Chapter 20: Electrochemistry

Electrochemistry is the study of the relationships between *electricity (movement of charge)* and *chemical reactions*.

It includes the study of both spontaneous and nonspontaneous processes.

Two incredibly important processes:

1. **Using electrons to make stuff (electrolytic cells).**

Examples: Electroplating. Production of Aluminum.

2. Using chemical reactions to produce electricity (Galvanic or voltaic cells).

Batteries.

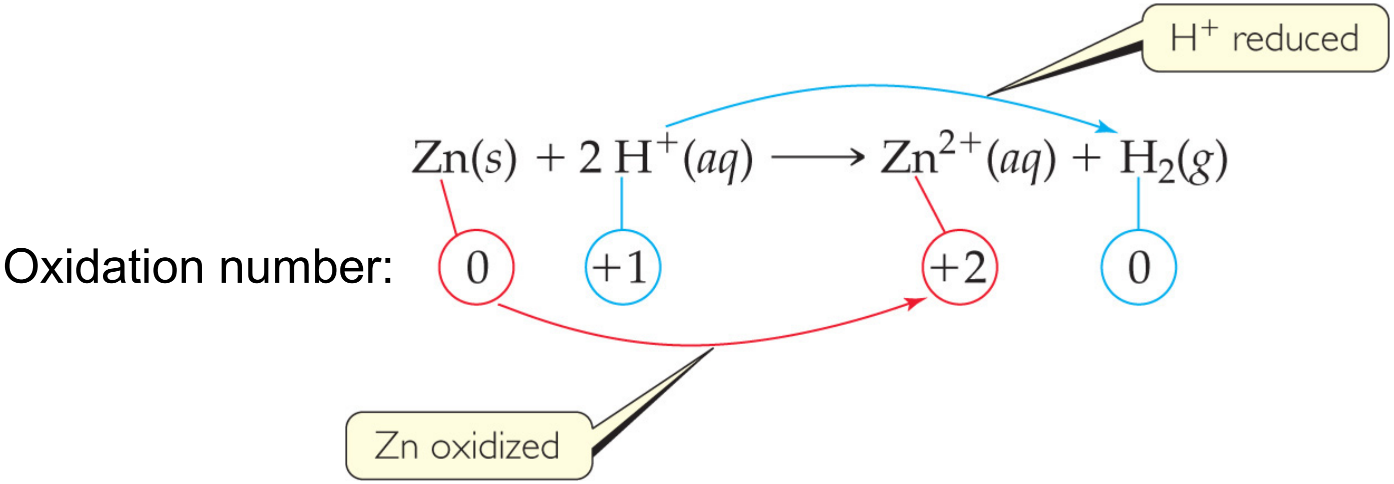
Liquid fuels (like gasoline): **chemical** energy **stored in atoms/compounds**
Batteries: Electrical energy stored in **atoms/ compounds.**

First step: Where do the electrons come from? Where do they go? Must Assign Oxidation Numbers (as a Reminder)

1. **Elements** (pure substance) = 0
2. Monatomic ion = charge
3. **F: –1**
4. **O: –2** (unless peroxide = –1)
5. **H: +1** (unless a metal hydride = –1)
6. The **sum** of the oxidation numbers **equals** the overall **charge** (0 in a compound).

Oxidation Numbers in “REDOX” reactions

- To keep track of which chemical species loses electrons and what gains them, we assign **oxidation numbers**.
- If the oxidation number **increases** for an element, that element is **oxidized** (loss of electron).
- If the oxidation number **decreases** for an element, that element is **reduced** (gain of electron).

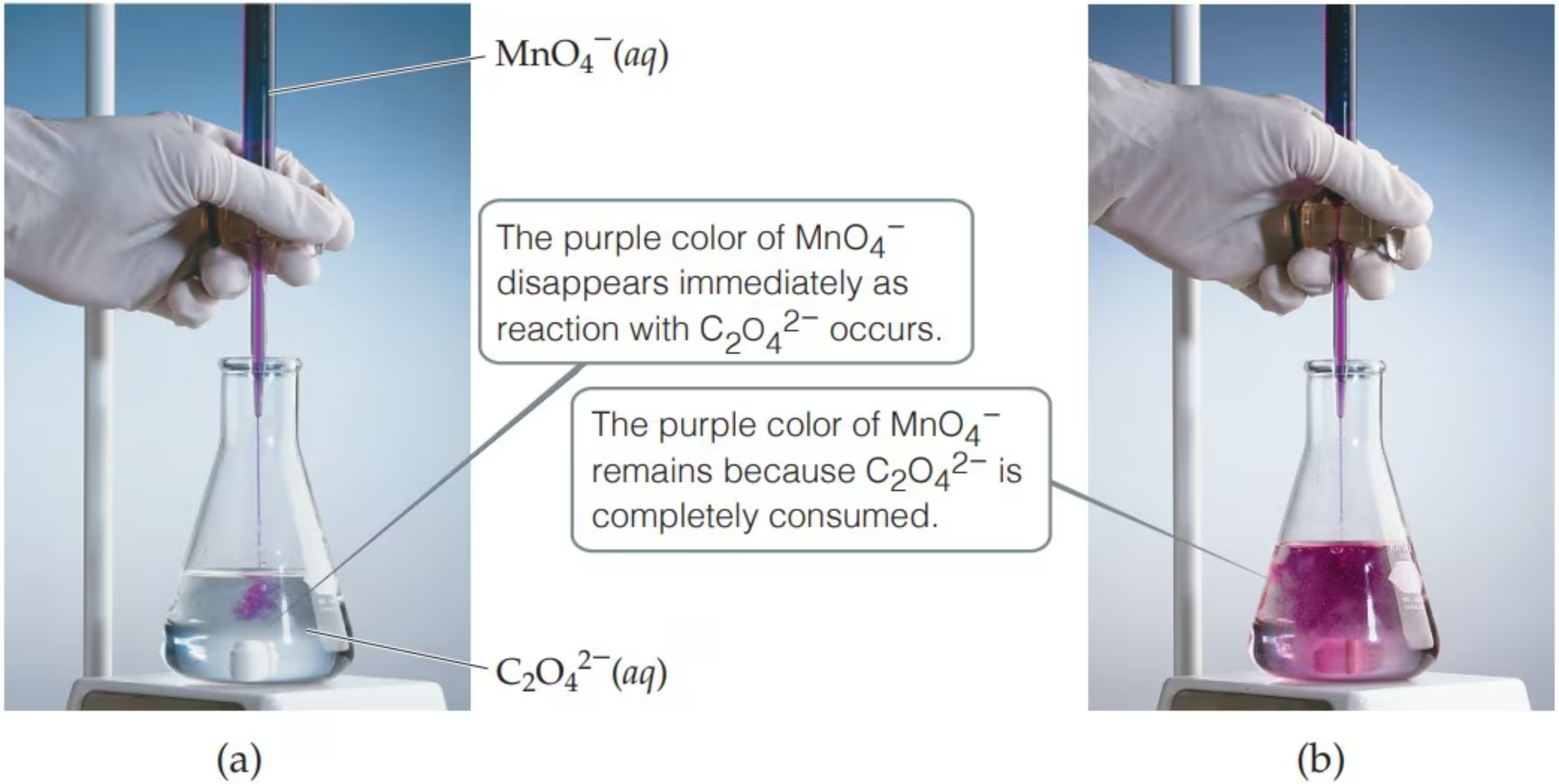


$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

- H$^+$ (when reduced) causes oxidation of something else (here, Zn). Thus, it is called an **“oxidizing agent**”
- Zn (when oxidized) causes reduction of something else (here H+). Thus, it is called a ”**reducing agent”.**

The Half-Reaction Method

Example: $MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$



The purple color of MnO_4^- disappears immediately as reaction with $C_2O_4^{2-}$ occurs.

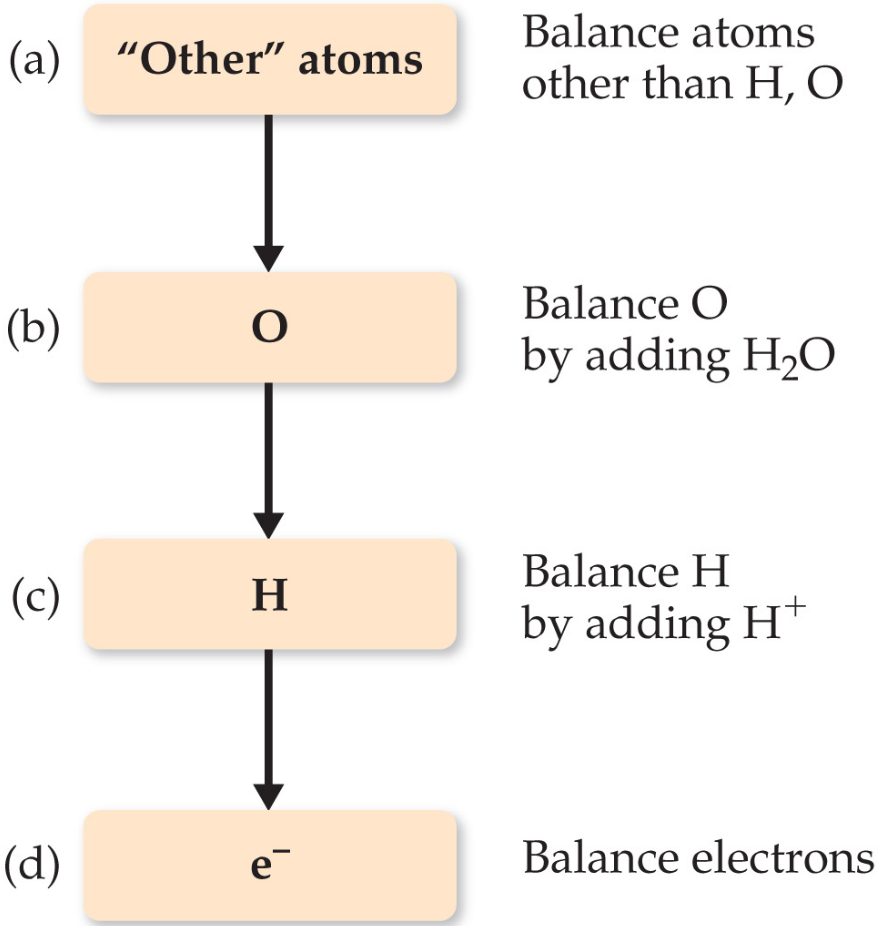
The purple color of MnO_4^- remains because $C_2O_4^{2-}$ is completely consumed.

(a)

(b)

Balancing Redox Equations: The Half-Reaction Method

1) Make two half-reactions (oxidation and reduction).
2) Balance elements **other** than O and H.
3) Balance O and H using H_2O/H^+.
4) Add **electrons** to balance **charges.**
5) Multiply by common factor to make electrons ***in each half-reaction*** equal.
6) **Add** the half-reactions.
7) Simplify by dividing by common factor or converting H^+ to OH^- if basic.
8) Double-check:
    1) Element balance
    2) charge balance!



(a) **"Other" atoms** — Balance atoms other than H, O

(b) **O** — Balance O by adding H_2O

(c) **H** — Balance H by adding H^+

(d) **e^-** — Balance electrons

The Half-Reaction Method

Example: $\overset{+7}{\mathrm{Mn}}\mathrm{O}_4^{-}(aq) + \overset{+3}{\mathrm{C}}_2\mathrm{O}_4^{2-}(aq) \longrightarrow \overset{+2}{\mathrm{Mn}}^{2+}(aq) + \overset{+4}{\mathrm{C}}\mathrm{O}_2(aq)$

2 half reactions:

Mn is **reduced** (+7 → +2), C is **oxidized** (+3 → +4).

The Half-Reaction Method

Example: $\overset{+7}{\mathrm{Mn}}\mathrm{O_4^-}(aq) + \overset{+3}{\mathrm{C}}\mathrm{_2O_4^{2-}}(aq) \longrightarrow \overset{+2}{\mathrm{Mn}}\mathrm{^{2+}}(aq) + \overset{+4}{\mathrm{C}}\mathrm{O_2}(aq)$

2 half reactions:

Mn is **reduced** (+7 → +2), C is **oxidized** (+3 → +4).

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$

a. Balance atoms other than O and H

The manganese is balanced;

b. Balance O with water.

to balance the oxygen, we must **add four waters** to the right side: $\mathbf{MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O}$

c. Balance H with H^+

To balance the hydrogen, we **add $8H^+$** to the left side:

$$8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

d. Balance charge with e^-

To balance the charge, we add $5e^-$ to the left side:

$$\boxed{5e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O}$$

The Half-Reaction Method

Example: $\overset{+7}{\mathrm{Mn}}\mathrm{O_4^-}(aq) + \overset{+3}{\mathrm{C}}_2\mathrm{O_4^{2-}}(aq) \longrightarrow \overset{+2}{\mathrm{Mn}}{}^{2+}(aq) + \overset{+4}{\mathrm{C}}\mathrm{O_2}(aq)$

2 half reactions:
Mn is **reduced** (+7 → +2), C is **oxidized** (+3 → +4).

Oxidation Half-Reaction

$$\mathrm{C_2O_4^{2-}} \longrightarrow \mathrm{CO_2}$$

a. Balance atoms other than O and H

To balance the carbon, we add a coefficient of 2:

$$\mathrm{C_2O_4^{2-}} \longrightarrow 2\ \mathrm{CO_2}$$

b. Balance O with water (skip)

The oxygen is now balanced as well.

c. Balance H with H⁺ (skip)

There is no H in the reaction.

d. Balance charge with e⁻

To balance the charge, we must add two electrons to the right side:

$$\boxed{\mathrm{C_2O_4^{2-}} \longrightarrow 2\ \mathrm{CO_2} + 2e^-}$$

The Half-Reaction Method: combine the two half-reactions

Oxidation Half-Reaction $$C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2e^-$$

Reduction Half-Reaction $$5e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$$

The Half-Reaction Method: combine the two half-reactions

Oxidation Half-Reaction $C_2O_4^{2-} \longrightarrow 2\ CO_2 + 2e^-$

Reduction Half-Reaction $5e^- + 8\ H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\ H_2O$

Balance the half reactions.

The number of electrons ***must*** be equal on each side,:

multiply the first reaction by 5, second by 2:

Oxidation Half-Reaction $5\ C_2O_4^{2-} \longrightarrow 10\ CO_2 + 10e^-$

Reduction Half-Reaction $10e^- + 16\ H^+ + 2\ MnO_4^- \longrightarrow 2\ Mn^{2+} + 8\ H_2O$

The Half-Reaction Method: combine the two half-reactions

Oxidation Half-Reaction $C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2e^-$

Reduction Half-Reaction $5e^- + 8\,H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$

Balance the half reactions. The number of electrons ***must*** be equal on each side,:

Oxidation Half-Reaction $5\,C_2O_4^{2-} \longrightarrow 10\,CO_2 + 10e^-$

Reduction Half-Reaction $10e^- + 16\,H^+ + 2\,MnO_4^- \longrightarrow 2\,Mn^{2+} + 8\,H_2O$

Add the two reactions
Cancel out electrons:

$$\cancel{10e^-} + 16\,H^+ + 2\,MnO_4^- + 5\,C_2O_4^{2-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2 + \cancel{10e^-}$$

The final equation:

$$16\,H^+ + 2\,MnO_4^- + 5\,C_2O_4^{2-} \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2$$

Verify that the equation is balanced by counting atoms and charges on each side!

The Half-Reaction Method

Example 2: $Cr_2O_7^{2-}{}_{(aq)} + Cl^-{}_{(aq)} \longrightarrow Cr^{3+}{}_{(aq)} + Cl_{2\,(g)}$

$14\ H^+ + Cr_2O_7^{2-}{}_{(aq)} + 6\ Cl^-{}_{(aq)} \longrightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O + 3\ Cl_{2\,(g)}$

The Half-Reaction Method

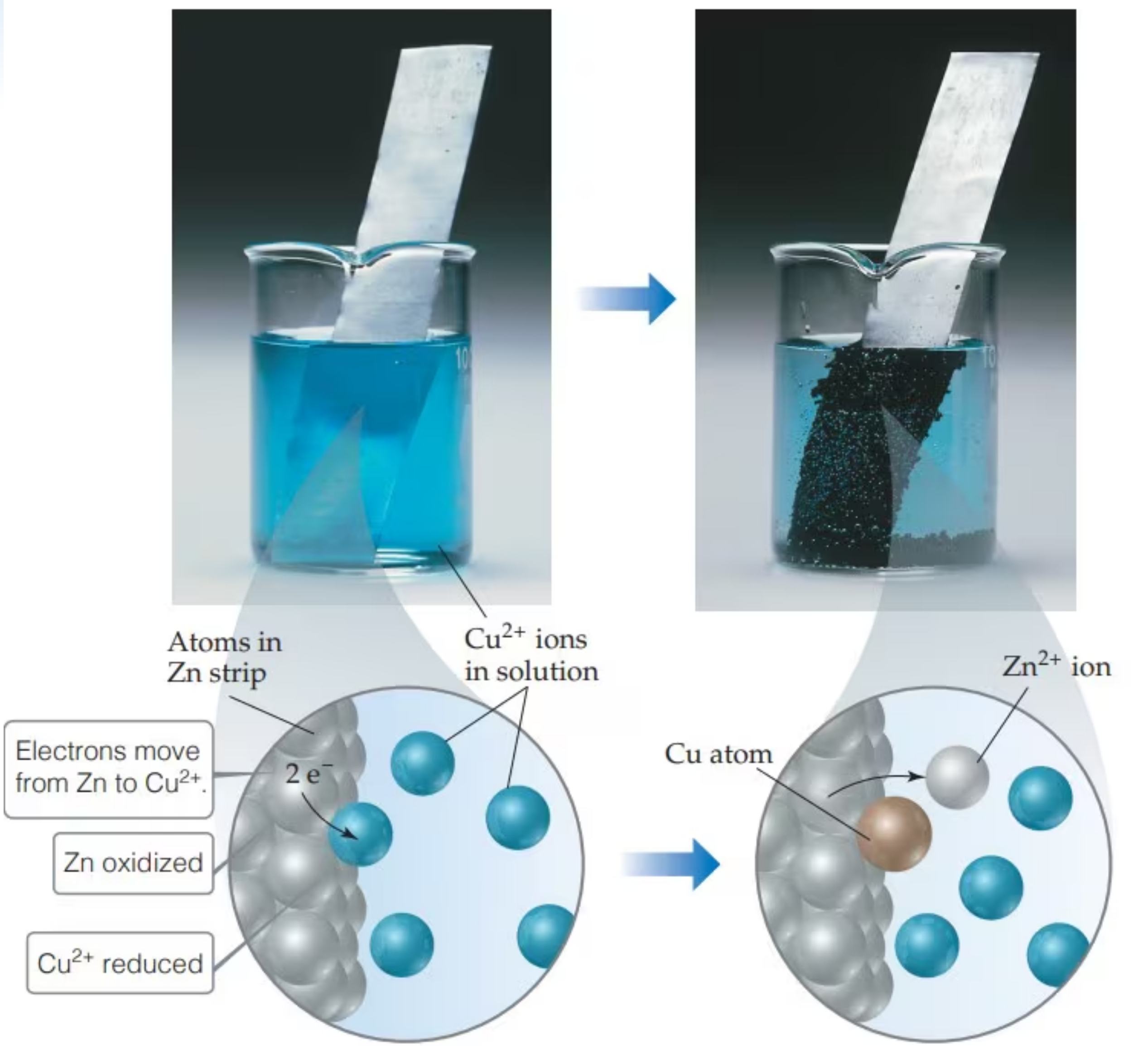
Example 2: $\underset{+6}{Cr_2O_7^{2-}}{}_{(aq)} + \underset{-1}{Cl^-}{}_{(aq)} \longrightarrow \underset{+3}{Cr^{3+}}{}_{(aq)} + \underset{0}{Cl_2}{}_{(g)}$

Oxidation Half-Reaction: $Cl^-_{(aq)} \longrightarrow Cl_{2\,(g)}$

Reduction Half-Reaction: $Cr_2O_7^{2-}{}_{(aq)} \longrightarrow Cr^{3+}{}_{(aq)}$

$14\ H^+ + Cr_2O_7^{2-}{}_{(aq)} + 6\ Cl^-_{(aq)} \longrightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O + 3\ Cl_{2\,(g)}$

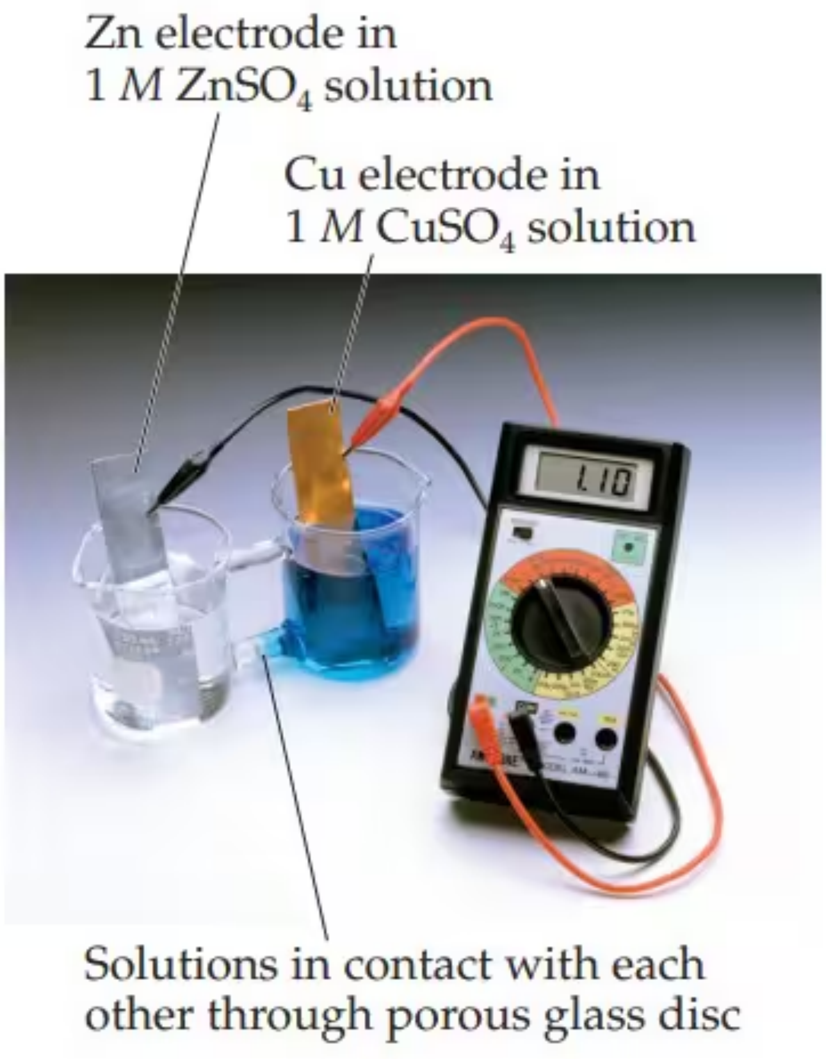
Spontaneous REDOX reaction



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

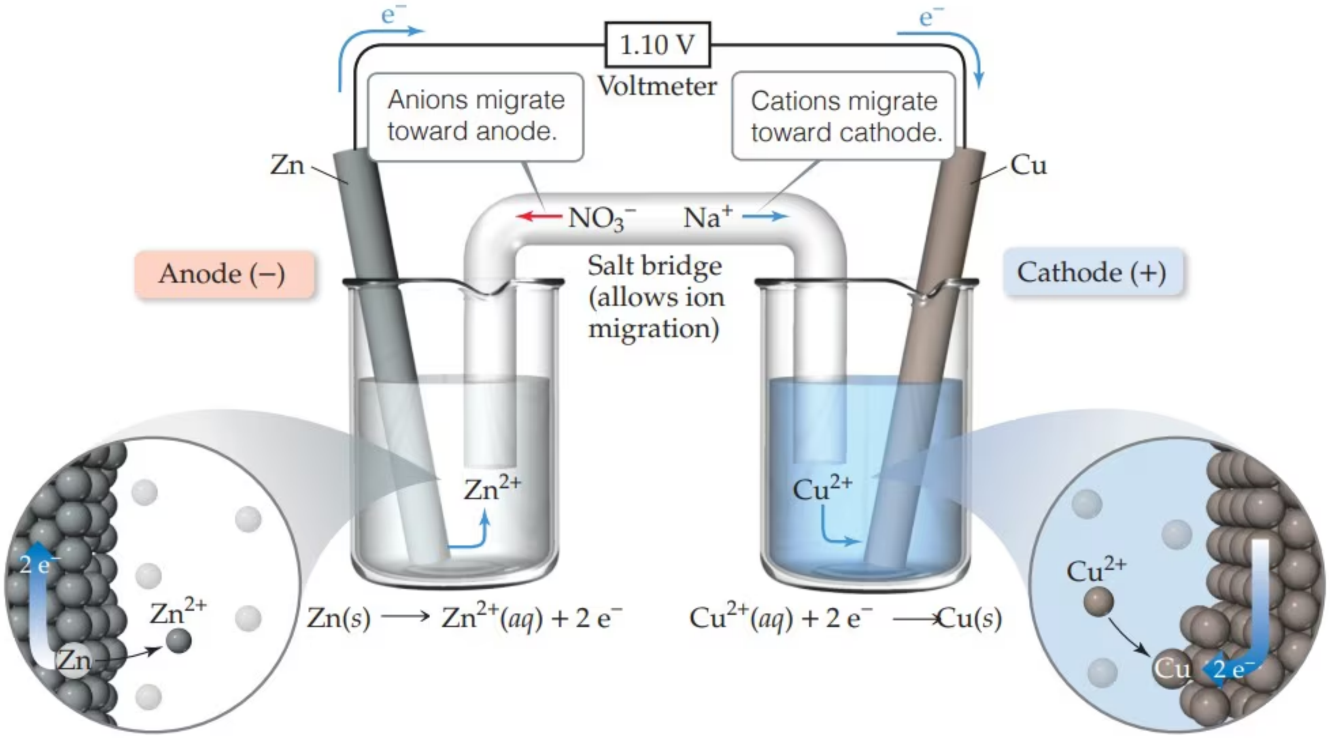
Galvanic (Voltaic) Cell

But what if you **SEPARATED** the two half reactions?



Galvanic (Voltaic) Cell

But what if you **SEPARATED** the two half reactions?
Electrons then run through a wire from one half reaction to the other.
A setup like this is called an **ELECTROCHEMICAL CELL**.



ANODE
the half side of a cell where
the <u>OXIDATION</u> occurs

BRIDGE
allows ions to flow
to close the circuit
(each side must remain
electrically neutral)

CATHODE
the half side of a cell where
the REDUCTION occurs

Galvanic (Voltaic) Cell

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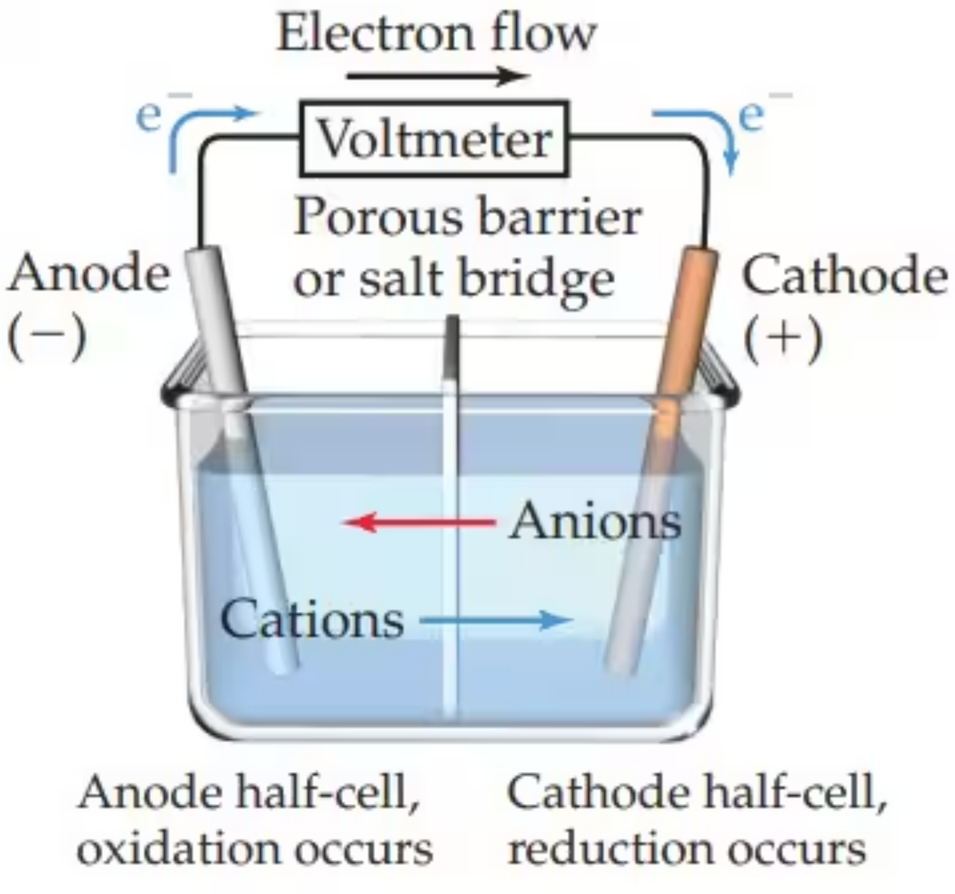

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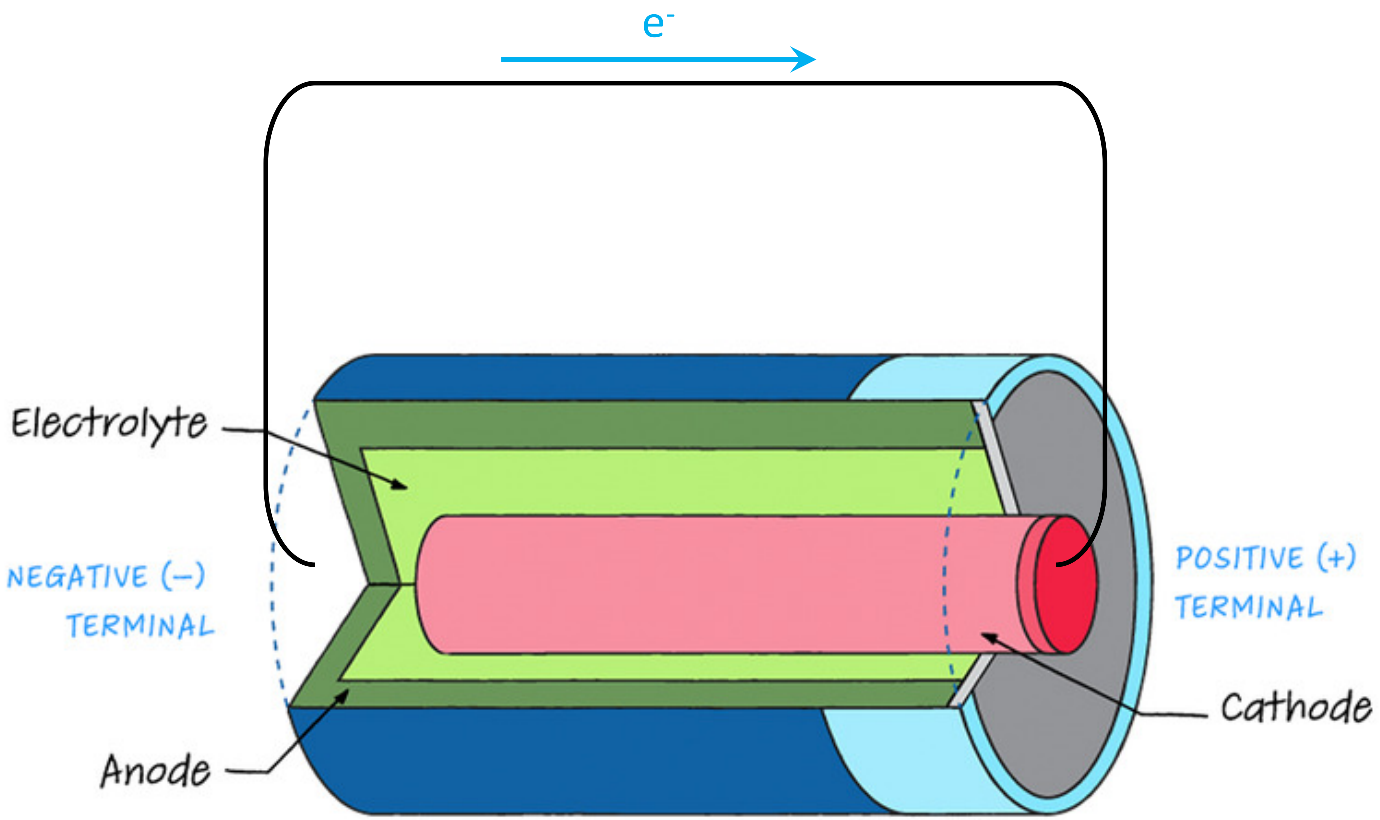


Mnemonics...

Reduction *always* occurs at the **cathode**
Oxidation *always* occurs at the **anode**

Two tricks to remember this:

1) Consonants with consonants, vowels with vowels:

Reduction at the **C**athode
Oxidation at the **A**node

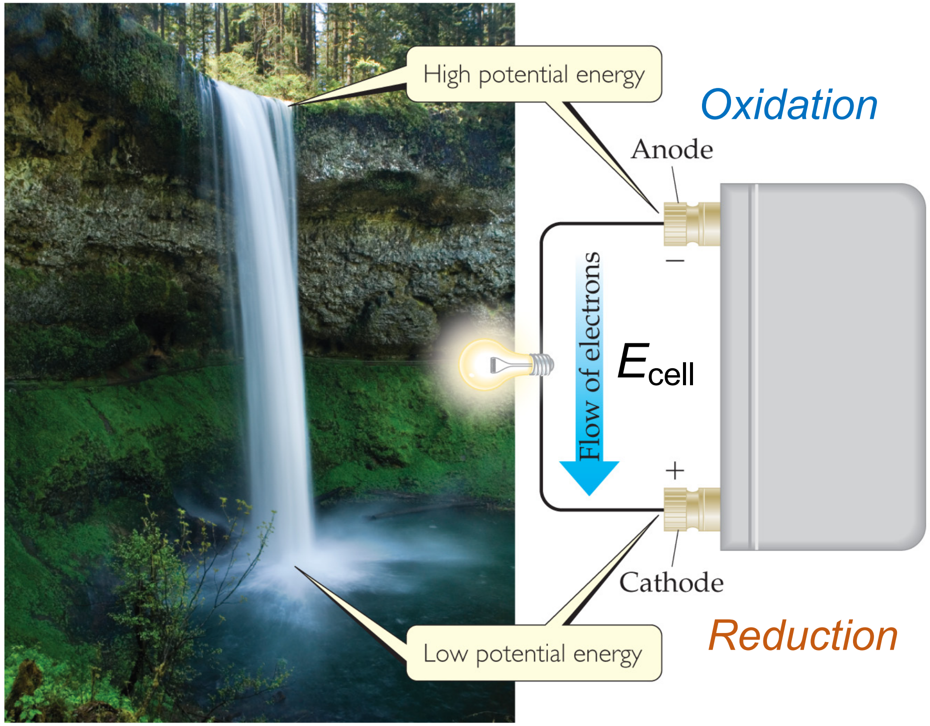
2)

REDCAT

REDuction at the **CAT**hode

ELECTROMOTIVE FORCE (EMF)

As **Water** flows ***spontaneously*** **Down** a waterfall…
electrons flow ***spontaneously one way*** in a redox reaction,
Both from high to low potential energy.



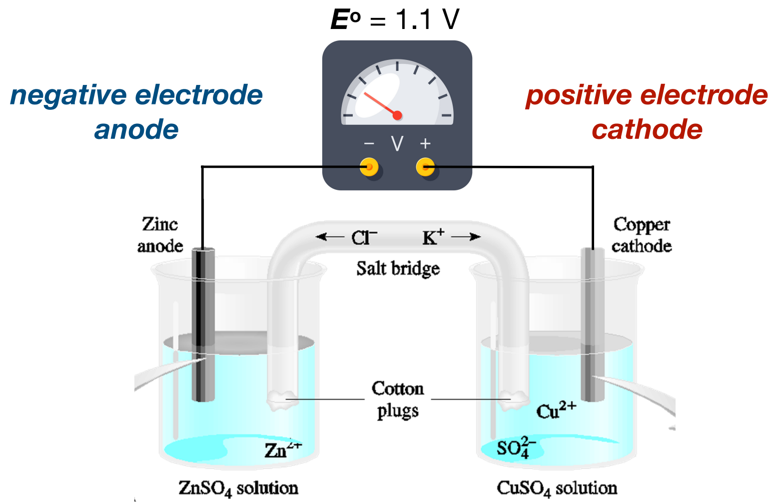
- **electromotive force (emf)** or
- **cell potential** designated $\boldsymbol{E_{cell}}$.
  - The potential difference between the anode and cathode
  - The relative propensity of one species to oxidize, versus another specie's propensity to reduce.
- measured in **volts (V)**.
  - volt = one joule per coulomb
  - (1 V = 1 J/C).

Standard Cell Potential/Reference cell potential

The **standard conditions** for electrochemical reaction:

- The concentration of all solutions is **1 M**
- Gas pressures are **1 bar** (often **1 atm** is used)
- **T = 25 °C (298 K)**, unless otherwise noted

Such "**standard cell potentials**" are denoted **E°**.

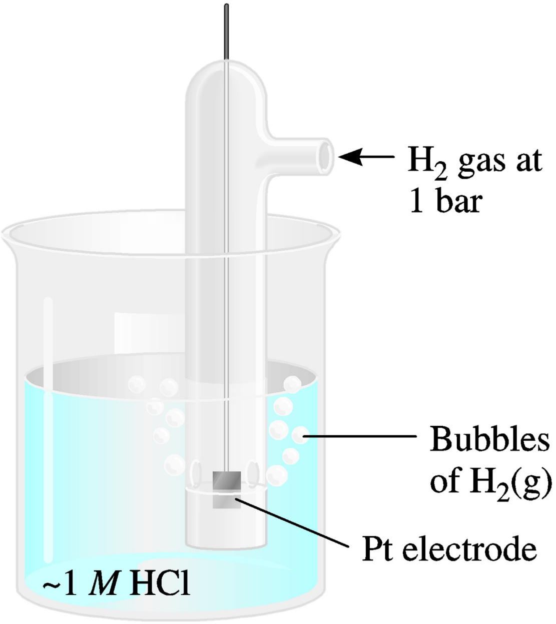


Reference electrode
(standard hydrogen electrode-SHE)

- All cell potentials are ***relative.***
- You need an **arbitrary** standard:
  - the REDUCTION potential for **hydrogen** is 0 V:
  - Every other potential is relative to hydrogen.

$$2\,H^+(aq,\,1M) + 2e^- \longrightarrow H_2(g,\,1\text{ atm})$$

E° = 0 V



Standard Cell Potentials

All standard half-cell potentials are compiled as **reduction potential**.

the species being reduced

the reduced form of that species

$$\underline{\mathrm{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \mathrm{Cu}_{(s)}}$$

a ***reduction*** reaction

$$E^{\circ}_{red}\left(\mathrm{Cu}^{2+}/\mathrm{Cu}\right) = 0.34\ \mathrm{V}\ vs.\ \mathrm{SHE}$$

a ***reduction*** potential

the **reference** potential

The standard potential of an **oxidation** reaction is the **negative** of the reduction. Just run it backwards, the sign changes.

$$\underline{\mathrm{Zn}^{2+}_{(aq)} + 2e^- \rightleftharpoons \mathrm{Zn}_{(s)}}$$

a ***reduction*** reaction

$$\underline{E^{\circ}_{red}\left(\mathrm{Zn}^{2+}/\mathrm{Zn}\right) = -0.76\ \mathrm{V}\ vs.\ \mathrm{SHE}}$$

this is what we find in a redox table

$$\underline{\mathrm{Zn}_{(s)} \rightleftharpoons \mathrm{Zn}^{2+}_{(aq)} + 2e^-}$$

an ***oxidation*** reaction
(inverse of reduction!)

$$E^{\circ}_{ox}\left(\mathrm{Zn}/\mathrm{Zn}^{2+}\right) = -E^{\circ}_{red}\left(\mathrm{Zn}^{2+}/\mathrm{Zn}\right)$$

$$= 0.76\ \mathrm{V}\ vs.\ \mathrm{SHE}$$

Standard Reduction Potentials

The more **positive** the reduction potential is, the easier it is for the species to **accept** an electron / be reduced / act as an oxidant.

More “positive” *E*°

- More easily reduced
- Better oxidants
- Electron **acceptors**
- Better cathode

Standard Reduction Potentials (vs. SHE) at 25 °C, in Aqueous Solutions

$E^\circ(\mathrm{F_2/F^-}) = 2.87\ \mathrm{V}$

$E^\circ(\mathrm{O_3,H^+/O_2}) = 2.08\ \mathrm{V}$

$E^\circ(\mathrm{S_2O_8^{2-}/SO_4^{2-}}) = 2.01\ \mathrm{V}$

$E^\circ(\mathrm{Ag^{2+}/Ag^+}) = 1.98\ \mathrm{V}$

$E^\circ(\mathrm{Au^+/Au}) = 1.83\ \mathrm{V}$

$E^\circ(\mathrm{Co^{3+}/Co^{2+}}) = 1.82\ \mathrm{V}$

$E^\circ(\mathrm{H_2O_2,H^+/H_2O}) = 1.76\ \mathrm{V}$

$E^\circ(\mathrm{PbO_2,H^+,SO_4^-/PbSO_4}) = 1.69\ \mathrm{V}$

$E^\circ(\mathrm{Au^{3+}/Au}) = 1.52\ \mathrm{V}$

$E^\circ(\mathrm{MnO_4^-,H^+/Mn^{2+}}) = 1.51\ \mathrm{V}$

$E^\circ(\mathrm{Cl_2/Cl^-}) = 1.36\ \mathrm{V}$

$E^\circ(\mathrm{Cr_2O_7^{2-},H^+/Cr^{3+}}) = 1.33\ \mathrm{V}$

$E^\circ(\mathrm{O_2,H^+/H_2O}) = 1.23\ \mathrm{V}$

$E^\circ(\mathrm{IO_3^-,H^+/I_2}) = 1.20\ \mathrm{V}$

$E^\circ(\mathrm{Br_2/Br^-}) = 1.07\ \mathrm{V}$

$E^\circ(\mathrm{NO_3^-,H^+/NO}) = 0.96\ \mathrm{V}$

$E^\circ(\mathrm{Hg^{2+}/Hg}) = 0.85\ \mathrm{V}$

$E^\circ(\mathrm{Ag^+/Ag}) = 0.80\ \mathrm{V}$

$E^\circ(\mathrm{Fe^{3+}/Fe^{2+}}) = 0.77\ \mathrm{V}$

$E^\circ(\mathrm{O_2,H^+/H_2O_2}) = 0.70\ \mathrm{V}$

$E^\circ(\mathrm{I_2/I^-}) = 0.54\ \mathrm{V}$

$E^\circ(\mathrm{I_3^-/I^-}) = 0.53\ \mathrm{V}$

$E^\circ(\mathrm{Cu^+/Cu}) = 0.52\ \mathrm{V}$

$E^\circ(\mathrm{O_2/OH^-}) = 0.40\ \mathrm{V}$

$E^\circ(\mathrm{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}}) = 0.36\ \mathrm{V}$

$E^\circ(\mathrm{Cu^{2+}/Cu}) = 0.34\ \mathrm{V}$

$E^\circ(\mathrm{AgCl/Ag}) = 0.22\ \mathrm{V}$

$E^\circ(\mathrm{Cu^{2+}/Cu^+}) = 0.16\ \mathrm{V}$

$E^\circ(\mathrm{Sn^{4+}/Sn^{2+}}) = 0.15\ \mathrm{V}$

$E^\circ(\mathrm{H^+/H_2}) = 0.00\ \mathrm{V}$

$E^\circ(\mathrm{Fe^{3+}/Fe}) = -0.04\ \mathrm{V}$

$E^\circ(\mathrm{CO_2,H^+/CO}) = -0.11\ \mathrm{V}$

$E^\circ(\mathrm{Pb^{2+}/Pb}) = -0.13\ \mathrm{V}$

$E^\circ(\mathrm{Sn^{2+}/Sn}) = -0.13\ \mathrm{V}$

$E^\circ(\mathrm{Ni^{2+}/Ni}) = -0.25\ \mathrm{V}$

$E^\circ(\mathrm{V^{3+}/V^{2+}}) = -0.26\ \mathrm{V}$

$E^\circ(\mathrm{Co^{2+}/Co}) = -0.28\ \mathrm{V}$

$E^\circ(\mathrm{In^{3+}/In}) = -0.34\ \mathrm{V}$

$E^\circ(\mathrm{Eu^{3+}/Eu^{2+}}) = -0.35\ \mathrm{V}$

$E^\circ(\mathrm{PbSO_4/Pb,SO_4^{2-}}) = -0.36\ \mathrm{V}$

$E^\circ(\mathrm{PbI_2/Pb}) = -0.37\ \mathrm{V}$

$E^\circ(\mathrm{Cd^{2+}/Cd}) = -0.40\ \mathrm{V}$

$E^\circ(\mathrm{Cr^{3+}/Cr^{2+}}) = -0.42\ \mathrm{V}$

$E^\circ(\mathrm{Fe^{2+}/Fe}) = -0.44\ \mathrm{V}$

$E^\circ(\mathrm{Cr^{3+}/Cr}) = -0.74\ \mathrm{V}$

$E^\circ(\mathrm{Zn^{2+}/Zn}) = -0.76\ \mathrm{V}$

$E^\circ(\mathrm{H_2O/H_2,OH^-}) = -0.83\ \mathrm{V}$

$E^\circ(\mathrm{V^{2+}/V}) = -1.13\ \mathrm{V}$

$E^\circ(\mathrm{Mn^{2+}/Mn}) = -1.19\ \mathrm{V}$

$E^\circ(\mathrm{Al^{3+}/Al}) = -1.66\ \mathrm{V}$

$E^\circ(\mathrm{Eu^{3+}/Eu}) = -1.99\ \mathrm{V}$

$E^\circ(\mathrm{Mg^{2+}/Mg}) = -2.37\ \mathrm{V}$

$E^\circ(\mathrm{Na^+/Na}) = -2.71\ \mathrm{V}$

$E^\circ(\mathrm{Ca^{2+}/Ca}) = -2.87\ \mathrm{V}$

$E^\circ(\mathrm{Sr^{2+}/Sr}) = -2.90\ \mathrm{V}$

$E^\circ(\mathrm{Ba^{2+}/Ba}) = -2.91\ \mathrm{V}$

$E^\circ(\mathrm{K^+/K}) = -2.93\ \mathrm{V}$

$E^\circ(\mathrm{Rb^+/Rb}) = -2.98\ \mathrm{V}$

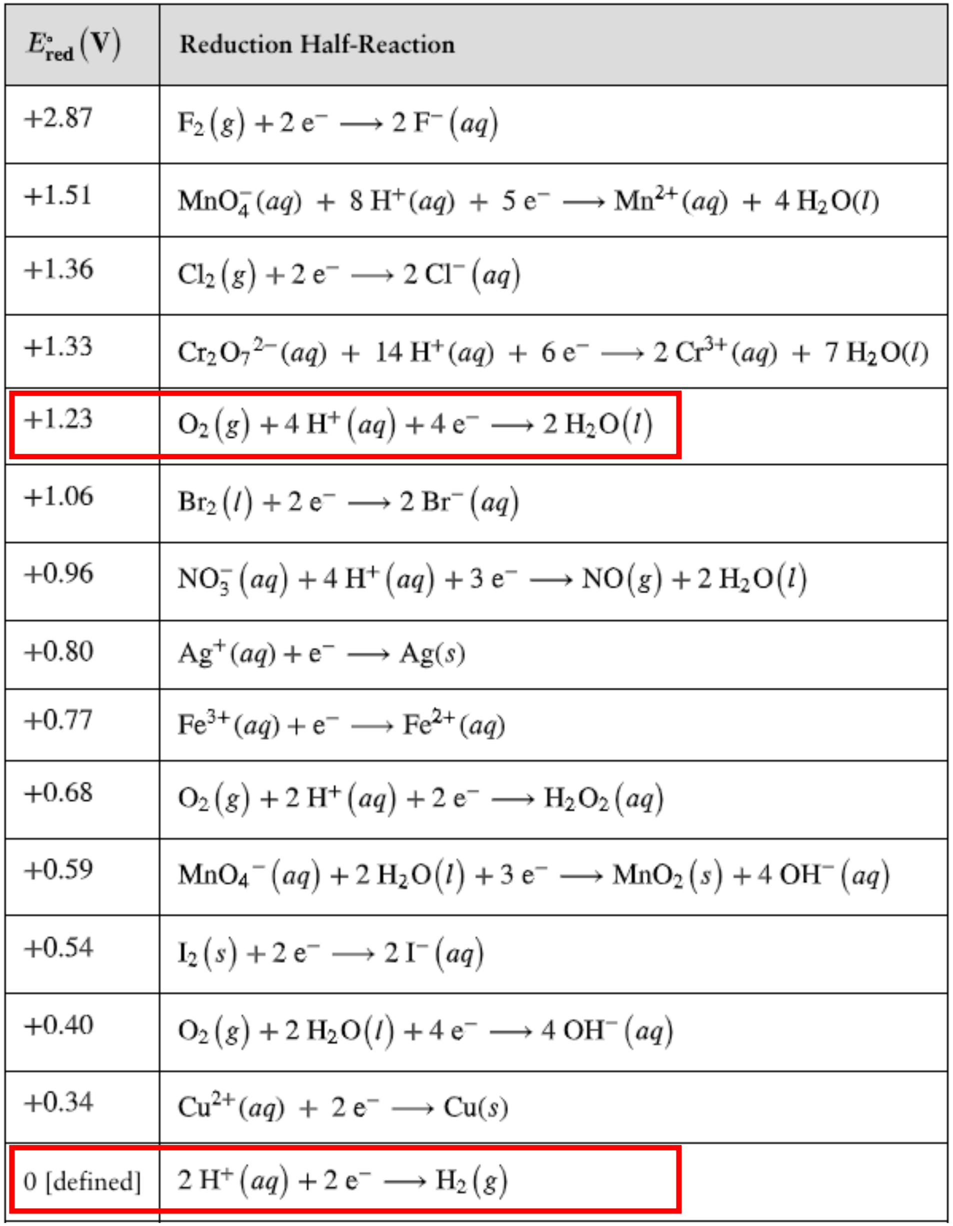
$E^\circ(\mathrm{Cs^+/Cs}) = -3.03\ \mathrm{V}$

$E^\circ(\mathrm{Li^+/Li}) = -3.04\ \mathrm{V}$

More “negative” *E*°

- More easily oxidized
- Better reducers
- Electron **givers**
- Better anode

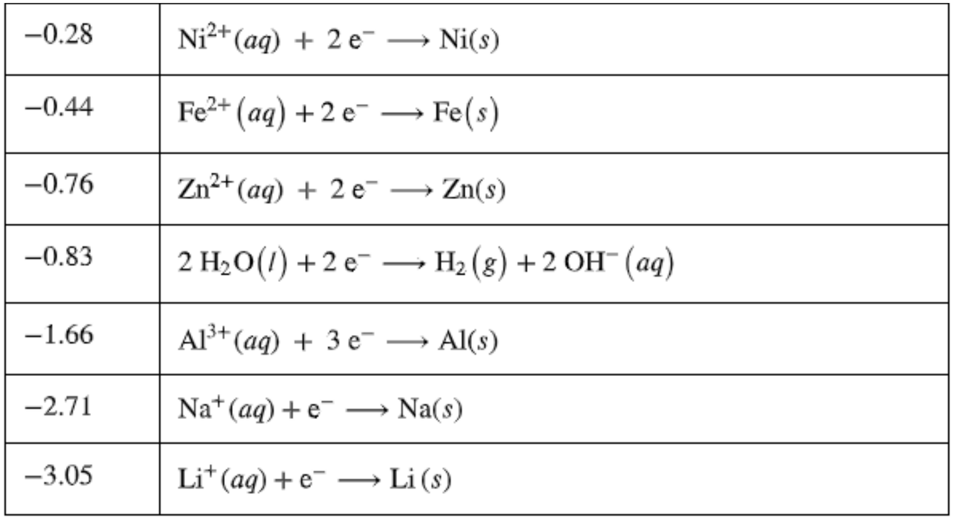
Standard Reduction Potentials



E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0 [defined]	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$

E°_{Red} is an intensive property

: does not scale with quantity



−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Standard Cell Potentials

Therefore: the total potential is the DIFFERENCE of the reduction potentials between the cathode and the anode (always “Reduction” part first):

$$E^{\circ}_{Cell} = E^{\circ}_{Red}(cathod) - E^{\circ}_{Red}(anode)$$

↑

Note! Also reduction!

ex: Daniell Cell

$$\underbrace{\mathrm{Zn}_{(s)}\big|\mathrm{Zn}^{2+}_{(aq)}}_{\text{anode half-cell}} \; \big\| \; \underbrace{\mathrm{Cu}^{2+}_{(aq)}\big|\mathrm{Cu}_{(s)}}_{\text{cathode half-cell}}$$

$$\begin{array}{rl} & E^{\mathrm{o}}_{red}\left(\mathrm{Cu}^{2+}/\mathrm{Cu}\right) = 0.34\ \mathrm{V}\ vs.\ \mathrm{SHE} \\ - & E^{\mathrm{o}}_{red}\left(\mathrm{Zn}^{2+}/\mathrm{Zn}\right) = -0.76\ \mathrm{V}\ vs.\ \mathrm{SHE} \\ \hline & E^{\mathrm{o}}_{tot} = 1.10\ \mathrm{V}\ vs.\ \mathrm{SHE} \end{array}$$

Potential and Thermodynamics

A galvanic cell is just another chemical reaction.

Therefore:
The laws of Thermodynamics should apply ***Exactly*** as it did for any other chemical reaction.

This means the relationships between **Work**, **Free Energy** and **Equilibrium** should be ***exactly the same*** as for any other chemical reaction

Potential and Thermodynamics

The relationship between the standard free energy and the standard redox potential:

$$\boxed{\Delta G^{o} = -nFE^{o}}$$

F = 96,485 C / mol

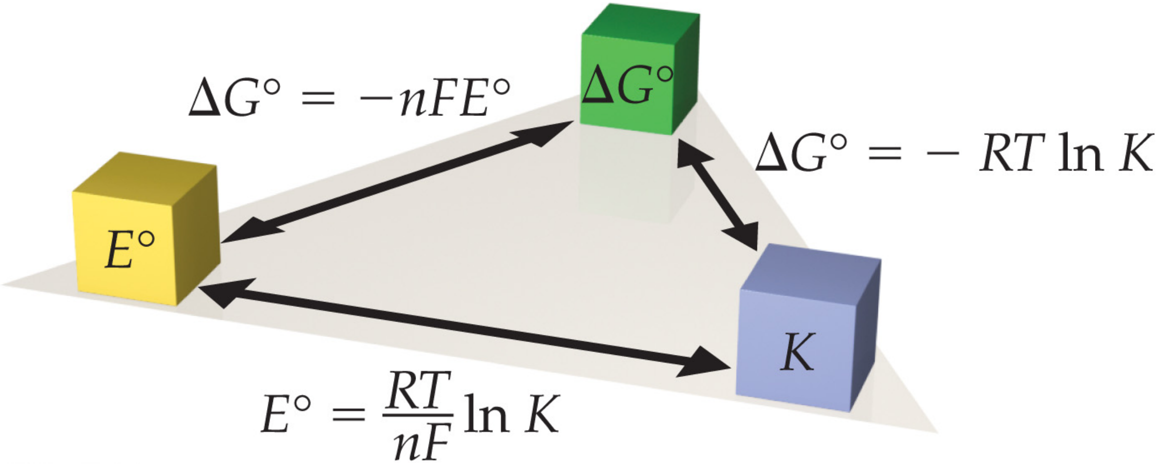
The relation between the free energy and the equilibrium constant:

$$\Delta G^{o} = -RT \ln K$$

Equating the two relationships: $-nFE^{o} = -RT \ln K$

Yielding the relationship between the standard redox potential and equilibrium constant:

$$\boxed{E^{o} = \frac{RT}{nF} \ln K}$$



Potential and Thermodynamics

Example: $4\ Ag_{(s)} + O_{2\,(g)} + 4\ H^+_{(aq)} \longrightarrow 4\ Ag^+_{(aq)} + 2\ H_2O_{(l)}$

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Reduction: $O_{2\,(g)} + 4\,H^+_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O_{(l)}$ E°_{Red}=+1.23 V

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$$\Delta G^\circ = -nFE^\circ = 4 \times 96{,}485 \times 0.43 = -1.7 \times 10^5\ J/mol$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{-1.7 \times 10^5}{RT}\right) = \exp(67) = 1.2 \times 10^{29}$$

Potential and Thermodynamics

What if we cut the reaction **in half**?

Example: $2\,Ag_{(s)} + \frac{1}{2}\,O_{2\,(g)} + 2\,H^+_{(aq)} \longrightarrow 2\,Ag^+_{(aq)} + H_2O_{(l)}$

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$$\Delta G^\circ = -nFE^\circ = 2 \times 96{,}485 \times 0.43 = -8.3 \times 10^4\ J/mol$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = 3.5 \times 10^{14}$$

The Nernst Equation

All the relationships that we derived only applies under standard conditions.

- -All reactants at **1 M** concentration
- -T=**298 K**.
- -Gases all at **1 atm**.

Why? Because we are using the Standard Reduction Potential:

$$-nFE^{\mathrm{o}} = -RT\ln K$$

And those are all at standard conditions.

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What happens if the reaction is under “**non-standard conditions**”?
What if the concentrations of the solutions are **not** all **1 M**?

NERNST EQUATION: The equation that gives the potential under non-standard conditions

Q = reaction quotient

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

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

potential under
any conditions

potential under
standard conditions

specific concentrations used
(if all concentrations = 1 M,
then $Q = 1$ and $\ln Q = 0$)

The Nernst Equation

Remember (chapter 19): $\Delta G = \Delta G^\circ + RT \ln Q$

and (this chapter) $\Delta G^\circ = -nFE^\circ$

Therefore,

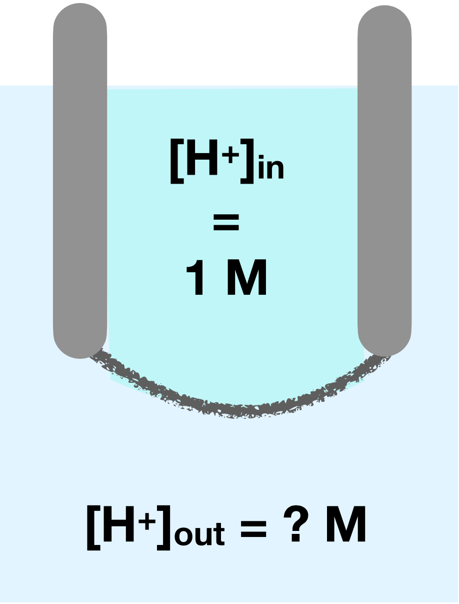
$$-nFE = -nFE^\circ + RT\,lnQ$$

$$\boxed{E = E^\circ - \frac{RT}{nF}\,lnQ}$$

NERNST EQUATION:

Concentration Cells: pH meters

In a pH meter, the measured potential comes from the difference in [H⁺] ion concentrations on both sides of the thin glass membrane of the sensing electrode.



We can think of the redox reactions as being:

$$E = -\frac{RT}{F}\ln\frac{[\mathrm{H}^+]_{\mathrm{out}}}{[\mathrm{H}^+]_{\mathrm{in}}} = -0.02569\ \mathrm{V}\ \ln\frac{[\mathrm{H}^+]_{\mathrm{out}}}{1\ \mathrm{M}}$$

To make things simpler, let's change the logarithm to a base 10:

$$\begin{aligned} E &= -2.30\times 0.02569\ \mathrm{V}\ \log_{10}[\mathrm{H}^+]_{\mathrm{out}} \\ &= 0.0592\ \mathrm{V}\times\left(-\log_{10}[\mathrm{H}^+]_{\mathrm{out}}\right) \\ &= 59.2\ \mathrm{mV}\times\mathrm{pH} \end{aligned}$$

The potential changes by **59.2 mV** every time the pH changes by one unit!

Electrolysis

Galvanic (voltaic) cells: **production** of electrical energy from the energy of a chemical reaction

Electrolysis: **Use** of electrical energy ***to create chemical reactions***.

Run **nonspontaneous** reactions using ***electrical energy***.

Reduction potentials:

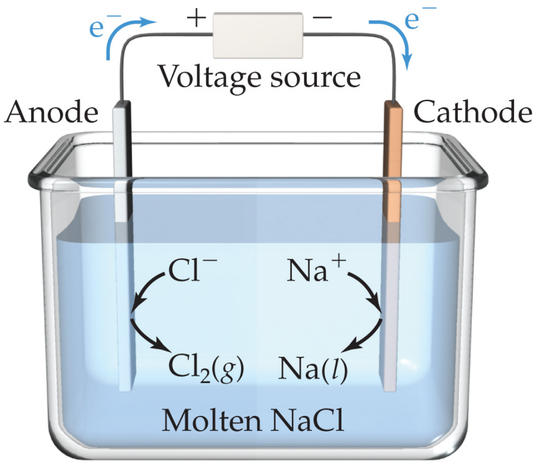
Anode: E^o_{Red} (Cl_2/Cl^-) = 1.36 V
Cathode: E^o_{Red} (Na^+/Na) = -2.71 V

$E^o_{Tot} = E^o_{Red}(Cl_2/Cl^-) - E^o_{Red}(Na^+/Na) = 4.07$ V

Anode : E^o_{Red} (Ni^{2+}/Ni) = -0.25 V
Cathode : E^o_{Red} (Ni^{2+}/Ni) = -0.25 V

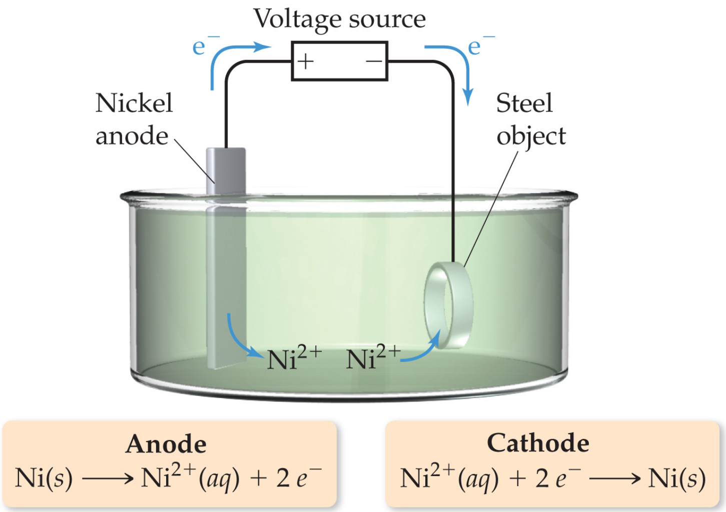
$E^o_{Tot} = E^o_{Red}(Ni^{2+}/Ni) - E^o_{Red}(Ni^{2+}/Ni) = 0$ V

Non-spontaneous can occur by the addition of external voltage source.



$$2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$$

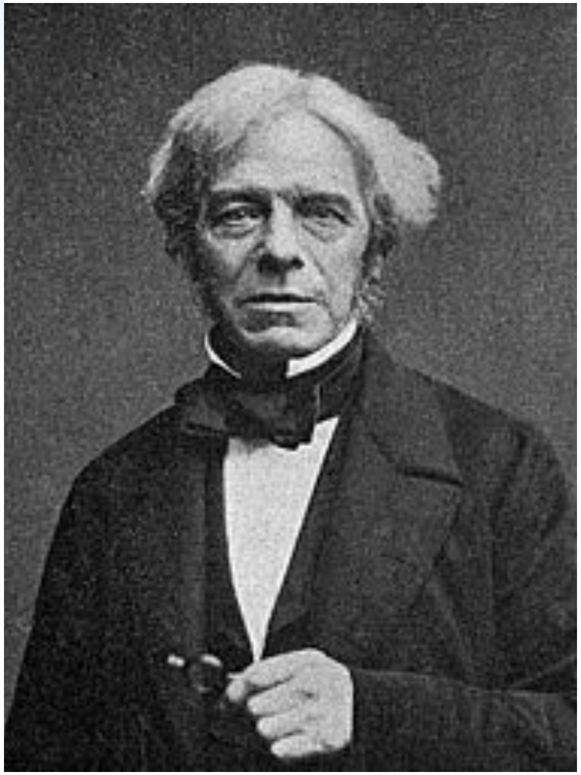
$$2\,Na^+ + 2\,e^- \longrightarrow 2\,Na(l)$$



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

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

Faraday's Law of Electrolysis



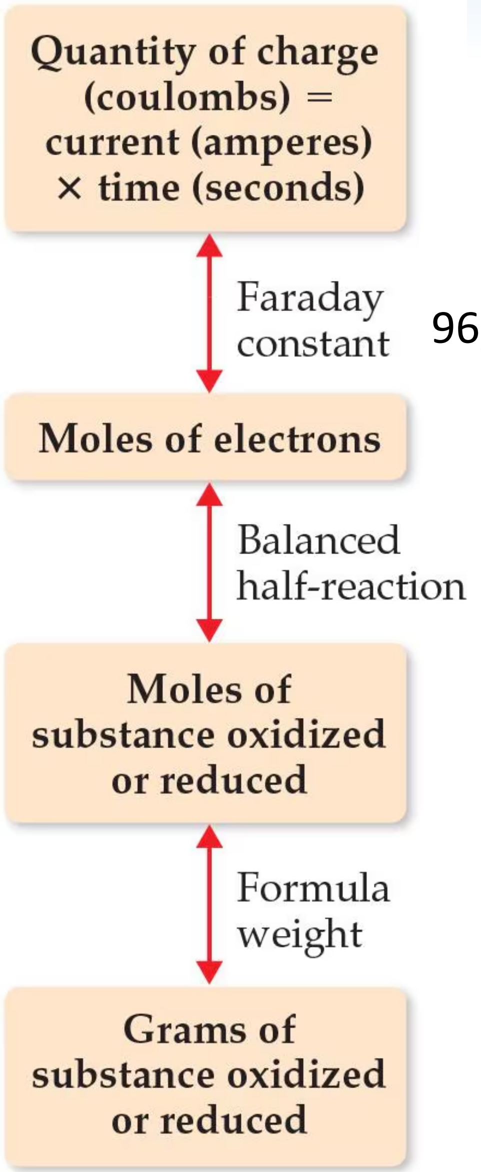
Michael Faraday
1791 - 1867
(England)

"The amount of substance created is directly proportional to the electrical charge passed through the cell."

$$\boxed{\text{mass}(\text{g}) = \frac{\text{charge}(\text{C}) \times \text{molar mass}(\text{g} \cdot \text{mol}^{-1})}{n \times F(\text{C} \cdot \text{mol}^{-1})}}$$

n → Number of electrons required to make one mol of substance

Using Faraday's Law



Quantity of charge (coulombs) = current (amperes) × time (seconds)

Faraday constant

96,485 C / mol

Moles of electrons

Balanced half-reaction

Moles of substance oxidized or reduced

Formula weight

Grams of substance oxidized or reduced

$$\boxed{\text{mass}(\text{g}) = \frac{\text{charge}(\text{C}) \times \text{molar mass}(\text{g} \cdot \text{mol}^{-1})}{n \times F(\text{C} \cdot \text{mol}^{-1})}}$$