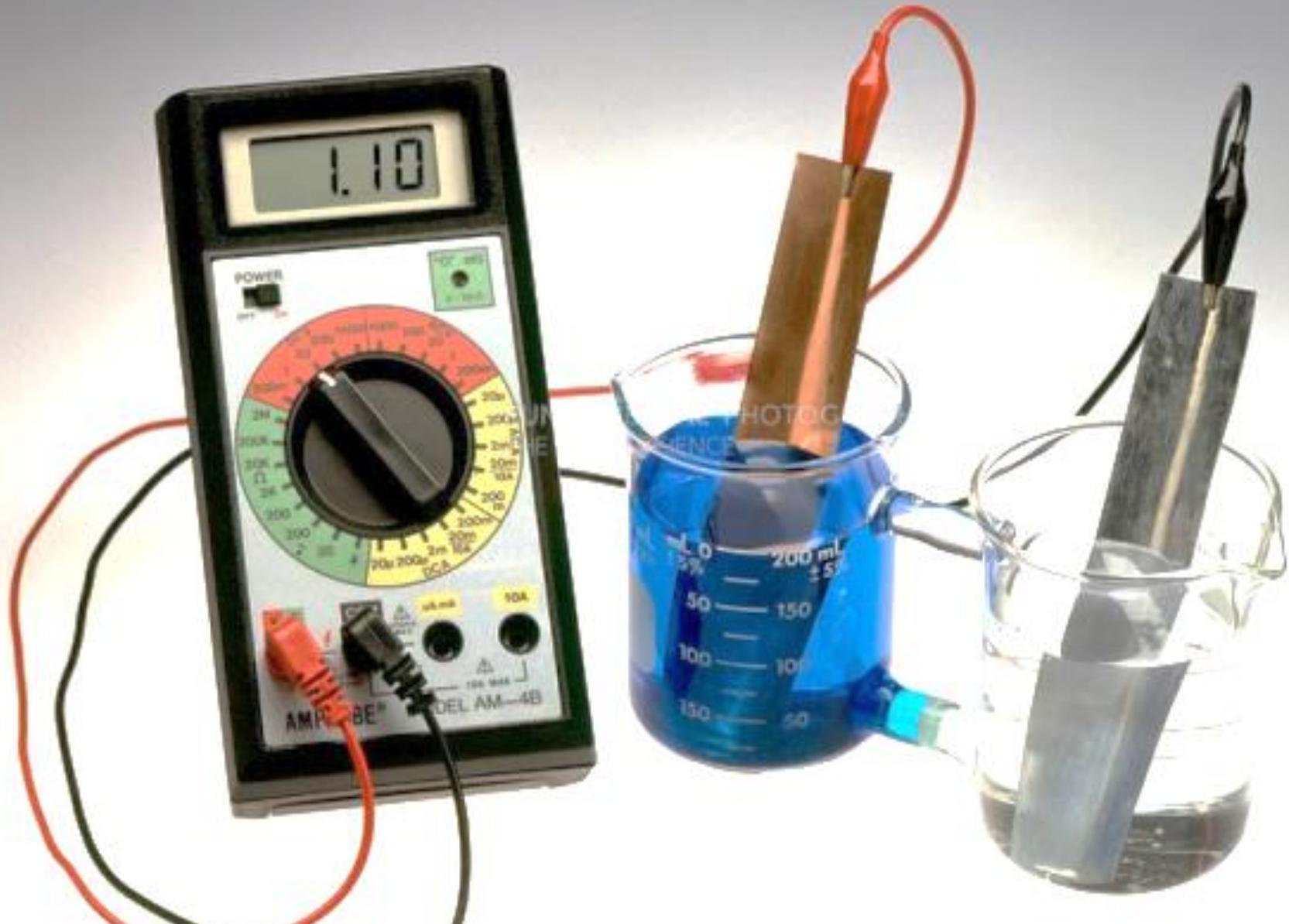


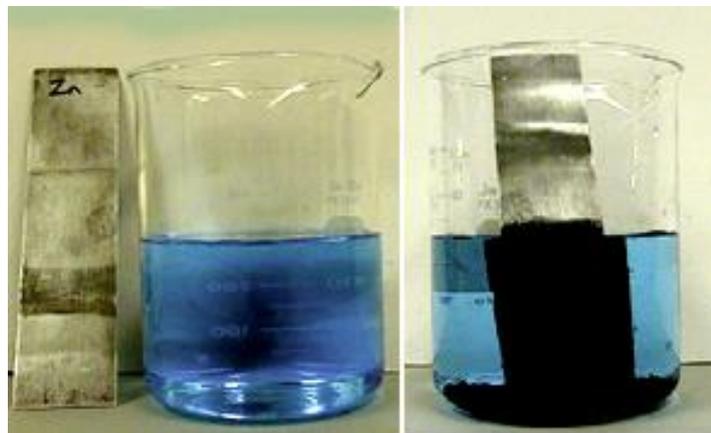
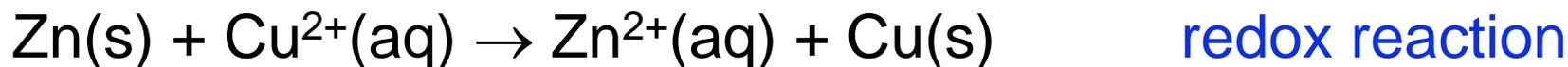
ELECTROCHEMISTRY



Oxidation and Reduction reactions (redox)

oxidation: it is the loss of electrons.

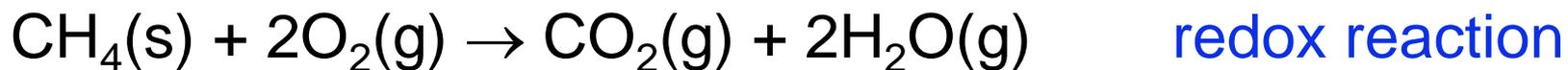
reduction: it is the gain of electrons.



Oxidation and Reduction reactions (redox)

oxidation: is the gain of oxygen / loss of hydrogen.

reduction: is the loss of oxygen / gain of hydrogen.



↓
C gains O and loses H
is oxidized
(reducing agent)

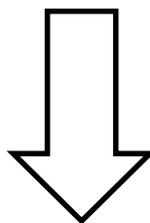
↘
O gains H
is reduced
(oxidizing agent)

single replacement reaction and combustion reactions → redox reactions

double replacement reactions → non redox

Oxidation States (Oxidation numbers)

Assigning charges to the various atoms in a compound.



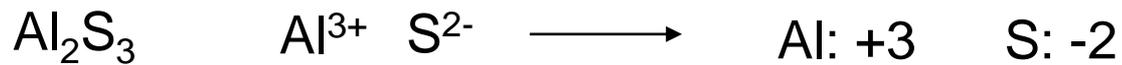
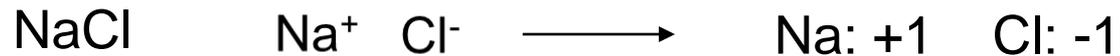
Keep track of electrons in redox reactions.

Rules for assigning oxidation states

1. Charge (oxidation state) of a uncombined element is zero.

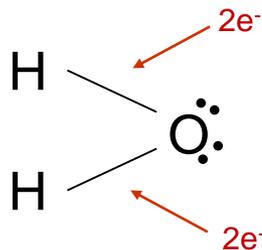


2. The oxidation state of a monatomic ion is the same as its charge.



Rules for assigning oxidation states

For covalent compounds assume the most electronegative atom controls or possesses the shared electrons.



O gained two e⁻ from H → Oxidation state = -2

H lost one e⁻ → Oxidation state = +1

4. The oxidation state of H is +1 and O is -2 in covalent compounds.

Exception: Peroxide (O₂²⁻) = -1 H₂O₂

Rules for assigning oxidation states

The most electronegative elements: F, O, N, and Cl

F: -1, O: -2, N: -3, Cl: -1

5. If two of these elements are found in the same compound, we assign them in order of electronegativity.

$F > O > N > Cl$



O: $2 \times (-2) = -4$ So N must be +4

Rules for assigning oxidation states

6. Sum of oxidation states = 0 in a neutral compound.

7. Sum of oxidation states = charge in an ion.



N must be +5 for an overall charge of -1 for NO_3^- .



S must be +6 for an overall charge of -2 for SO_4^{2-} .

Rules for assigning oxidation states



$$\text{K} = +1; \text{Cr} = +6; \text{O} = -2$$



$$\text{C} = +4; \text{O} = -2$$



$$\text{Mn} = +4; \text{O} = -2$$



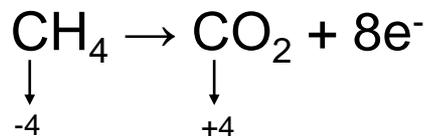
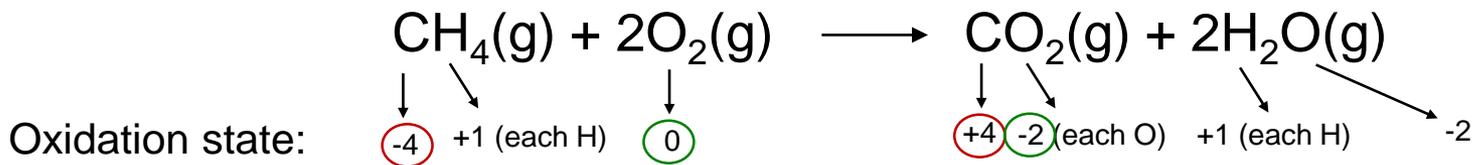
$$\text{P} = +5; \text{Cl} = -1$$



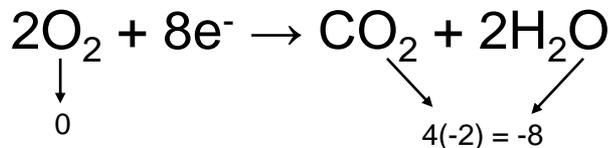
$$\text{S} = +4; \text{F} = -1$$

Oxidation-Reduction Reactions

In some redox reactions **ions are not produced** (all nonmetals).



C is oxidized.
CH₄ is a reducing agent.



O is reduced.
O₂ is an oxidizing agent.

Oxidation-Reduction Reactions

Oxidation: is an increase in oxidation state (a loss of e^-).

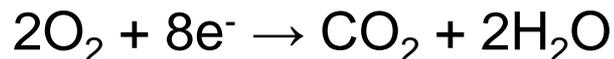
Reduction: is a decrease in oxidation state (a gain of e^-).

Oxidizing agent (electron acceptor): the reactant containing the element that is reduced.

Reducing agent (electron donor): the reactant containing the element that is oxidized.

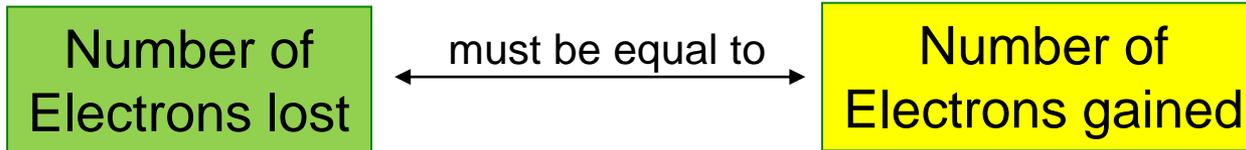
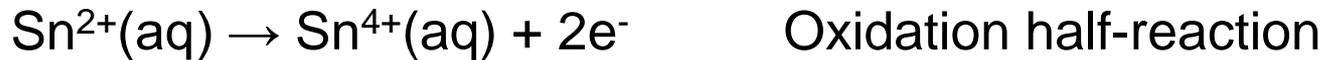
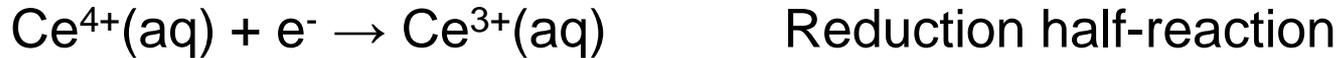
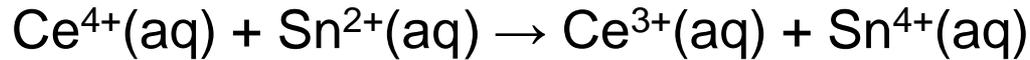


C is oxidized.
CH₄ is a reducing agent.

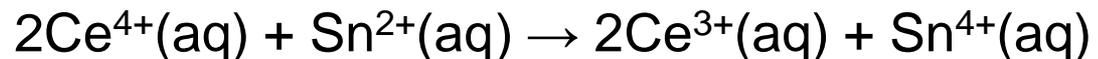


O is reduced.
O₂ is an oxidizing agent.

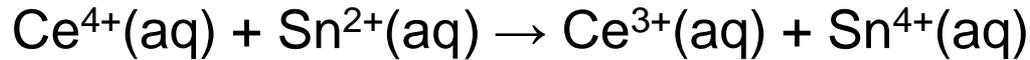
Half-Reaction Method for balancing



Multiply by 2:



Redox Couple



$\text{Sn}^{2+}(\text{aq})$ and $\text{Sn}^{4+}(\text{aq})$ are jointly formed, so we refer to these as **couples**, and written as $\text{Sn}^{4+}/\text{Sn}^{2+}$.

Oxidized form/Reduced form

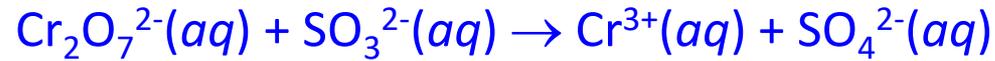
A note on *formalism*: Couples are written as reductions, so $\text{Sn}^{4+}/\text{Sn}^{2+}$ implies $\text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{e}^{-}$

The Cerium couple is written as $\text{Ce}^{4+}/\text{Ce}^{3+}$.

Half-Reaction Method for balancing

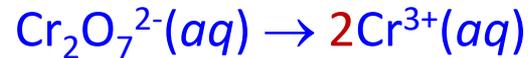
1. Identify and write the equations for the oxidation and reduction half-reactions.
2. For each half-reaction:
 - A. Balance all the elements except H and O.
 - B. Balance O using H_2O .
 - C. Balance H using H^+ .
 - D. Balance the charge using electrons.
3. If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.
4. Add the half-reactions, and cancel identical species.
5. Check that the elements and charges are balanced.

Half-Reaction Method for balancing



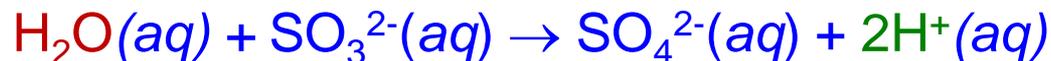
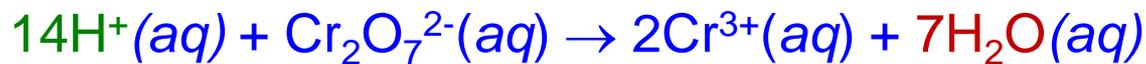
How can we balance this equation?

1. Separate into half-reactions.
2. Balance elements except H and O.



Half-Reaction Method for balancing

3. Balance O's with H₂O and H's with H⁺.

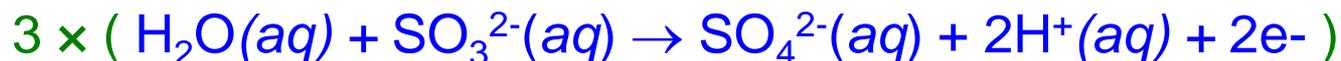


4. How many electrons are involved in each half-reaction? Balance the charges.

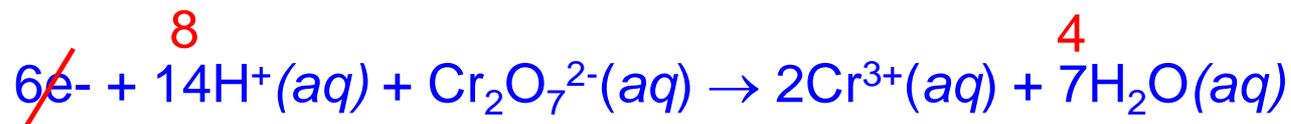


Half-Reaction Method for balancing

5. Multiply whole reactions by a whole number to make the number of electrons gained equal the number of electrons lost.



6. Combine half-reactions cancelling out those reactants and products that are the same on both sides, especially the electrons.



Electrochemistry

Galvanic Cells



Galvanic Cells

Galvanic cells are *spontaneous* reactions generating electric current.

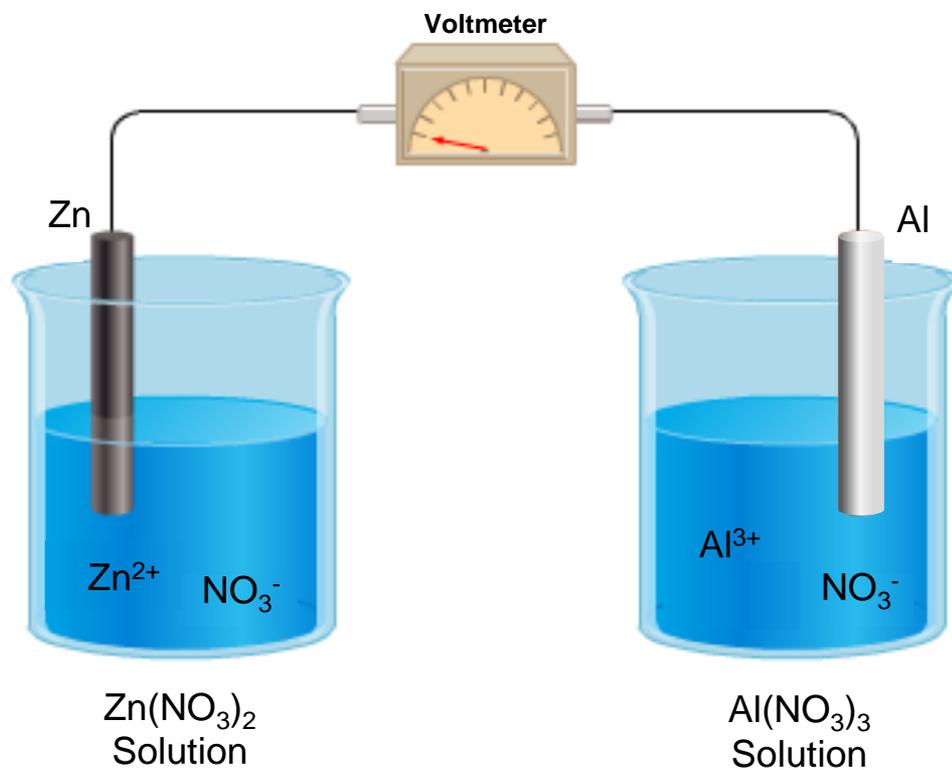
Batteries are a collection of galvanic cells joined in series, where the total voltage is the sum of each cell.

Voltage is the **ability** to push an electric current through a circuit.

The formal term for “voltage” is potential difference, measured in volts:
 $1 \text{ V} = \text{J} \cdot \text{C}^{-1}$ (more on this later)

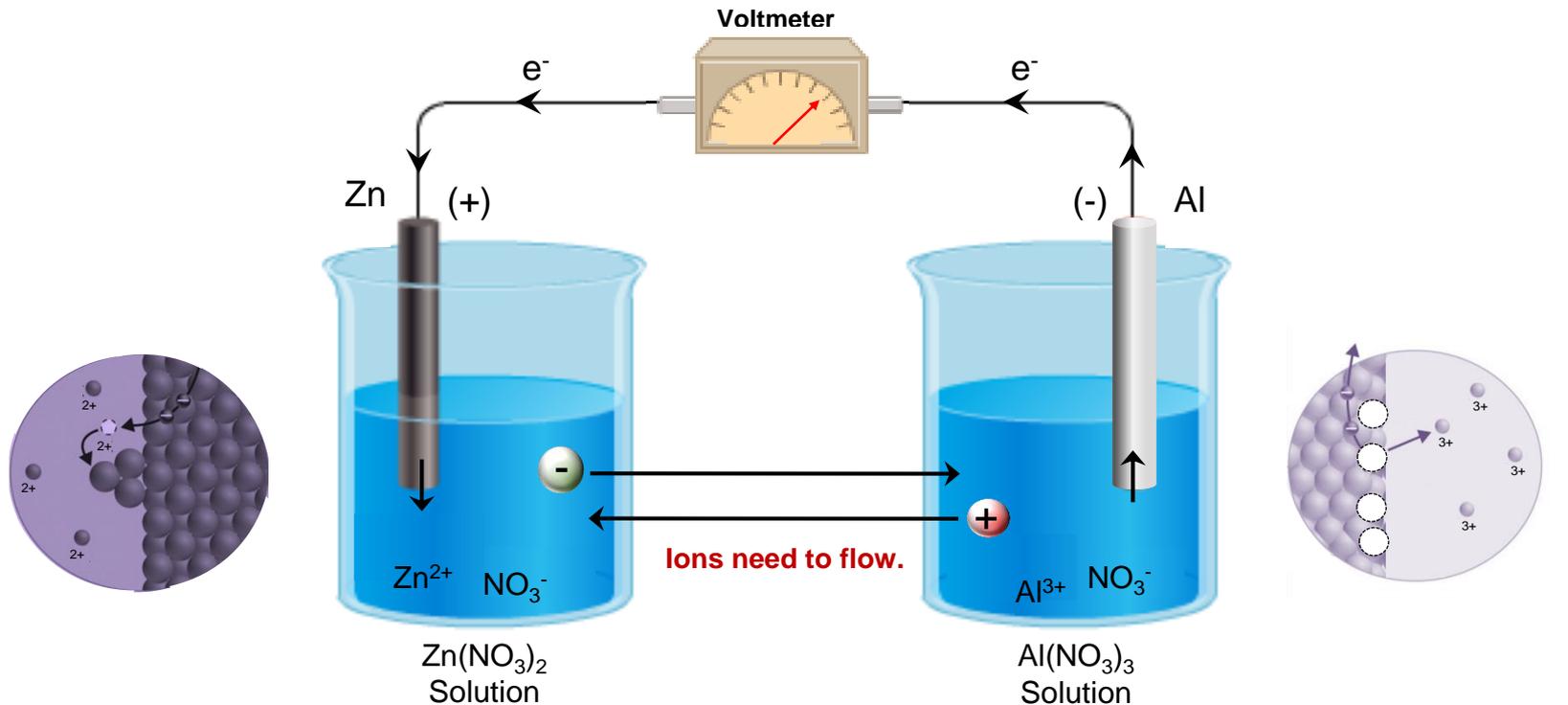
Galvanic cells are also known as voltaic cells.

Galvanic Cells



Galvanic Cell (Electrochemical Battery)

Soon electrons **stop moving**: the anodes "+" pulls electrons back *and* repulsion of the "-" cathode.



Cathode

Reduction



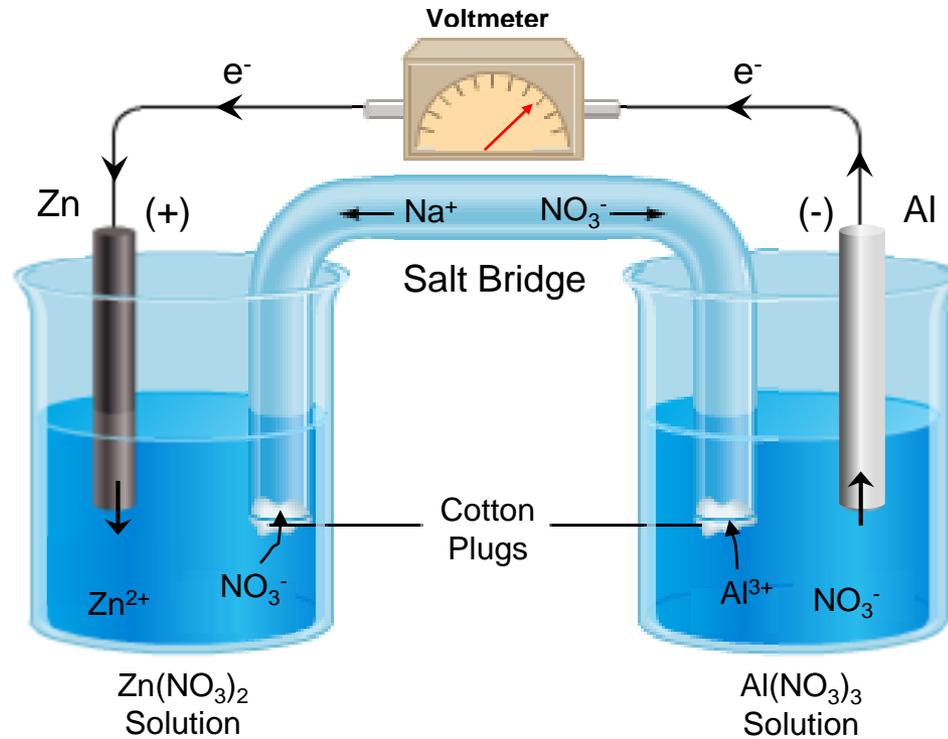
Anode

Oxidation



Redox reaction

Galvanic Cell (Electrochemical Battery)



The **Salt Bridge** allows *ion exchange* thereby **electrically neutralizing** the anode and cathode.

Chemical Reaction \Rightarrow Electric Energy

Standard Reduction Potentials

Potential (E in volt): pressure of e^- to flow from one electrode to the other in a battery.
 E is the *ability* of a cell to *force* electrons through a circuit.

Ionic Concentration 1 M in water at 25°C, 1 atm.

Half-Reaction	E° (volts)	Half-Reaction	E° (volts)
$F_2(g) + 2e^- \rightarrow 2F^-$	+2.87	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
$Au^{3+} + 3e^- \rightarrow Au(s)$	+1.50	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.26
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.36	$Co^{2+} + 2e^- \rightarrow Co(s)$	-0.28
$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.23	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.45
$4H^+ + O_2(g) + 4e^- \rightarrow 2H_2O$	+1.23	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
$4H^+ + MnO_2(s) + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.22	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.09	$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$	-0.83
$Hg^{2+} + 2e^- \rightarrow Hg(l)$	+0.85	$Mn^{2+} + 2e^- \rightarrow Mn(s)$	-1.19
$Ag^+ + e^- \rightarrow Ag(s)$	+0.80	$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	+0.80	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.37
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$Na^+ + e^- \rightarrow Na(s)$	-2.71
$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
$Cu^+ + e^- \rightarrow Cu(s)$	+0.52	$Sr^{2+} + 2e^- \rightarrow Sr(s)$	-2.89
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.34	$Ba^{2+} + 2e^- \rightarrow Ba(s)$	-2.91
$4H^+ + SO_4^{2-} + 2e^- \rightarrow SO_2(aq) + 2H_2O$	+0.17	$Cs^+ + e^- \rightarrow Cs(s)$	-2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$K^+ + e^- \rightarrow K(s)$	-2.93
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00	$Rb^+ + e^- \rightarrow Rb(s)$	-2.98
		$Li^+ + e^- \rightarrow Li(s)$	-3.04

Zn is a better oxidizing agent → It is reduced

Al is a better reducing agent → It is oxidized

Cell Potential

Exhausted batteries at equilibrium have no pushing or pulling power, the **cell potential** is zero.

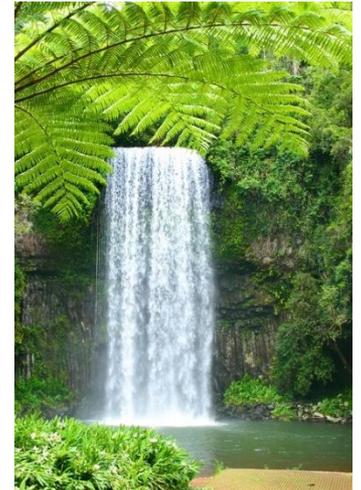
The SI unit of potential is the volt (V) defined as the charge of one coulomb (1 C) falling through a potential difference of one volt (1 V) releasing one joule (1 J) of energy:

$$\text{Volts: } 1 \text{ V} = \text{J} \cdot \text{C}^{-1}$$

One coulomb is the magnitude of charge delivered one ampere flowing for one second: $1 \text{ C} = 1 \text{ A} \cdot \text{s}$

Each water drop is like an electron.

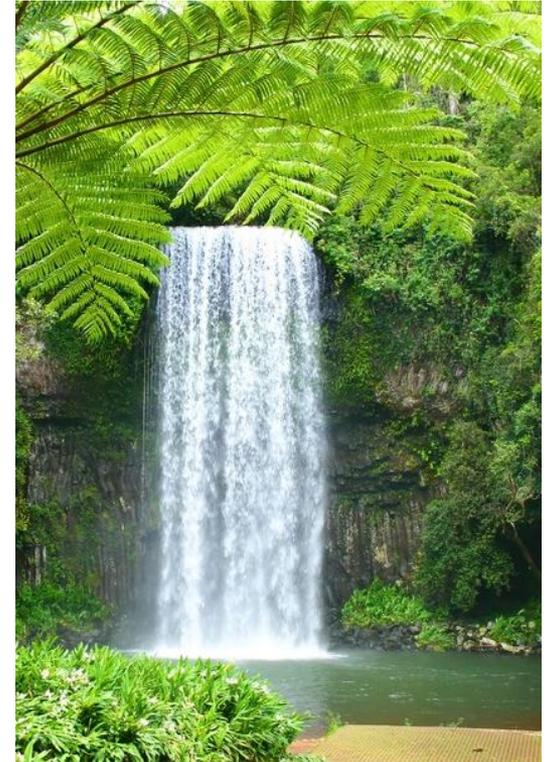
The larger waterfall represents a higher **volume of electrons delivered per second**.



Cell Potential and Reaction Gibbs Free Energy

Work of a waterfall is due to **gravitational** force, a change in **pressure** and **volume** due to mass.

However, **electrical work** is **neither** a change in pressure nor volume.



Electrical work is **nonexpansion work** (section 9.14).

Gibbs free energy is the measure of the **maximum non expansion work** that a reaction can do at constant pressure and temperature: $\Delta G = w_e$

Cell Potential and Reaction Gibbs Free Energy

$$\Delta G = w_e = -nFE$$

F: 96,485 C·mol⁻¹ (Faraday's constant, it is the *magnitude* of the charge *per mole* of electrons).

n = number of moles (electrons traveling)

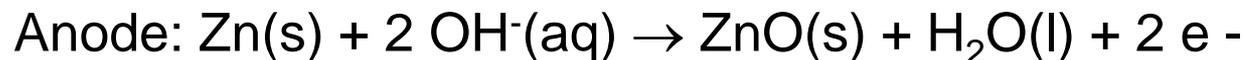
E: The maximum amount of work is the maximum cell potential produced in the reaction and is called the **electromotive force**, **emf**, of a cell.

From now on, E will always be taken to represent this emf.

[Note: The definition of **reversibility**, Section 8.3, requires the pushing force balance against an *equal* and opposite force. Under these conditions the **maximum work** occurs for a reversible process.]

Example 1: The reaction taking place in the silver cell used in some cameras and wristwatches is $\text{Ag}_2\text{O}(\text{s}) + \text{Zn}(\text{s}) \rightarrow 2 \text{Ag}(\text{s}) + \text{ZnO}(\text{s})$, and the emf of the cell when new is 1.6V. What is the reaction Gibbs free energy?

Table values:



This is a 2 electron process.

Use $\Delta G = -nFE$ to determine a reaction Gibbs free energy.

$$\Delta G = -nFE, = - (2 \text{ mol}) \times (96,485 \text{ C}\cdot\text{mol}^{-1}) \times (1.6 \text{ V}) = - 3.09 \times 10^5 \text{ C}\cdot\text{V}$$

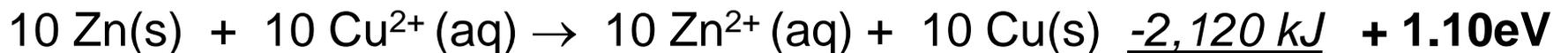
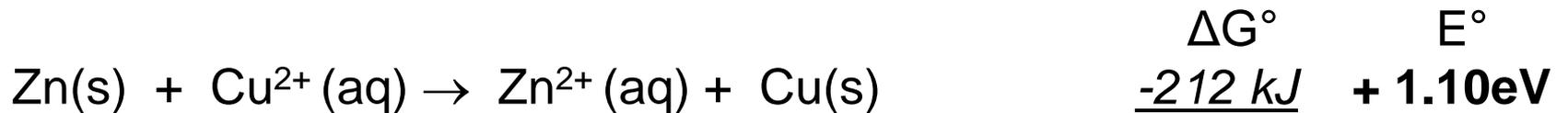
Because $1 \text{ C}\cdot\text{V} = 1 \text{ J}$, we can conclude that the Gibbs free energy of reaction is -309 kJ (spontaneous)

Standard Reaction

For standard E° or standard emf we can write $\Delta G^\circ = -nFE^\circ$.

Meaning 1 bar of pressure, 1 M solutions.

The value of E is the same, regardless of how we write the equation, but the value of ΔG° depends on the **stoichiometric coefficients** in the chemical equation.



You would get the same voltage if you had a battery that could fit in your hand or were the size an Olympic sized swimming pool (only amperage would change).

The Notation (Diagram) for a Daniell Cell

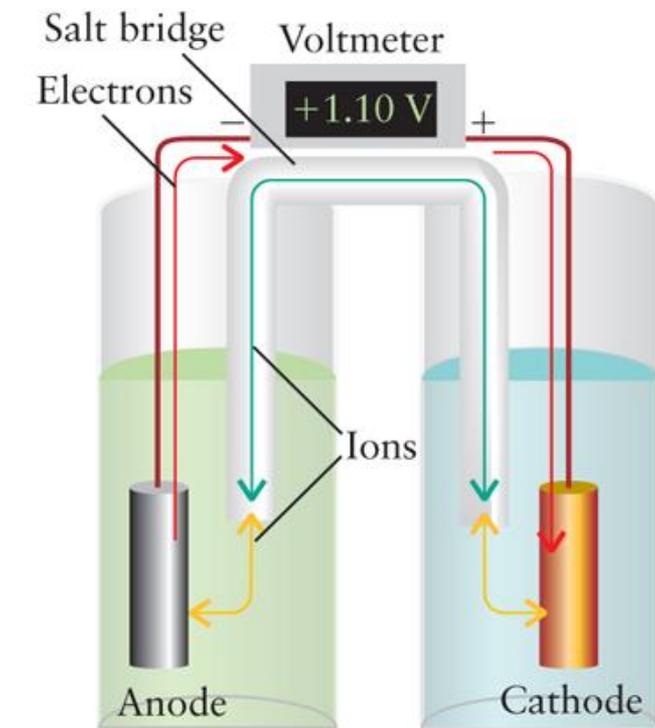
Anode electrode | anode electrolyte || cathode electrolyte | cathode electrode

“|” means phase change like an electrode and solution.

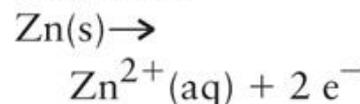
“||” means a salt bridge.

The anode is also called the anodic compartment, and cathodic compartment for the cathode.

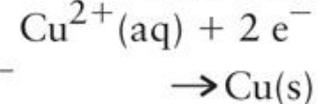
The salt bridge allows ions to move back and forth.



Oxidation:



Reduction:



Inert Electrodes

The field of electrochemistry would be very small if we only had metallic electrodes, how about gasses?

If the oxidized and reduced form of a redox couple are **water soluble**:

Inert electrode allow electrons to pass, yet it will **not react**. Platinum, gold, and carbon are just a few common inert electrodes.

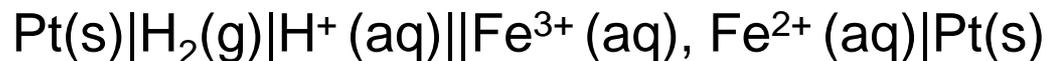
For instance measuring the potential of two aqueous ions:



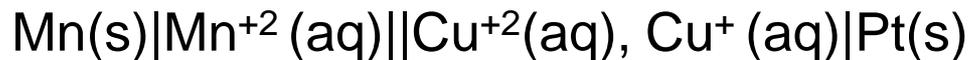
Or a gas: $||\text{H}^{+}(\text{aq})|\text{H}_2(\text{g})|\text{Pt}(\text{s})$

Only species and not the electrode go through Redox.

Example 2: Write the diagram for a cell with a hydrogen electrode on the left and an iron(III)/iron(II) electrode on the right. The two electrode compartments are connected by a salt bridge and platinum is used as the conductor at each electrode.



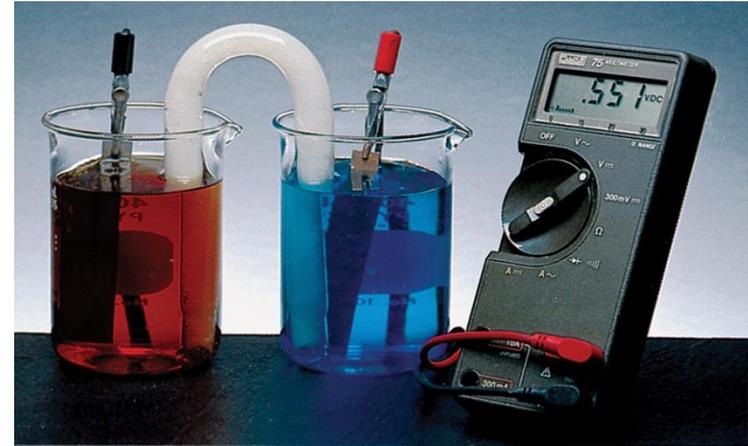
Example 3: Write the diagram for a cell that has an electrode consisting of a manganese wire dipping into a solution of manganese(II) ions on the left, a salt bridge, and a copper(II)/copper(I) electrode on the right with a platinum wire.



Electronic Voltmeter

Electronic voltmeter: $\Delta G^\circ = -nFE^\circ$

Voltmeters (aka potentiometer) measure voltage.



Voltage for $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$ is $E = + 1.10 \text{ V}$. Zn is the anode, (-), and Cu is the cathode (+).

Here $E > 0$, so $G < 0$, so this is a **spontaneous** cell.

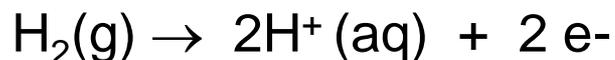
Switching the leads around would read electrons flowing in the opposite direction, $\text{Cu(s)}|\text{Cu}^{2+}(\text{aq})||\text{Zn}^{2+}(\text{aq})|\text{Zn(s)}$ then $E = -1.10 \text{ V}$

Here $E < 0$, so $G > 0$, so this is a **nonspontaneous** cell.

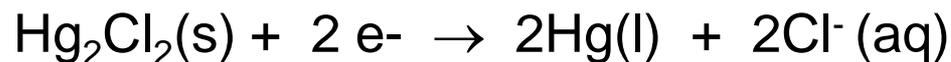
Example 4: Write the cell reaction for the cell



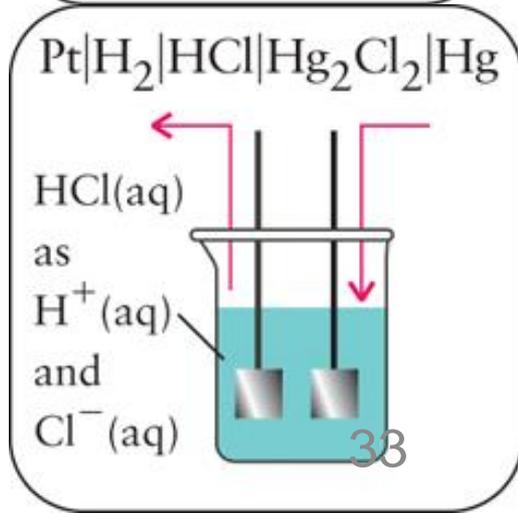
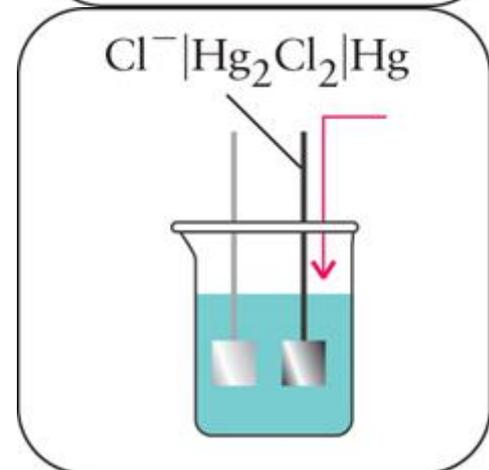
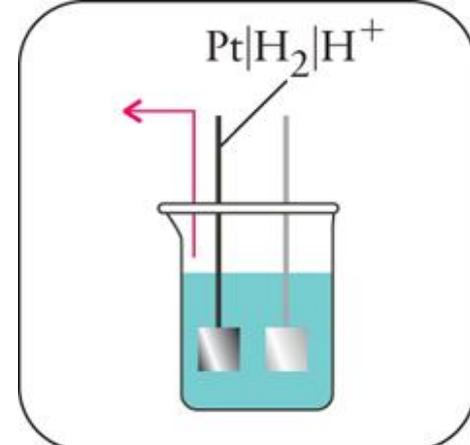
We note there is **no salt bridge**, so this is done in a single beaker. The anode is where oxidation takes place, this is the hydrogen electrode,



The cathode is where reduction takes place, this is the Hg.



Combine the two half reactions:



Standard Potential

Each electrode makes it's own characteristic contribution to the cell potential called *its* **standard potential**, E° , a measure of it's **electron-pulling power**.

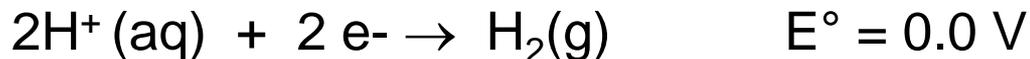
Galvanic cells measure the overall pulling power of the cell, called the **cell's standard emf**; a **difference** of the **standard potentials of the two electrodes**.

The difference is written as: $E^\circ = E^\circ(\text{cathode}) - E^\circ(\text{anode})$

Ionic Concentrations 1 M in Water at 298 K, 101.3 kPa			
Half-Reaction	E° (volts)	Half-Reaction	E° (volts)
$F_2(g) + 2e^- \rightarrow 2F^-$	+2.87	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
$Au^{3+} + 3e^- \rightarrow Au(s)$	+1.50	$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.26
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	+1.36	$Co^{2+} + 2e^- \rightarrow Co(s)$	-0.28
$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.23	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.45
$4H^+ + O_2(g) + 4e^- \rightarrow 2H_2O$	+1.23	$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
$4H^+ + MnO_2(s) + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.22	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.09	$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$	-0.83
$Hg^{2+} + 2e^- \rightarrow Hg(l)$	+0.85	$Mn^{2+} + 2e^- \rightarrow Mn(s)$	-1.19
$Ag^+ + e^- \rightarrow Ag(s)$	+0.80	$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	+0.80	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.37
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$Na^+ + e^- \rightarrow Na(s)$	-2.71
$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
$Cu^+ + e^- \rightarrow Cu(s)$	+0.52	$Sr^{2+} + 2e^- \rightarrow Sr(s)$	-2.89
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.34	$Ba^{2+} + 2e^- \rightarrow Ba(s)$	-2.91
$4H^+ + SO_4^{2-} + 2e^- \rightarrow SO_2(aq) + 2H_2O$	+0.17	$Cs^+ + e^- \rightarrow Cs(s)$	-2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$K^+ + e^- \rightarrow K(s)$	-2.93
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00	$Rb^+ + e^- \rightarrow Rb(s)$	-2.98
		$Li^+ + e^- \rightarrow Li(s)$	-3.04

Standard Potential

Instead, an electrode is chosen to be the standard against which all other electrodes are measured; it's the hydrogen electrode.



This is called the **Standard Hydrogen Electrode** (SHE).

For example, for the cell the cell potential is:



Since the hydrogen electrode is zero, the emf is **attributed entirely to the copper** electrode, and we write:

spontaneous $E > 0$ ($\Delta G^\circ = -nFE^\circ$)

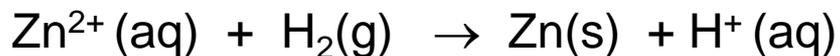


Additionally, **the hydrogen electrode is usually the anode.**

The *more positive the potential:*

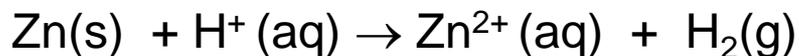
1. the greater the **electron-pulling power** of the reduction half-reaction;
2. It is a stronger oxidizing agent.

Example 5: For Pt(s)|H₂(g)|H⁺ (aq)||Zn²⁺ (aq)|Zn(s): emf is -0.76 V



The reaction is **nonspontaneous** $E < 0$ ($\Delta G^\circ = -nFE^\circ$). Zinc ion (Zn²⁺) has a poor electron-pulling ability, therefore it is a poor oxidizing agent when compared to H⁺.

The reverse of the cell reaction,



The emf is +0.76 V, this is **spontaneous** so zinc metal has a strong electron-pulling ability, therefore zinc is a better oxidizing agent when compared to hydrogen (H₂).

Example 6: For $\text{Zn(s)}|\text{Zn}^{+2}(\text{aq})||\text{Sn}^{4+}(\text{aq}),\text{Sn}^{2+}(\text{aq})|\text{Pt(s)}$ the emf, E° , is +0.91 V.

The standard potential of a zinc electrode is -0.76 V. What is the standard potential of the $\text{Sn}^{4+}/\text{Sn}^{2+}$ electrode?

Written as anode||cathode so Zn is the anode or getting oxidized and Sn is getting reduced.

We know $E^\circ = E_{\text{cat}}^\circ - E_{\text{anode}}^\circ$

And $E^\circ = +0.91\text{V}$, and $E_{\text{anode}}(\text{Zn}) = -0.76\text{V}$

$E^\circ = E^\circ = E_{\text{cat}}^\circ - E_{\text{anode}}^\circ$, $+0.91\text{V} = E_{\text{cat}}^\circ - (-0.76\text{V})$,

$E_{\text{cat}}^\circ = +0.91\text{V} - 0.76\text{V} = +0.15\text{V}$

Easiest to oxidize, strongest reducing agents

	1	2	13/III	14/IV	15/V	16/VI	17/VII
2	Li -3.05	Be -1.85	B	C	N	O +1.23	F +2.87
3	Na -2.71	Mg -2.36	Al -1.66	Si	P	S -0.48	Cl +1.36
4	K -2.93	Ca -2.87	Ga -0.49	Ge	As	Se -0.67	Br +1.09
5	Rb -2.93	Sr -2.89	In -0.34	Sn -0.14	Sb	Te -0.84	I +0.54
6	Cs -2.92	Ba -2.91	Tl -0.34	Pb -0.13	Bi +0.20	Po	At
7	Fr	Ra -2.92					

Hardest to oxidize, strongest oxidizing agents.

Note that the most negative values are in the s-block and that the most positive values are close to fluorine.

Standard Potentials and Equilibrium Constants

In Section 10.3 the standard reaction Gibbs free energy, ΔG_r° , is related to the *equilibrium constant* $\Delta G_r^\circ = -RT \ln K$.

In this chapter, the standard reaction Gibbs free energy is related to the *standard emf* $\Delta G^\circ = -nFE^\circ$.

We can rearranged to the following:

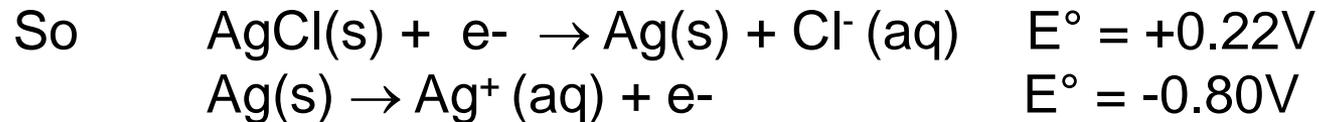
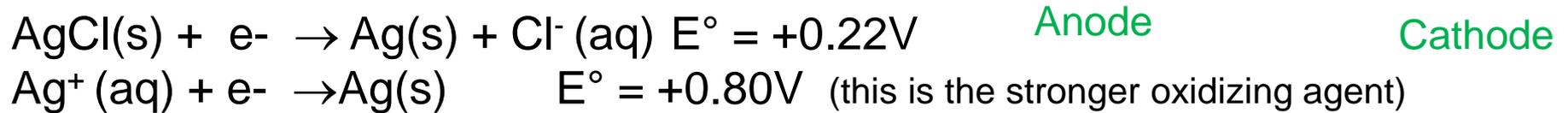
$$\ln K = \frac{nFE^\circ}{RT} \quad \text{For } \frac{RT}{F} = 0.025693\text{V} \quad \text{so} \quad \ln K = \frac{nE^\circ}{0.025693\text{V}}$$

So K increases exponentially with E° . So a large E° means $K \gg \gg 1$ (product favored)

Example 7: Calculate the equilibrium constant at 25.00°C for the reaction
 $\text{AgCl(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The equilibrium constant is the solubility product, $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$.

$$\ln K = \frac{nE^\circ}{0.025693\text{V}} \quad \text{To find } K, \text{ we need } E^\circ$$



$$\ln K = \frac{nE^\circ}{0.025693\text{V}} = \frac{(1) \times (-0.58\text{V})}{0.025693\text{V}}, \quad K = e^{\frac{(1) \times (-0.58\text{V})}{0.025693\text{V}}} = 1.6 \times 10^{-10}$$

The Nernst Equation

As a reaction proceeds, reactants are consumed, the concentrations change and eventually the battery becomes “dead.” This happens when ΔG approaches zero or at equilibrium, zero potential is generated.

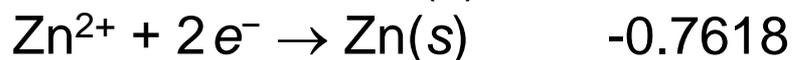
The Nernst equations is a quantitative measure of a cell potential at different concentrations.

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (RT/F = 0.025693V, \text{ and using Log})$$

$$E = E^\circ - \frac{0.025693V}{n} \ln Q$$

The Nernst equation is widely used to estimate the emf of cells under nonstandard conditions.

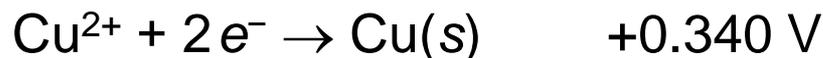
Example 8: Calculate the emf at 25°C of a Daniell cell in which the concentration of Zn^{2+} ions is $0.10 \text{ mol}\cdot\text{L}^{-1}$ and that of the Cu^{2+} ions is $0.0010 \text{ mol}\cdot\text{L}^{-1}$.



$$E = E^{\circ} - \frac{0.025693\text{V}}{n} \ln Q$$

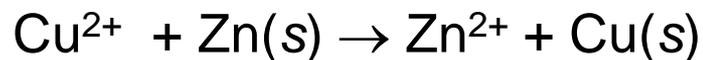
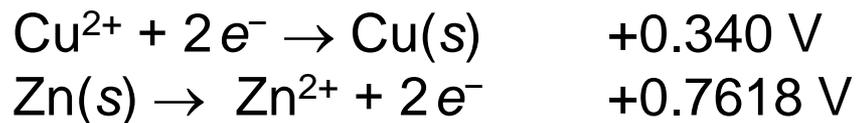
We solve for E, so we need to find E° and Q, $n = 2$

For a Daniell cell E is positive, since Cu^{2+} is a stronger oxidizing agent, Zn will get oxidized.



(note: reaction and sign are reversed)

Example 8: Calculate the emf at 25°C of a Daniell cell in which the concentration of Zn^{2+} ions is $0.10 \text{ mol}\cdot\text{L}^{-1}$ and that of the Cu^{2+} ions is $0.0010 \text{ mol}\cdot\text{L}^{-1}$.



$$E^{\circ} = E_{\text{ox}} + E_{\text{red}} = +0.340 \text{ V} + 0.7618 \text{ V} = +1.102 \text{ V}$$

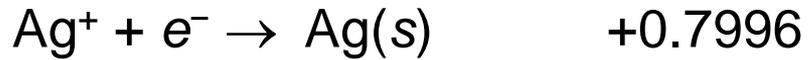
$$Q = \frac{\text{products}}{\text{reactants}} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.10 \text{ mol}\cdot\text{L}^{-1}}{0.0010 \text{ mol}\cdot\text{L}^{-1}}$$

$$E = E^{\circ} - \frac{0.025693\text{V}}{n} \ln Q ,$$

$$E = 1.102 \text{ V} - \frac{0.025693\text{V}}{2} \ln \frac{0.10 \text{ mol}\cdot\text{L}^{-1}}{0.0010 \text{ mol}\cdot\text{L}^{-1}}$$

$$= +1.04 \text{ V}$$

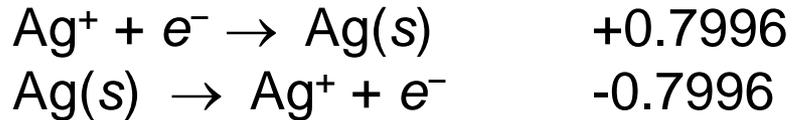
Example 9: Calculate the emf of the concentration cell
 $\text{Ag(s)}|\text{Ag}^+(\text{aq}, 0.0010 \text{ mol}\cdot\text{L}^{-1}) || \text{Ag}^+(\text{aq}, 0.010 \text{ mol}\cdot\text{L}^{-1})|\text{Ag(s)}$.



$$E = E^\circ - \frac{0.025693\text{V}}{n} \ln Q$$

We solve for E, so we need to find E° and Q, $n = 1$

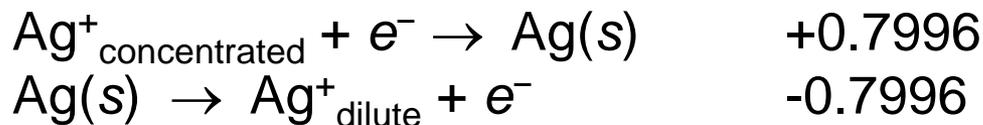
For a Daniell cell E is positive, in this case



$$E^\circ = E_{\text{ox}} + E_{\text{red}} = +0.7996 - 0.7996 = 0$$

Example 9: Calculate the emf of the concentration cell
 $\text{Ag(s)}|\text{Ag}^+(\text{aq}, 0.0010 \text{ mol}\cdot\text{L}^{-1}) || \text{Ag}^+(\text{aq}, 0.010 \text{ mol}\cdot\text{L}^{-1})|\text{Ag(s)}$.

The cell notation is written as anode||cathode, or

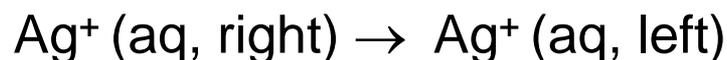


$$Q = \frac{\text{products}}{\text{reactants}} = \frac{[\text{Ag}^+_{\text{dilute}}]}{[\text{Ag}^+_{\text{concentrated}}]} = \frac{0.0010 \text{ mol}\cdot\text{L}^{-1}}{0.010 \text{ mol}\cdot\text{L}^{-1}}$$

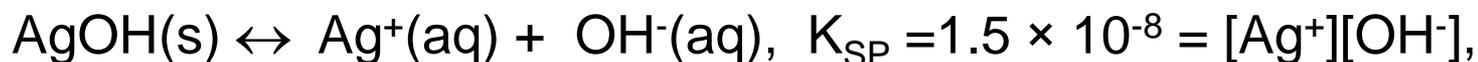
$$E = E^\circ - \frac{0.025693\text{V}}{n} \ln Q = 0 \text{ V} - \frac{0.025693\text{V}}{1} \ln \frac{0.0010 \text{ mol}\cdot\text{L}^{-1}}{0.010 \text{ mol}\cdot\text{L}^{-1}} = +0.059 \text{ V}$$

An interesting cell driven by a difference in concentration.

Example 10: Calculate the emf of a cell constructed with two silver electrodes. The electrolyte in one compartment is 1.0 M $\text{AgNO}_3(\text{aq})$. In the other compartment NaOH has been added to a AgNO_3 solution until the $\text{pH} = 12.5$ at 298 K



$$\text{pH} + \text{pOH} = 14, \quad 14 - 12.5 = 1.5 = \text{pOH}, \quad [\text{OH}^-] = 0.032\text{M}$$



$$\text{solve for } [\text{Ag}^+] = 1.5 \times 10^{-8} / 0.032 = 4.7 \times 10^{-7}$$

$$E = E^\circ - \frac{0.025693\text{V}}{n} \ln Q, \quad \text{here } E^\circ = 0, \quad \text{so}$$

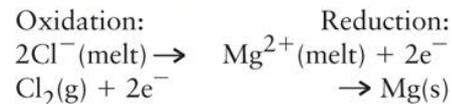
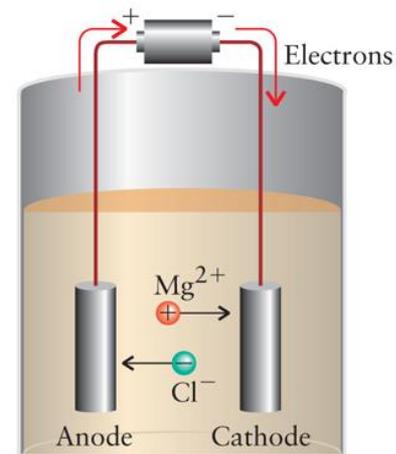
$$E = \frac{-0.025693\text{V}}{1} \ln \frac{4.7 \times 10^{-7}}{1.0\text{M}} = +0.37\text{V}$$

Electrolytic Cells

Electrolytic cells are **nonspontaneous** cells, where a current is forced in the opposite direction to drive the reaction.

This process is called electrolysis, and is the **opposite of a Galvanic cell**.

Whereas electrons flow spontaneously in a **Galvanic cell** from the anode to cathode, **Electrolytic cells** apply an emf at the cathode, making the **cathode “-”** and the **anode “+.”**

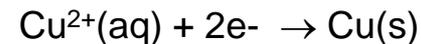
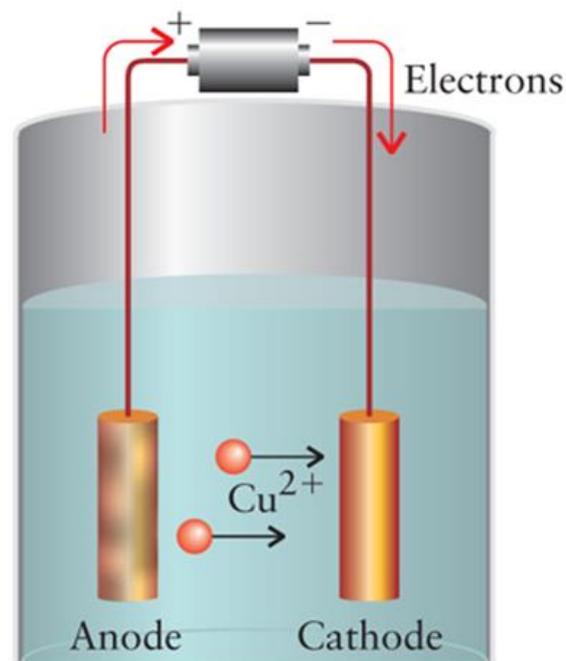


Electrolytic Cells

Reduction still takes place at the cathode, $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$, here though, electrons are being pumped in, from an **external power source** (e^- are not coming from the anode).

Oxidation still takes place at the anode, $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ except now the electrons are being pulled toward the higher potential, they are falling upstream, like salmon during a spawning-run, in order to create new Cu^{2+} .

[The new Cu^{2+} serves both to create neutrality, as well as be pulled toward the cathode to be plated.]



Electrolytic Cells

A nonspontaneous reaction, driven by an external power supply.



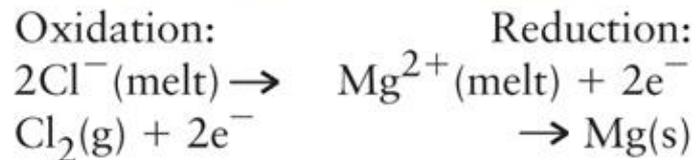
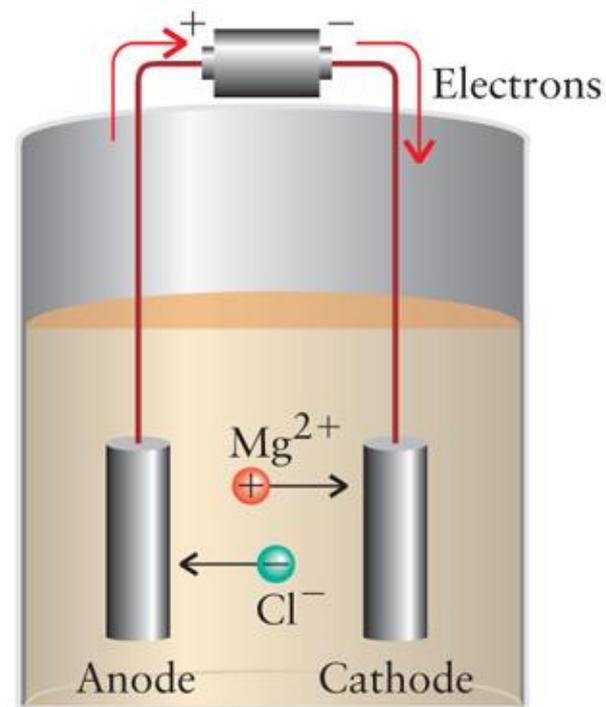
["melt" signifies molten salt]

Note that only the **sign changes**.

Electrons are forced into the cathode and are drawn toward a higher potential anode.

Notice the **lack of a salt bridge**.

The Dow process

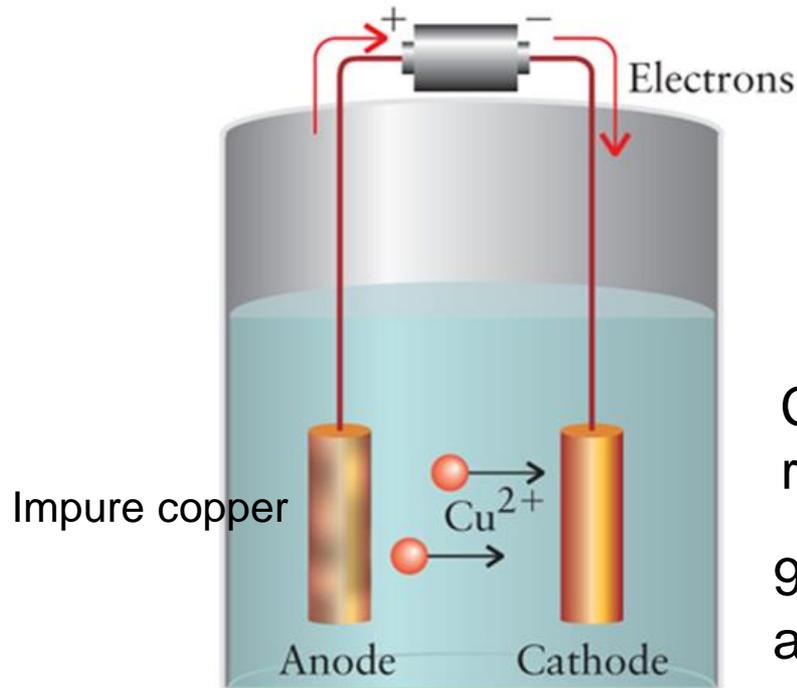


Electrolysis

Copper is refined electrolytically by using an impure form of copper metal called **blister copper** as the anode in an electrolytic cell. Supplied current drives the oxidation of the blister copper to copper(II) ions, Cu^{2+} , which are then reduced to pure copper metal at the cathode:

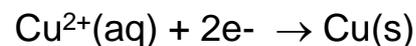
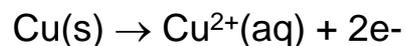


Michael Faraday



Copper is 100% recyclable

99.99% pure, aqueous!



Electrolysis

$$Q = I \times t$$

Q: quantity of electricity passed through the electrolysis cell (in coulombs (C))

I: current (in ampere (A))

t: time (in second (s))

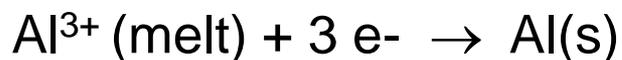
$$n = \frac{Q}{F} = \frac{It}{F}$$

F: 96,485 C·mol⁻¹ (Faraday's constant, it is the *magnitude* of the charge *per mole* of electrons).

n: amount (moles) of electrons

Example 11: Aluminum is produced by electrolysis of its oxide dissolved in molten cryolite (Na_3AlF_6). Find the mass of aluminum that can be produced in 1.00 day (d) in an electrolytic cell operating continuously at 1.00×10^5 A. The cryolite does not react.

The half reaction we're interested in is



This is a 3 mol $\text{e}^- \simeq 1$ mol Al

$$1 \text{ day} = 24 \text{ hr} = 24 \times 3600 \text{ s}$$

$$F = 96,485 \text{ C} \cdot \text{mol}^{-1}$$

$$n = \frac{Q}{F} = \frac{It}{F} = \frac{(1.00 \times 10^5 \text{ A})(24 \times 3600 \text{ s})}{96,485 \text{ C} \cdot \text{mol}^{-1}} = 8.95 \times 10^4 \text{ mol e}^-$$

$$8.95 \times 10^4 \text{ mol e}^- \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 8.05 \times 10^5 \text{ g Al}$$

Example 12: How many hours are required to plate 25.00 g of copper metal from 1.00 M CuSO₄(aq) by using a current of 3.00 A?

For the reaction $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Cu}(\text{s})$

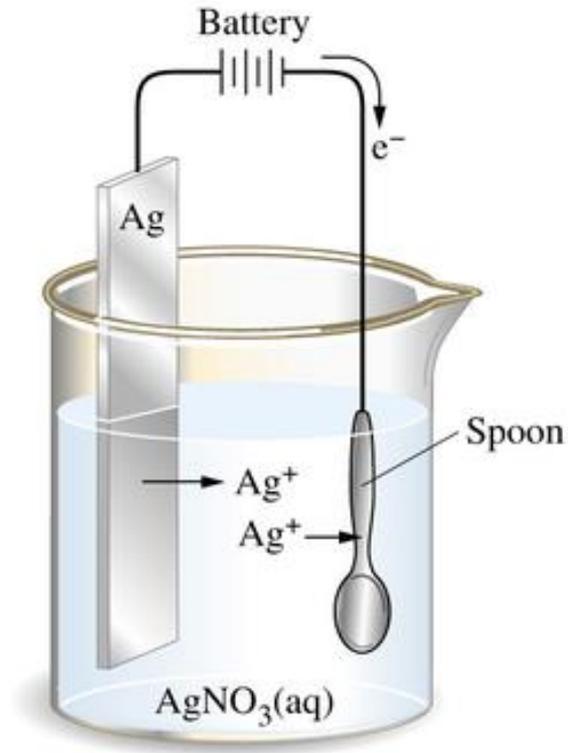
This is a 2 mol e⁻ ≅ 1 mol Cu(s)

$$25.00 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.54 \text{ g Cu}} \times \frac{2 \text{ mol e}^{-}}{1 \text{ mol Cu}} = 0.7869 \text{ mol e}^{-}$$

$$n = 0.7869 \text{ mol e}^{-} = \frac{It}{F} = \frac{(3.00 \text{ A})(t)}{96,485 \text{ C}\cdot\text{mol}^{-1}} \rightarrow t = 2.52 \times 10^5 \text{ s} = 7.0 \text{ hr}$$

Electrolysis

Nonspontaneous



Electric Energy



Chemical Reaction

Electrolysis

