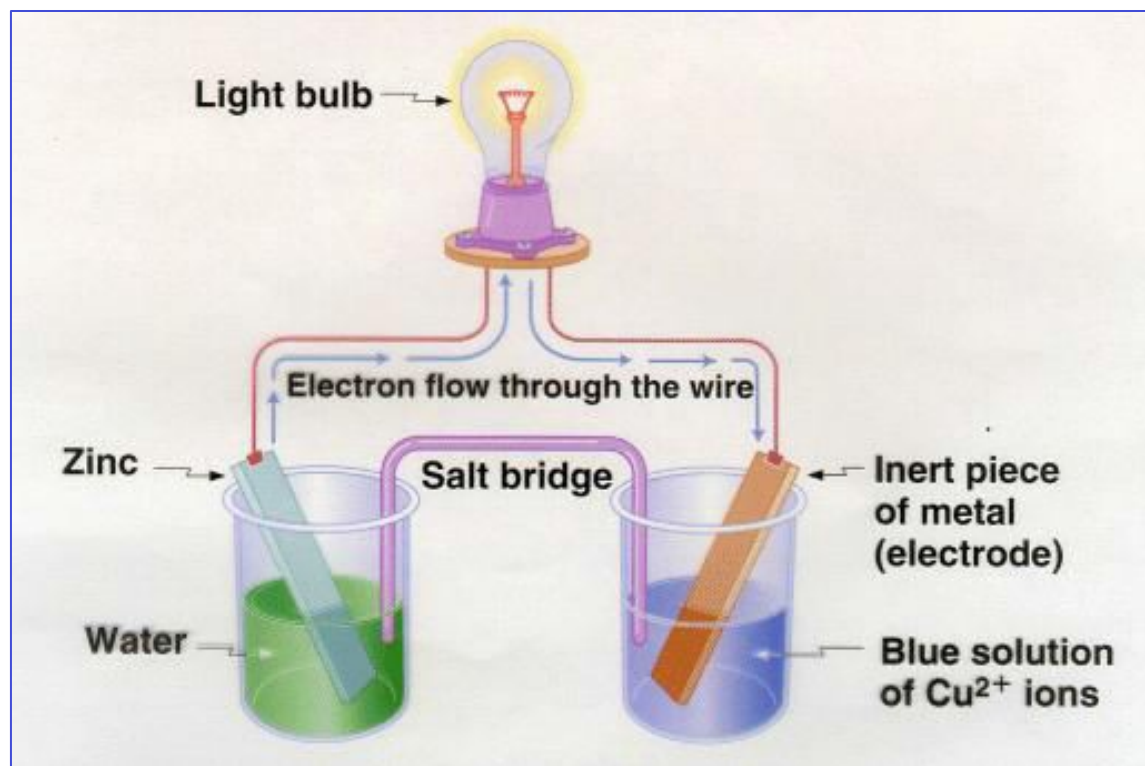
The reaction takes place on the surface of the electrode, and the electrons involved in the reaction are transferred through the electrode of Pt



# An example



1 *active* electrode (Zn) & 1 *passive (inert)* electrode (Pt)





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

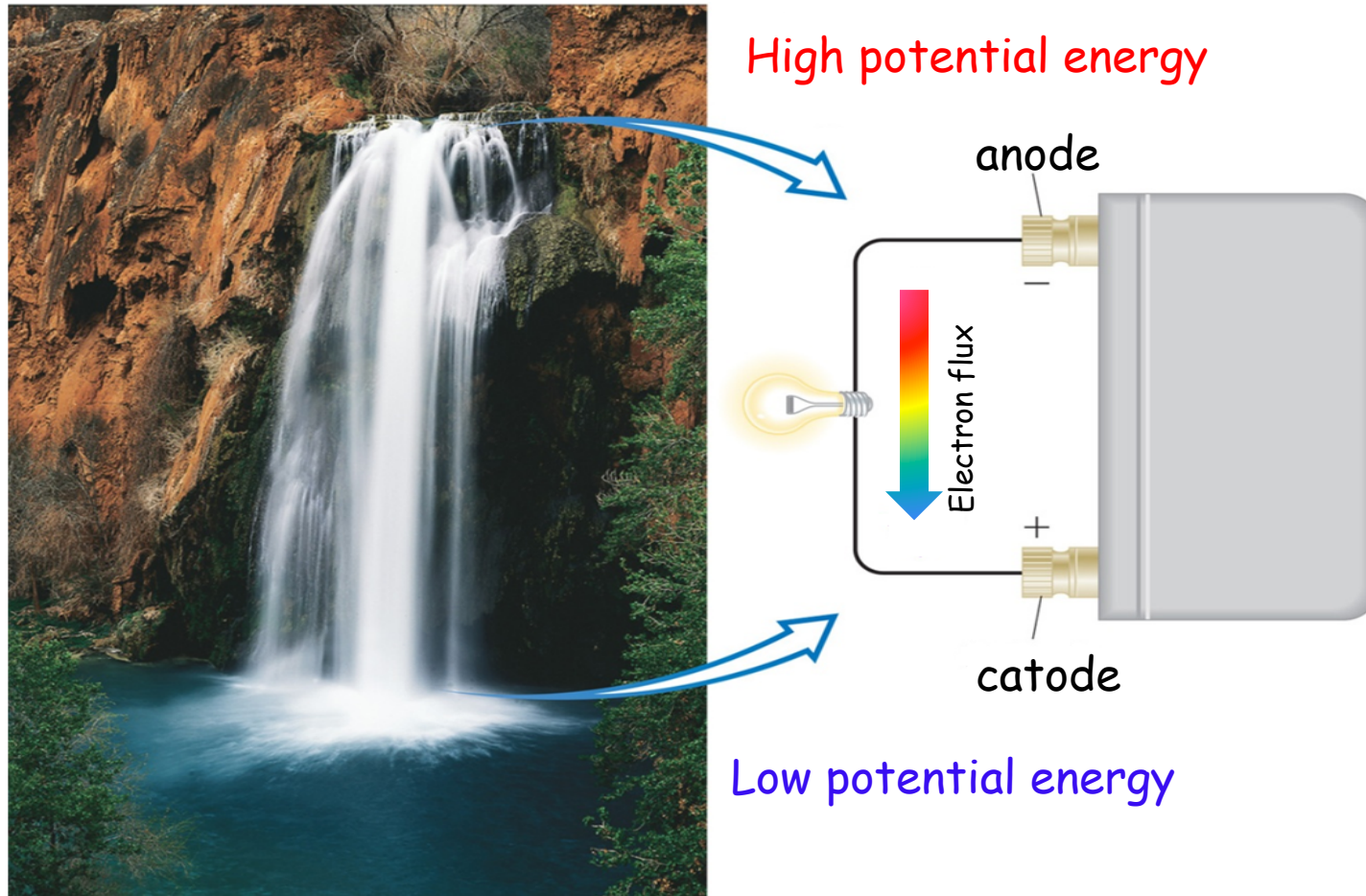


Is written as:



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)

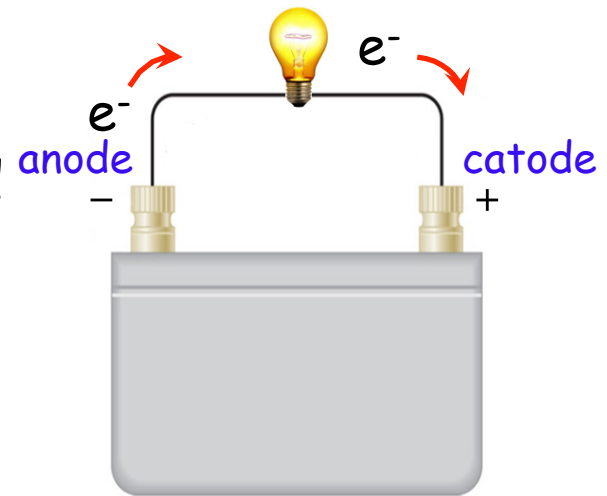


- $H_2O$  flows in one direction in a waterfall
- Electrons flow spontaneously from high to low potential energy.

# 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)
- **1 volt** is the potential difference necessary to transfer **1 joule** of energy to an electrical charge of **1 coulomb** ( $1 \text{ V} = 1 \text{ J} \times 1 \text{ C}$ )
- **1 coulomb** is the amount of electric charge that passes through a circuit when a current of **1 ampere** flows for **1 second** ( $1 \text{ C} = 1 \text{ A} \times 1 \text{ s}$ )

# Measurement of standard electrochemical potentials

We want to study the voltage of 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** :

- $T = 298 \text{ K}$
- Solutes at  $1 \text{ M}$  and gases at  $1 \text{ bar}$

A potential measured at standard conditions is called standard potential  $\Delta E^\circ_{\text{cell}}$

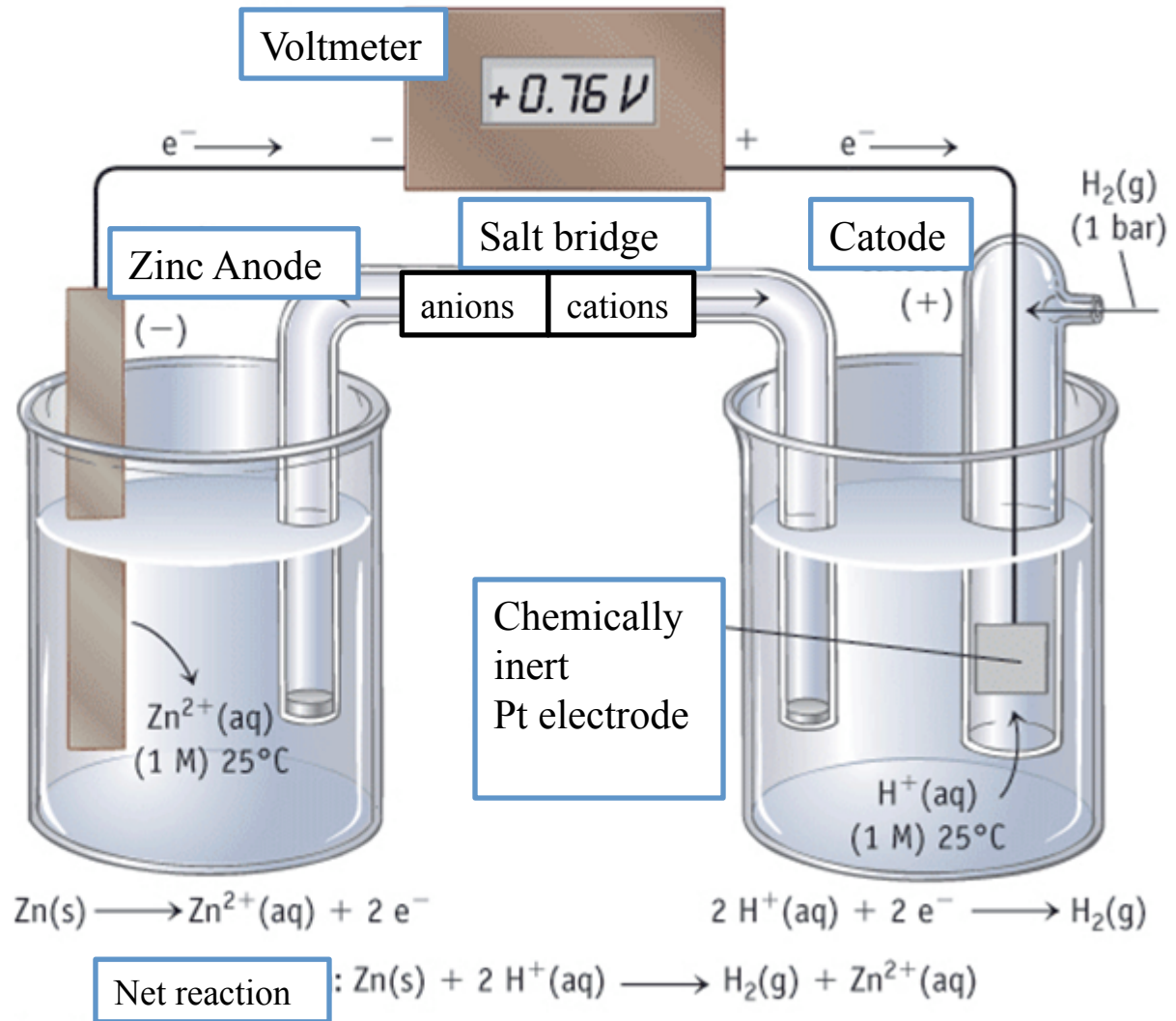
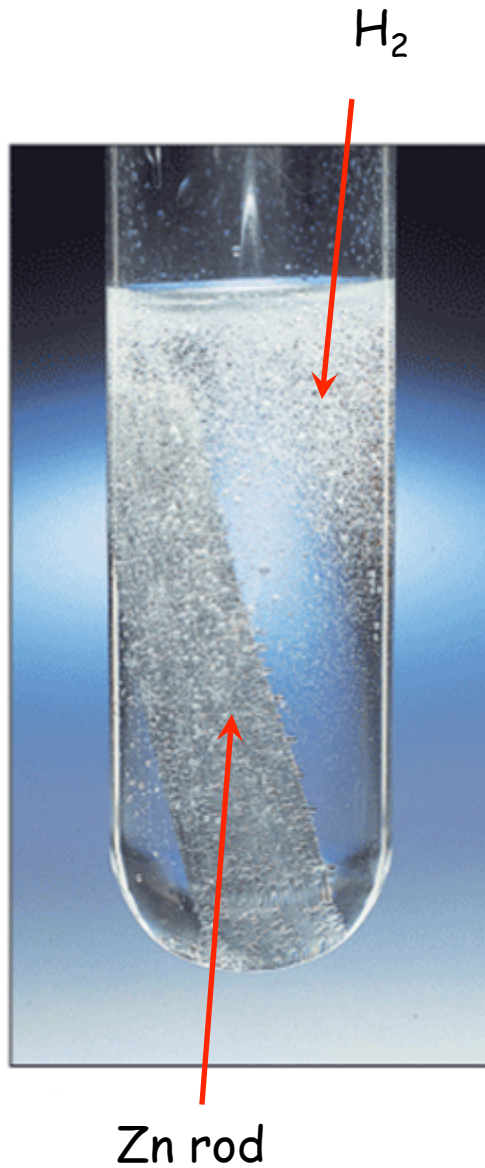
In thermochemistry and thermodynamics standard conditions are: (STP acronym of Standard Temperature Pressure)  $25^{\circ}\text{C}$  -  $298,15\text{ K}$ - and  $1\text{ atm}$ .

These refer to reactions in which gases are formed and consumed. In these cases, normally, one considers gas volumes and not moles.

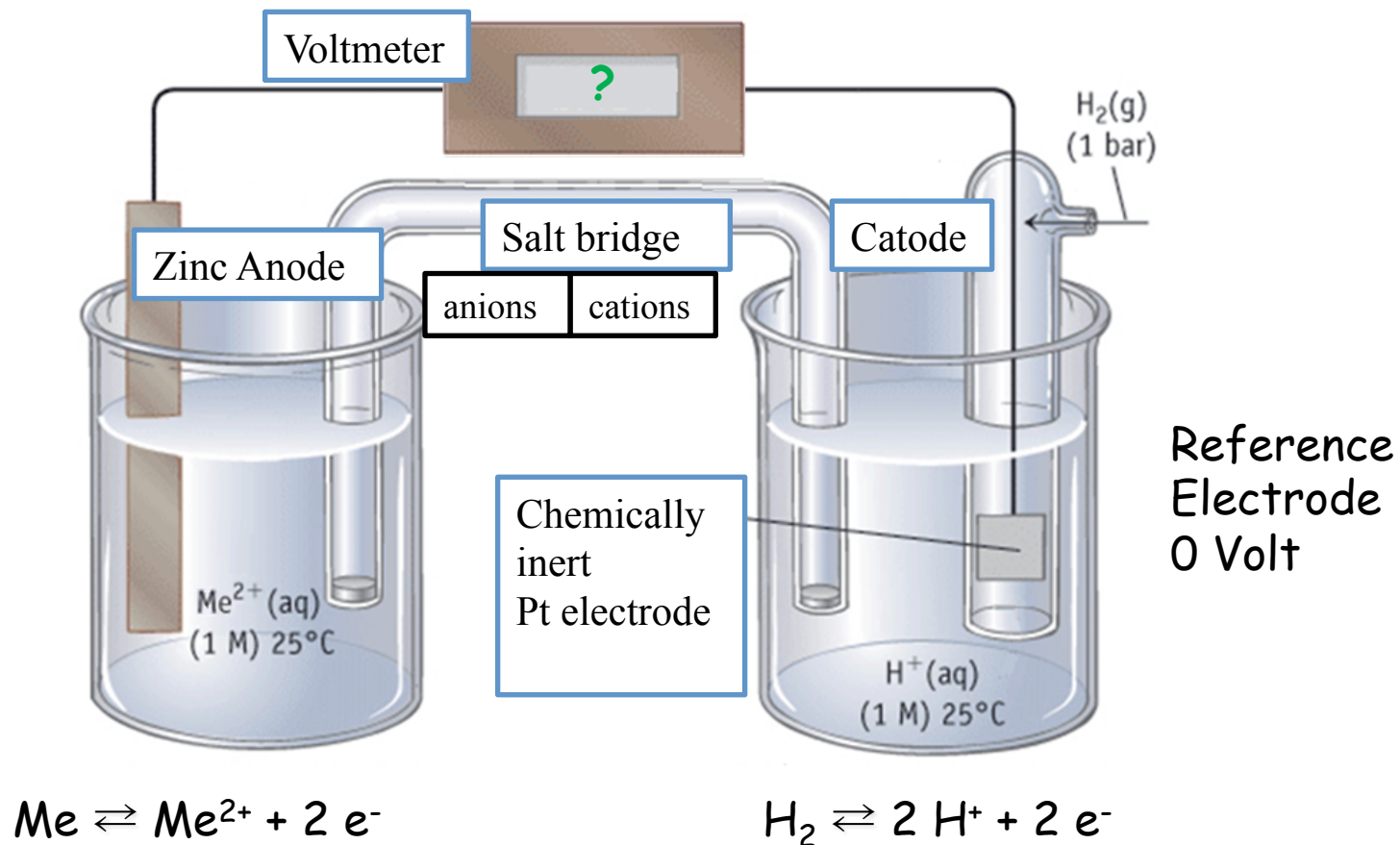
If unspecified one intends normal conditions  $273,15\text{ K}$  ( $20^{\circ}\text{C}$ ) e  $1\text{ atm}$ .

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

# A battery at standard conditions



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

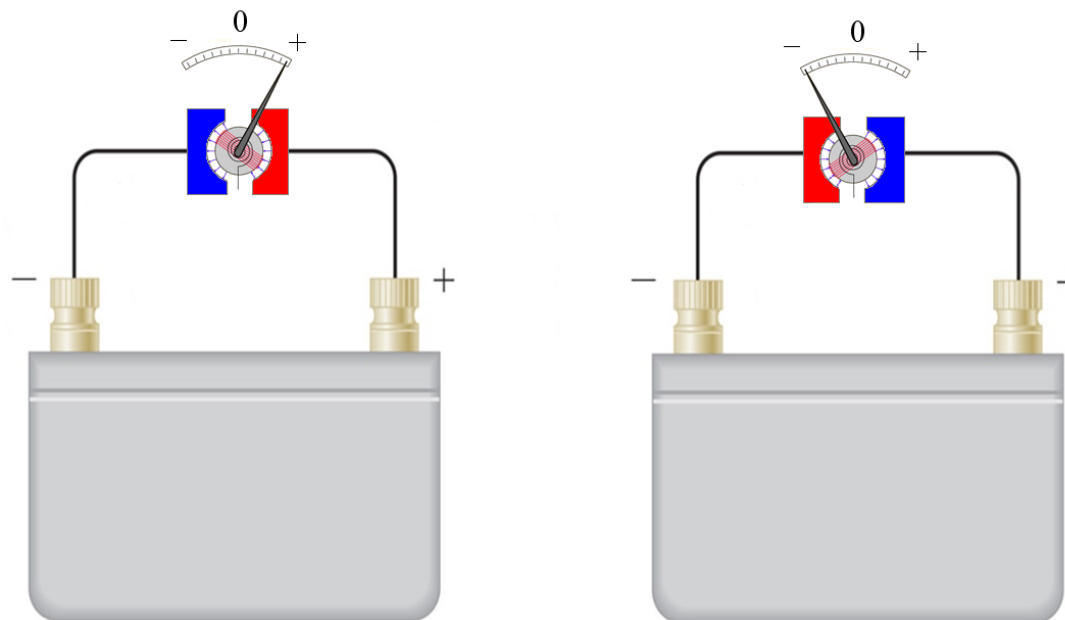


What will be the reaction's direction? Which one is the catode and which one is the anode?

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

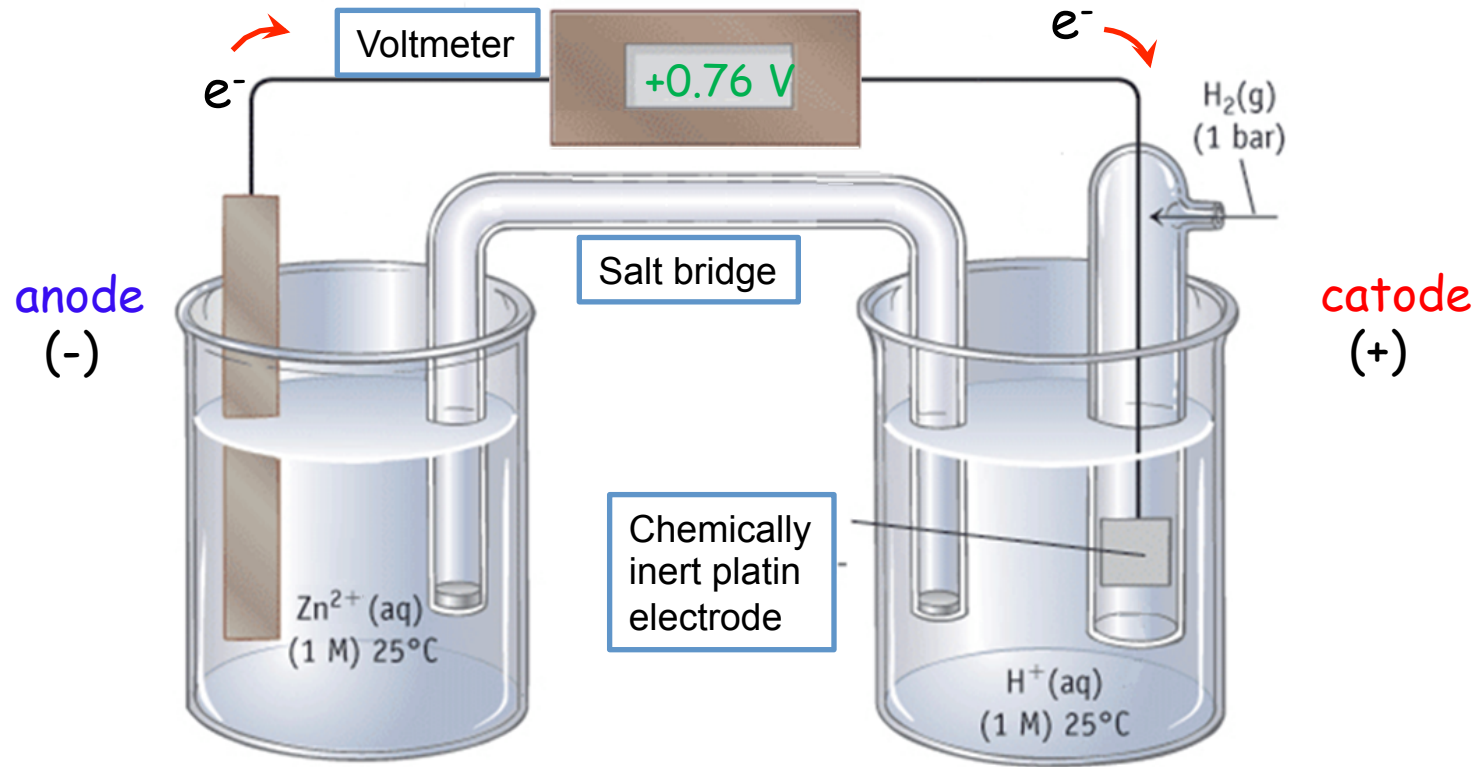
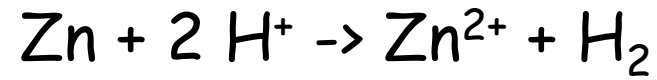
In a voltaic cell, electrons go from positive to negative, moving from anode to catode.

A voltmeter allows one to establish the flow direction.



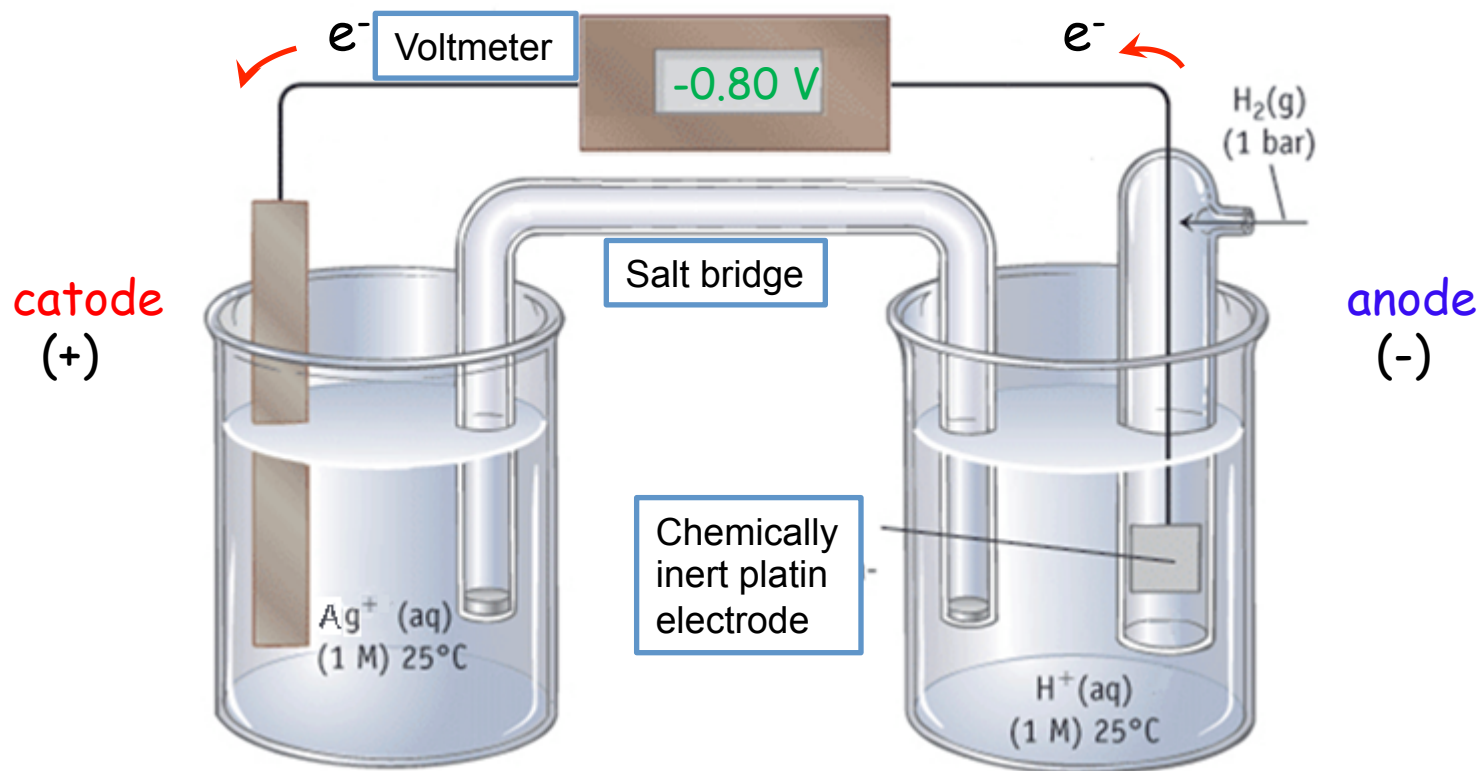
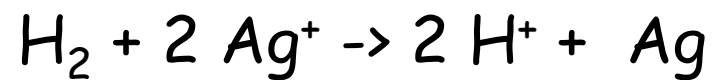
We measure a positive potential if the positive terminal of the voltmeter is connected to the catode (and vice versa).





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

right half cell  
 $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$



Left half cell  
 $\text{Ag} \leftarrow \text{Ag}^+ + e^-$

Right half cell  
 $2 \text{H}^+ + 2 e^- \leftarrow \text{H}_2$

## Standard redox potentials

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



$$\Delta E^\circ_{\text{cell}} = E^\circ_{\text{catode}} - E^\circ_{\text{anode}}$$

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

- knowing  $E^\circ_{\text{catode}}$  and  $E^\circ_{\text{anode}}$  one can calculate the standard redox potential  $\Delta E^\circ_{\text{cell}}$  of a voltaic cell
- when  $\Delta E^\circ_{\text{cell}}$  is positive the reaction is spontaneous

TABLE 18.1

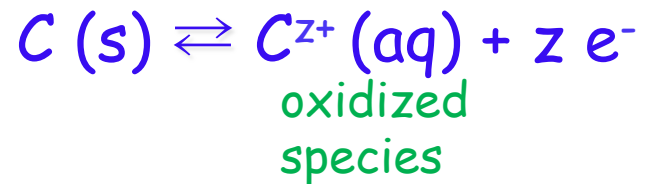
Standard Reduction Potentials at 25°C

	Reduction Half-Reaction	$E^\circ$ (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			
	Weaker oxidizing agent	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$		-0.13	Stronger reducing agent
		$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$		-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			
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04			

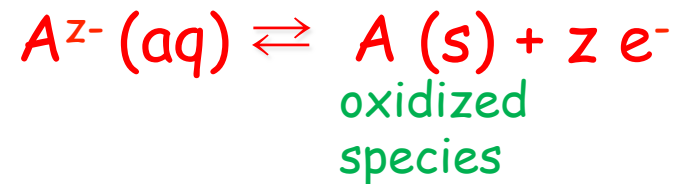
# Nernst equation

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

reduced  
species



reduced  
species



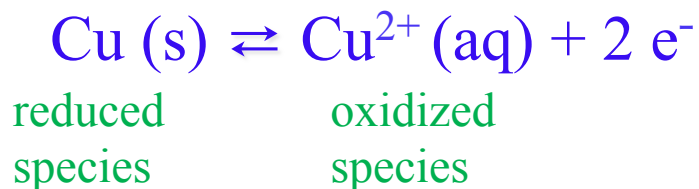
One can demonstrate that the half cell potential is:

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

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

## Nernst law

Example 1: we prepare a Cu electrode in equilibrium with Cu(II) ions  
[Cu<sup>2+</sup>] = 0.1 M, knowing that E° = 0.34 V a 25 °C

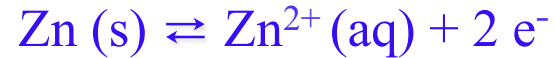


$$E = E^{\circ} + \frac{RT}{zF} \ln \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

The electrode potential (compared to the hydrogen reference one)

$$\begin{aligned} E_{\text{Cu/Cu}^{2+}} &= E^{\circ}_{\text{Cu/Cu}^{2+}} + \frac{RT}{2F} \ln[\text{Cu}^{2+}] \\ &= 0.34 + \frac{8.314 \cdot 298}{2 \cdot 96487} \ln(0.1) = 0.31 \text{ V} \end{aligned}$$

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



The electrode potential (compared to the hydrogen reference one)

$$\begin{aligned} E_{Zn/Zn^{2+}} &= E_{Zn/Zn^{2+}}^\circ + \frac{RT}{2F} \ln[Zn^{2+}] \\ &= -0.76 + \frac{8.314 \cdot 298}{2 \cdot 96487} \ln(0.1) = -0.79 \text{ V} \end{aligned}$$

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

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

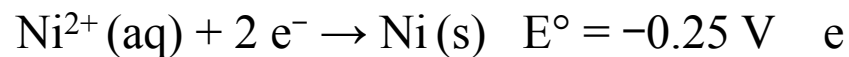
Example 2: a voltaic cell is:

Half cell a:  $\text{Al (s)} \mid \text{Al}^{3+} \text{ (aq)} \text{ (0.001 M)}$

Half cell b:  $\text{Ni (s)} \mid \text{Ni}^{2+} \text{ (aq)} \text{ (0.5 M)}$

Calculate the cell potential.

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



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





In standard conditions the emf is:

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



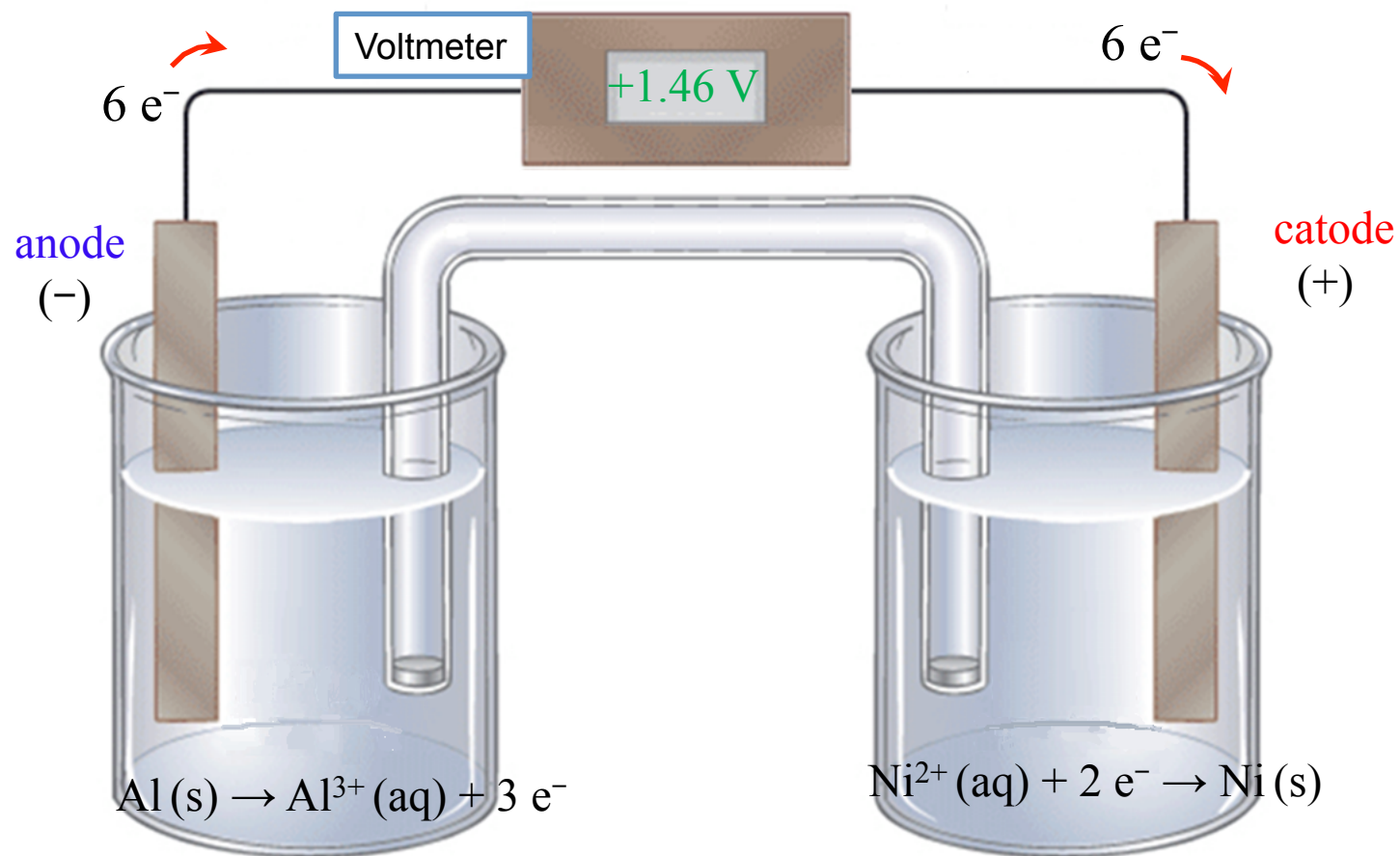
TABLE 18.1

Standard Reduction Potentials at 25°C

	Reduction Half-Reaction	$E^\circ$ (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	
	Weaker oxidizing agent	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-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	
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	

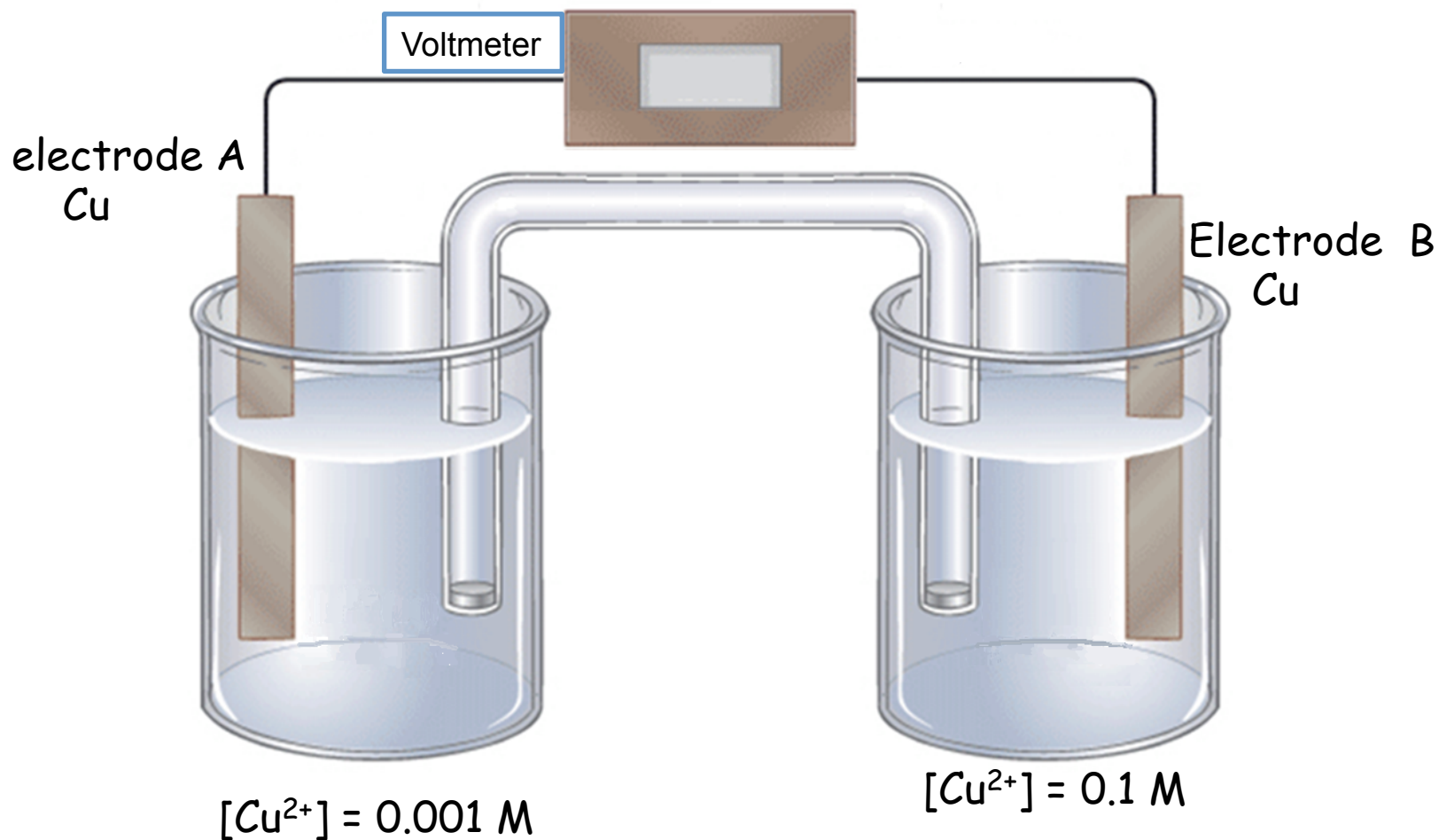


$$\Delta E_{\text{cell}} = \Delta E_{\text{cell}}^0 + \frac{RT}{nF} \ln \frac{[\text{Ni}^{2+}]^3}{[\text{Al}^{3+}]^2} = 1.41 + \frac{8.314 \cdot 298}{6 \cdot 96487} \ln \frac{0.5^3}{0.001^2} = 1.46 \text{ V}$$

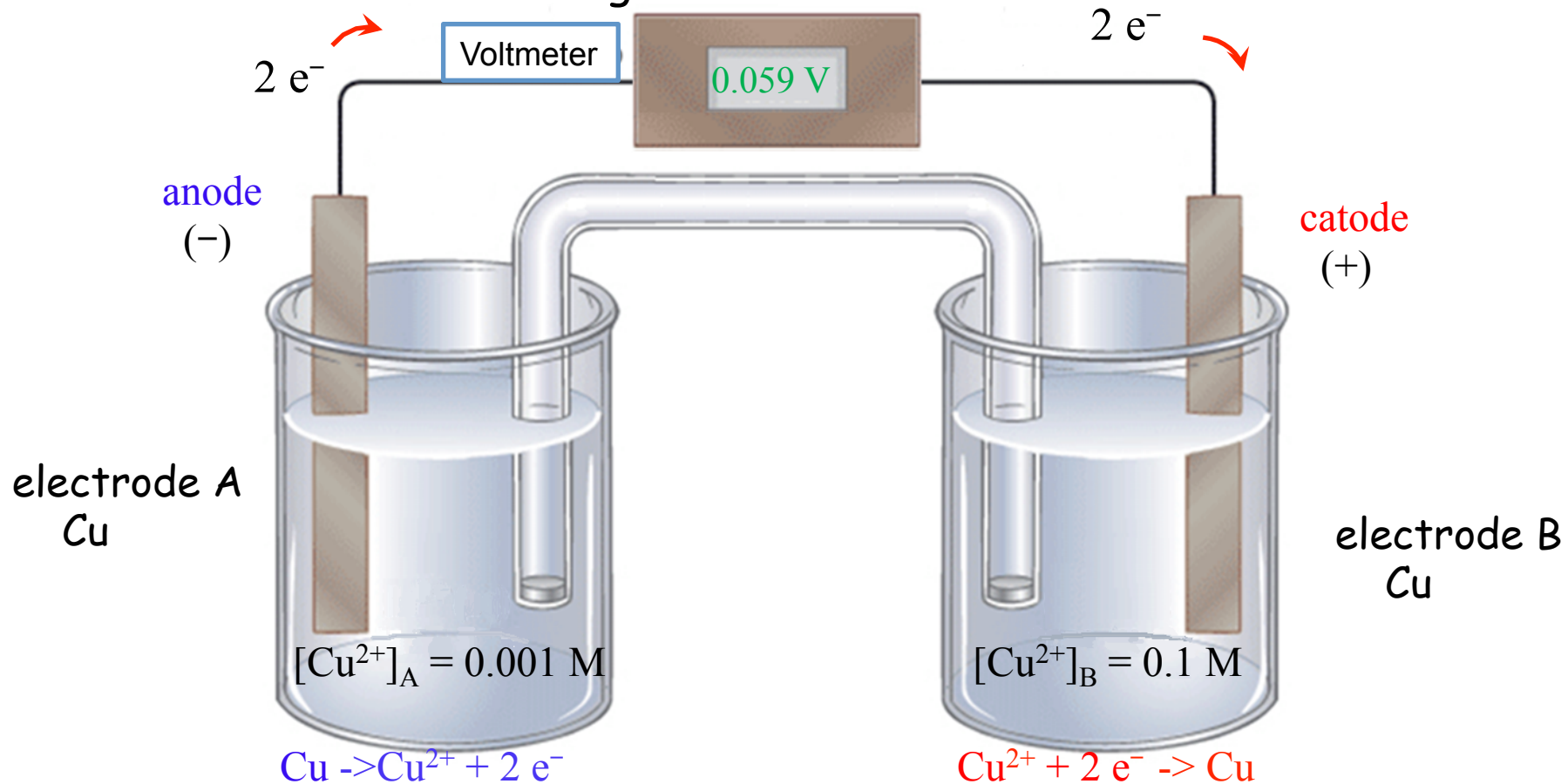


## Concentration cell

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



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



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

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

# A relevant application of the concentration electrode: the pHmeter



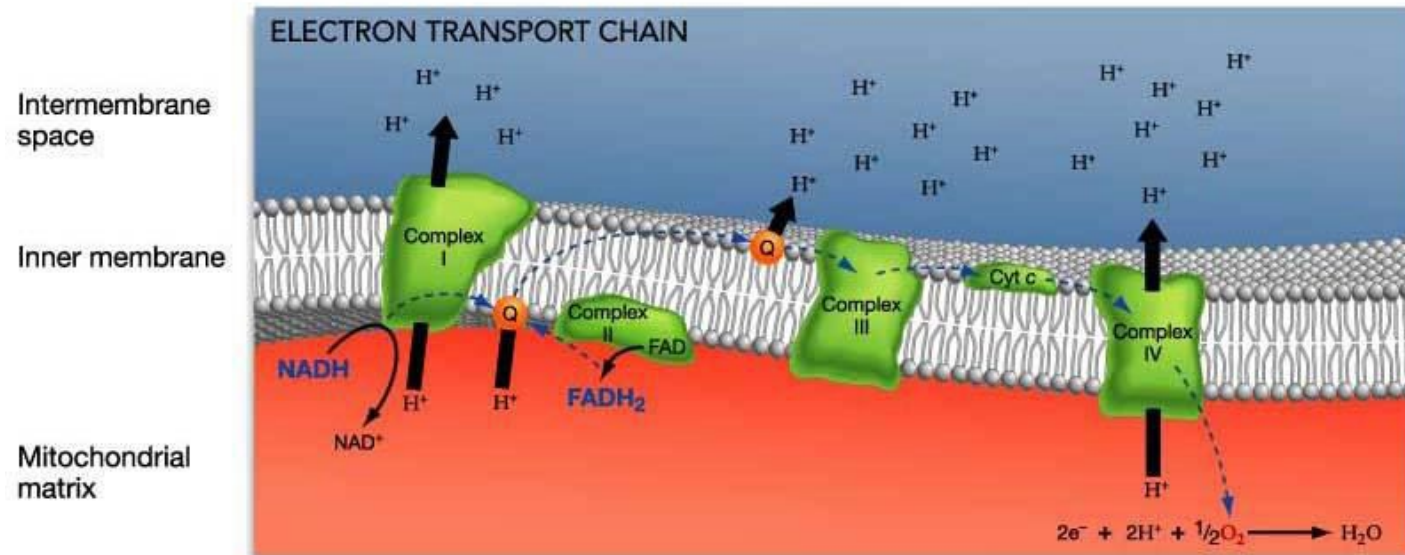
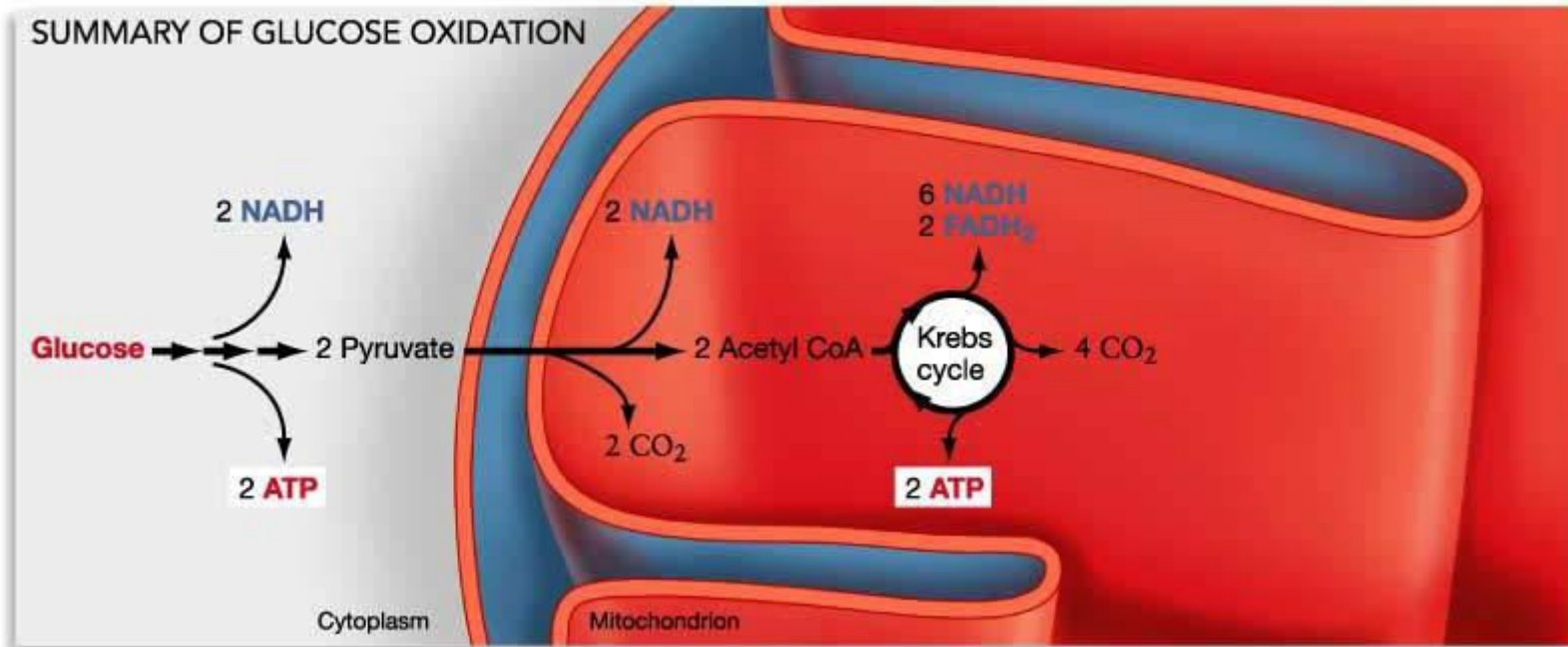
## Relationship between emf and the equilibrium constant K

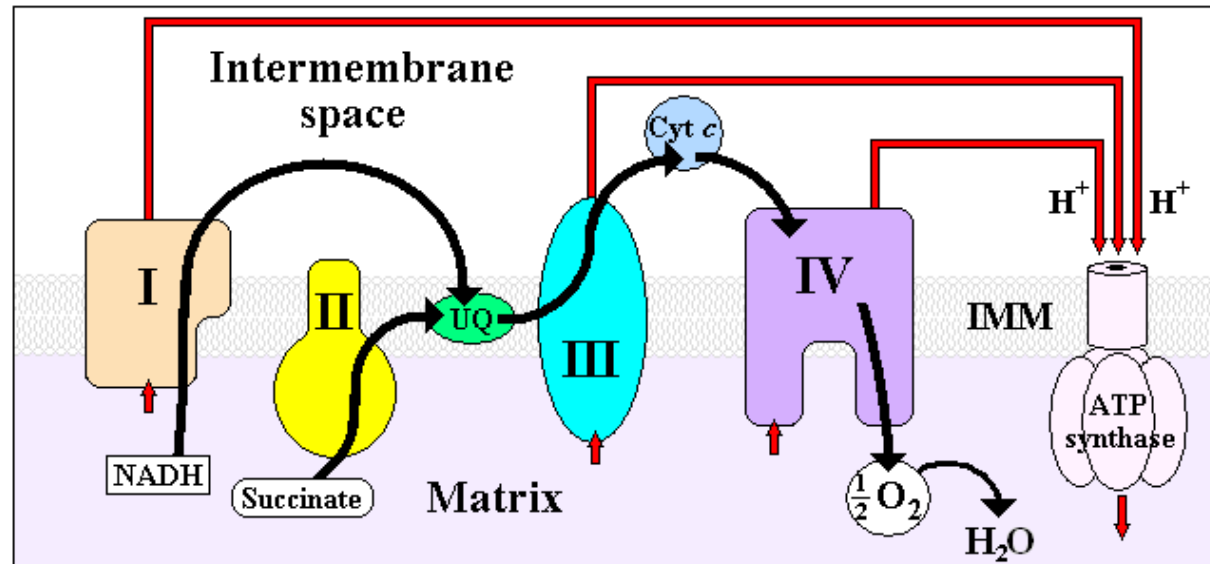
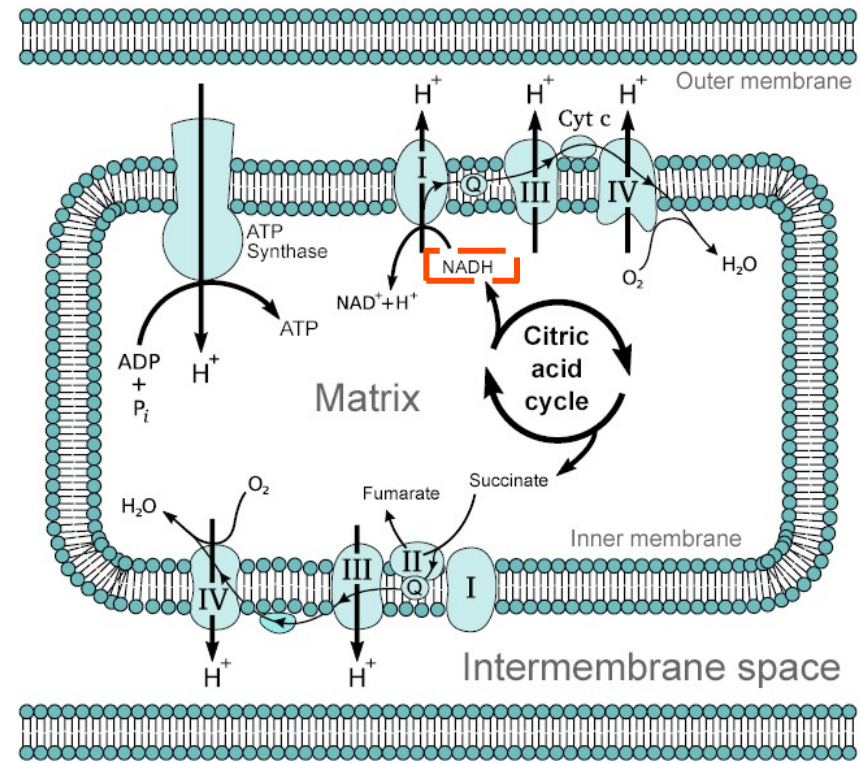
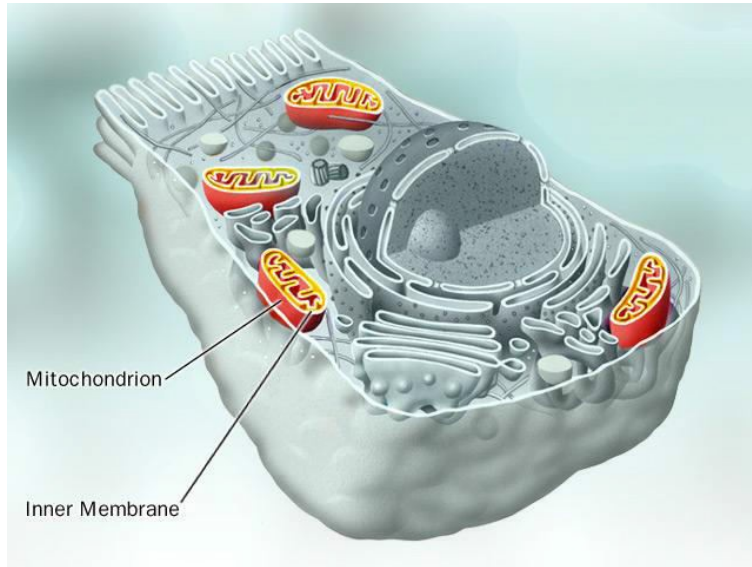
Using thermodynamics it is possible to demonstrate that the free energy change of a reaction is equal to the maximum useful work that that reaction can produce to T and P constants. This corresponds to the electric work produced by a cell, and referring to reagents and products in standard conditions:

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

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

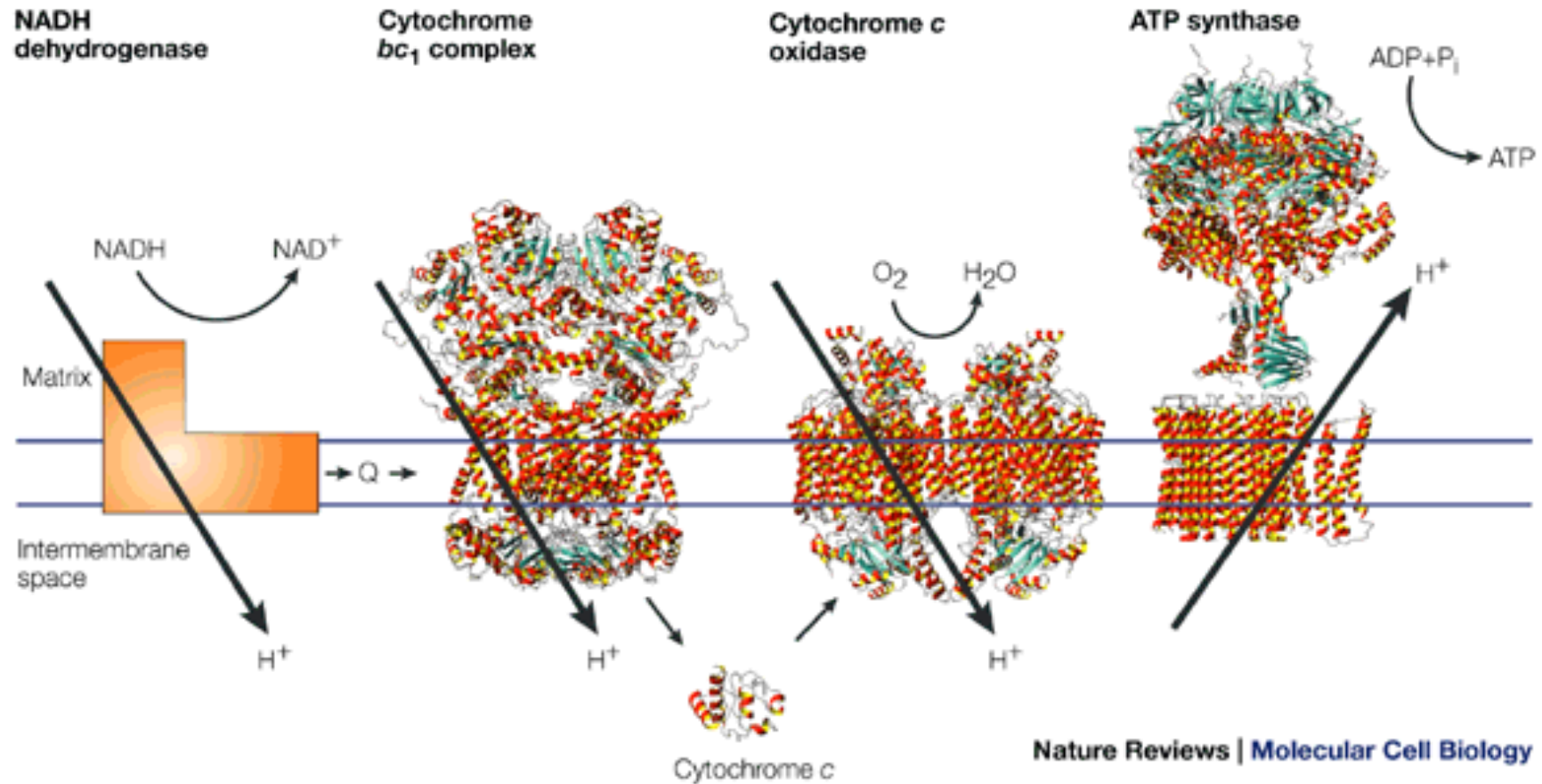
$$\Delta G^{\circ} = -z \cdot F \cdot \Delta E^{\circ} = -RT \ln K_{\text{EQ}}$$







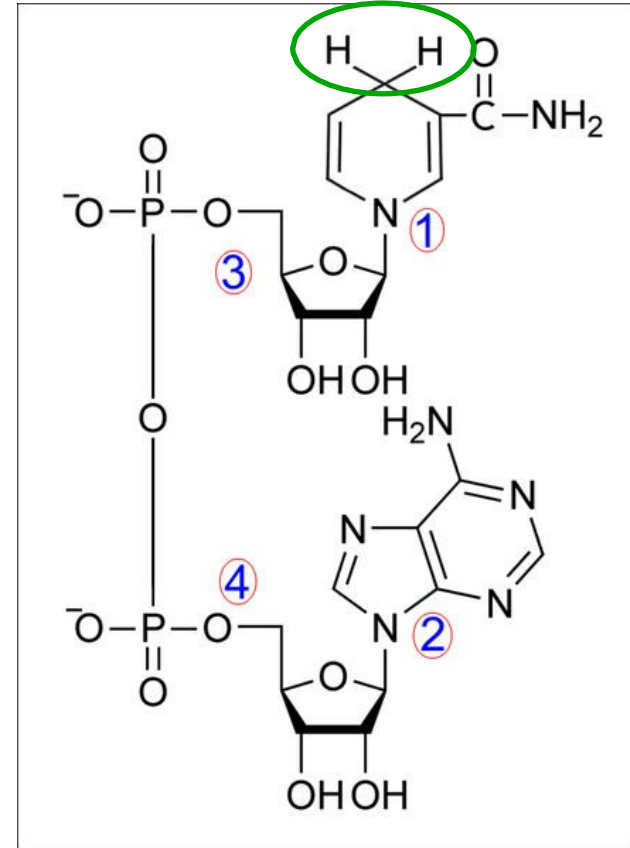
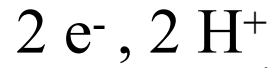
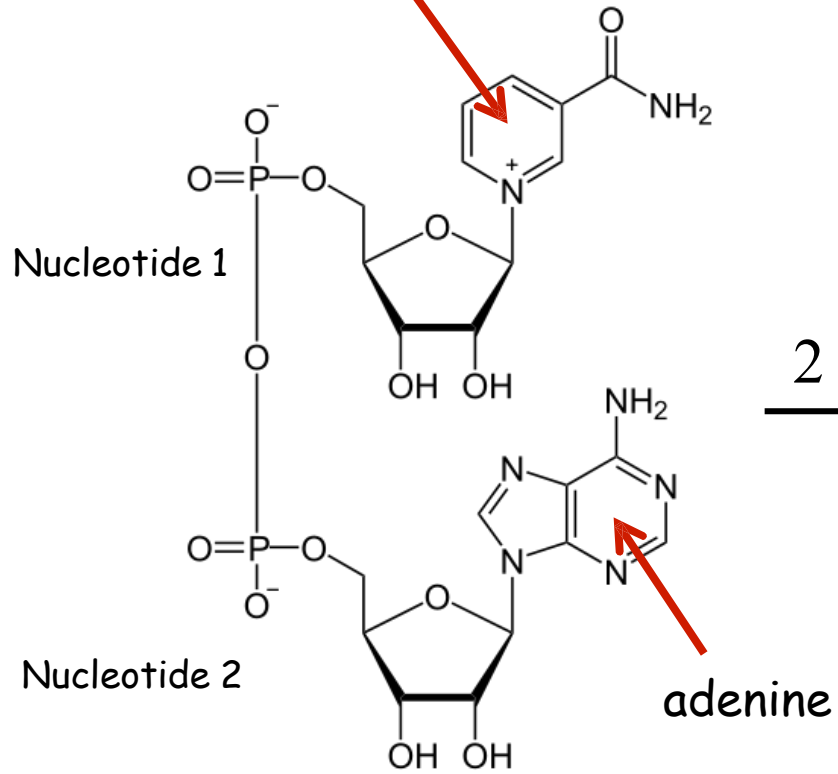
# The Respiratory Chain

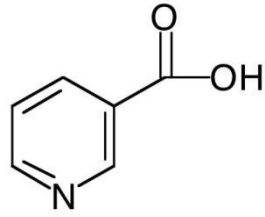


Yoshida et al. (2001)

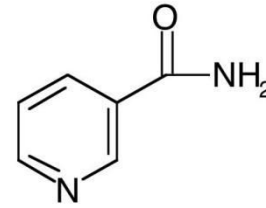
# NADH

nicotinamide

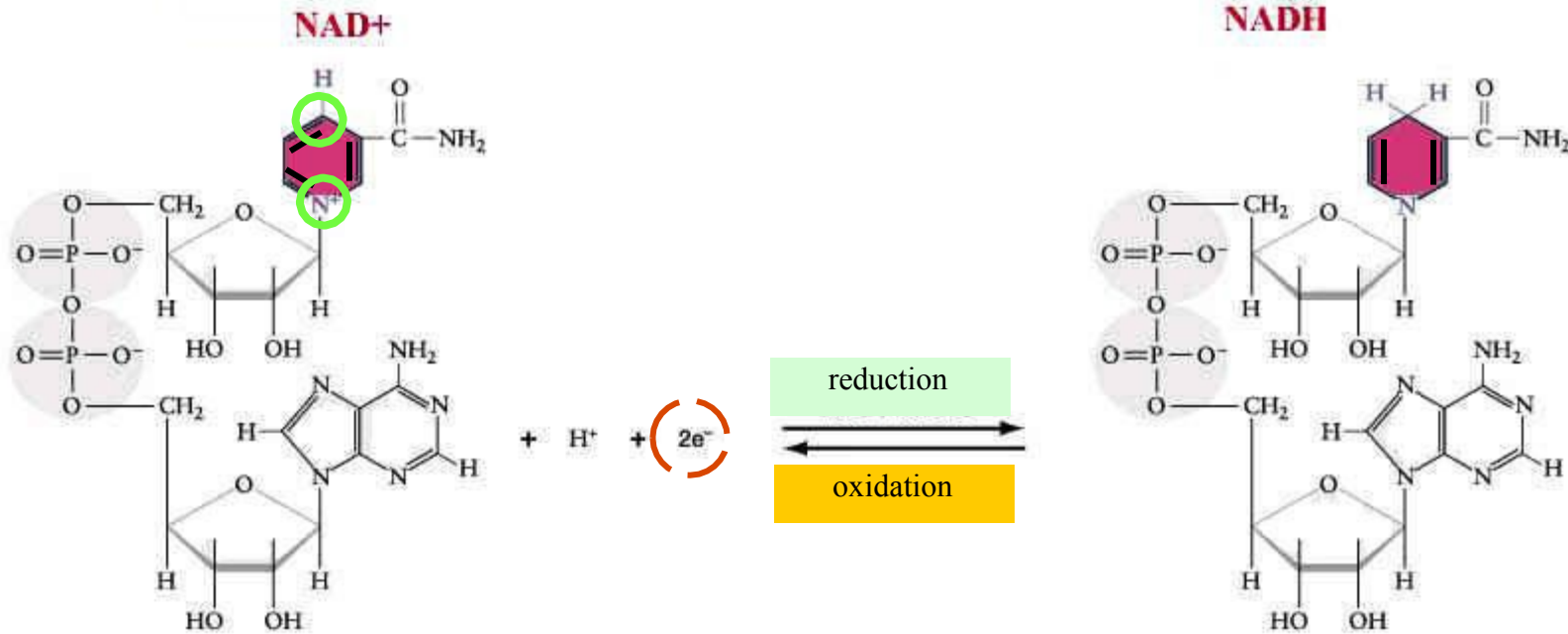




Nicotinic acid



nicotinamide

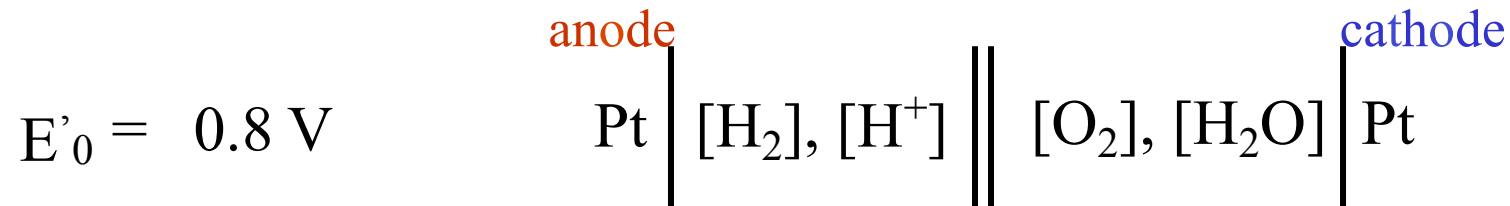


(standard potential)  $E^{\circ} = -0.28 \text{ V}$  (NAD<sup>+</sup>/NADH)

*emf* of respiratory chain (mitochondria)



*E'\_0 (approx.)*



$$\Delta E = fem = 0.8 - (-0.3) \approx 1.1 \text{ V}$$

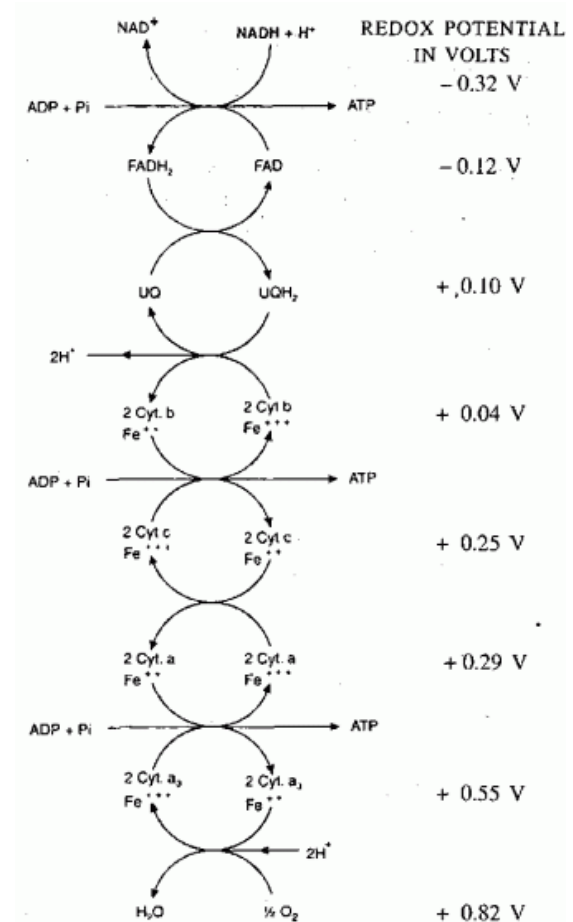
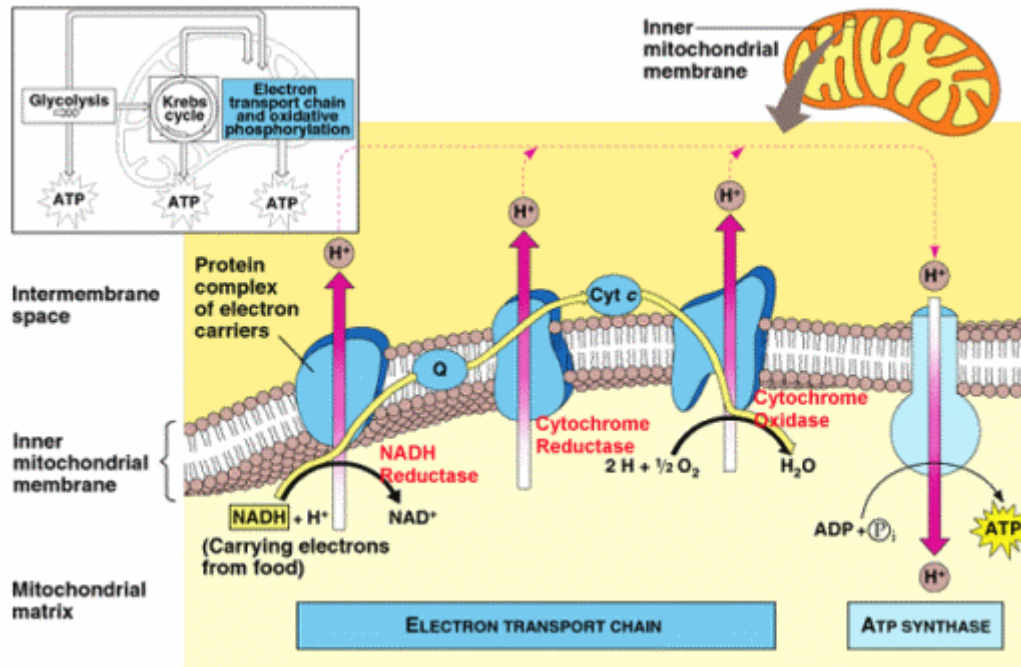


Fig. 5.3.3.3 : Electron transport system and oxidative phosphorylation

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