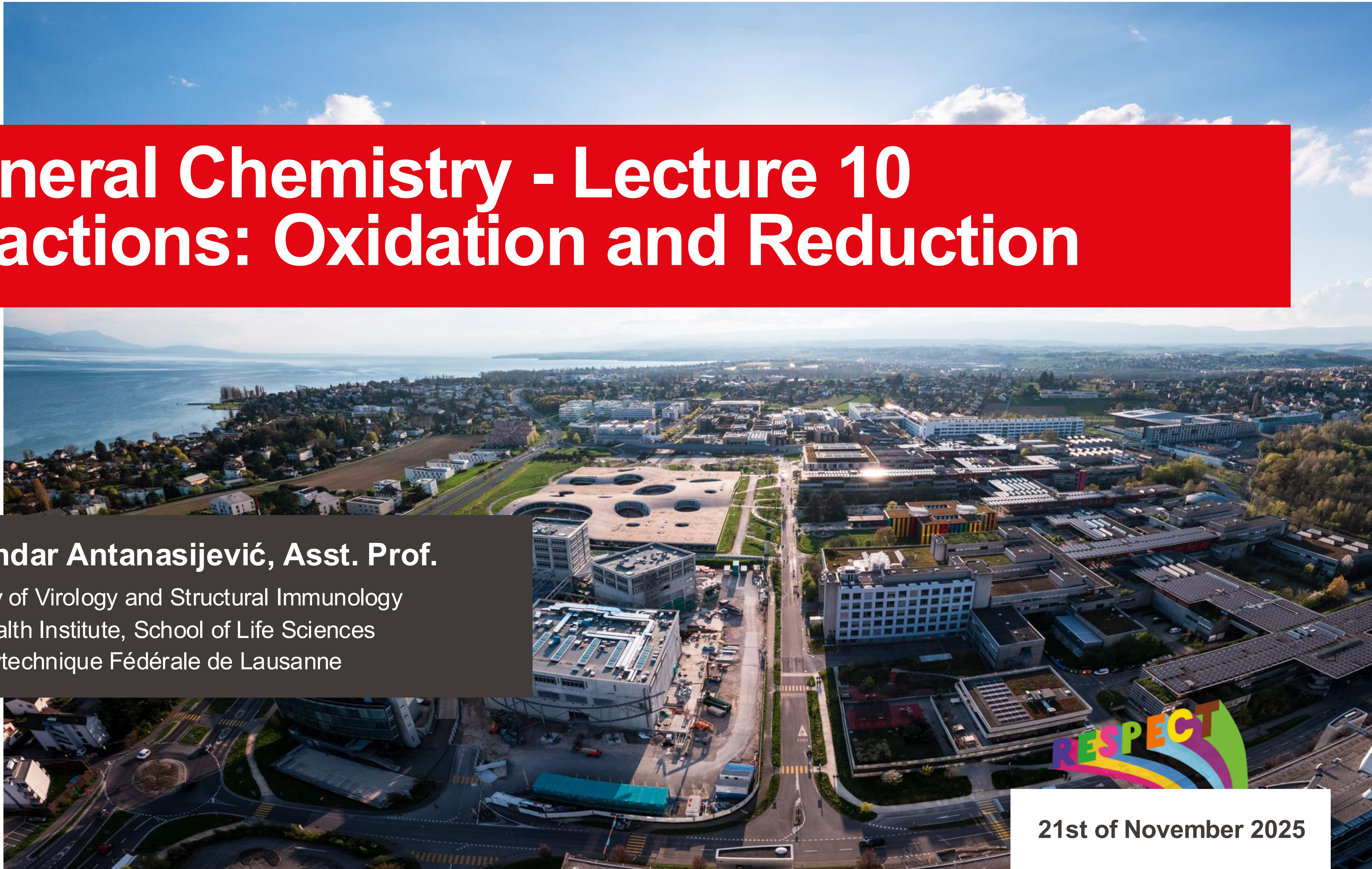

General Chemistry - Lecture 10
Reactions: Oxidation and Reduction

Aleksandar Antanasijević, Asst. Prof.
Laboratory of Virology and Structural Immunology
Global Health Institute, School of Life Sciences
École Polytechnique Fédérale de Lausanne

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polytechnique
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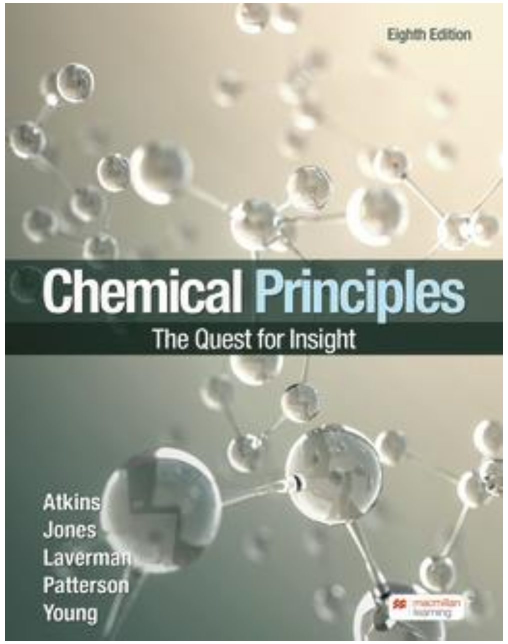
Learning Objectives

- Learning the basic redox processes and their origins
- Understanding the transfer of electrons in chemical reactions
- Learning the basic concepts of electrochemistry
- Understanding how electrodes work in galvanic cells
- Electrolysis

Reading suggestions

- Chemical Principles: The Quest of Insight
  - Chapter 6

Also revise **Lecture 2** of this course



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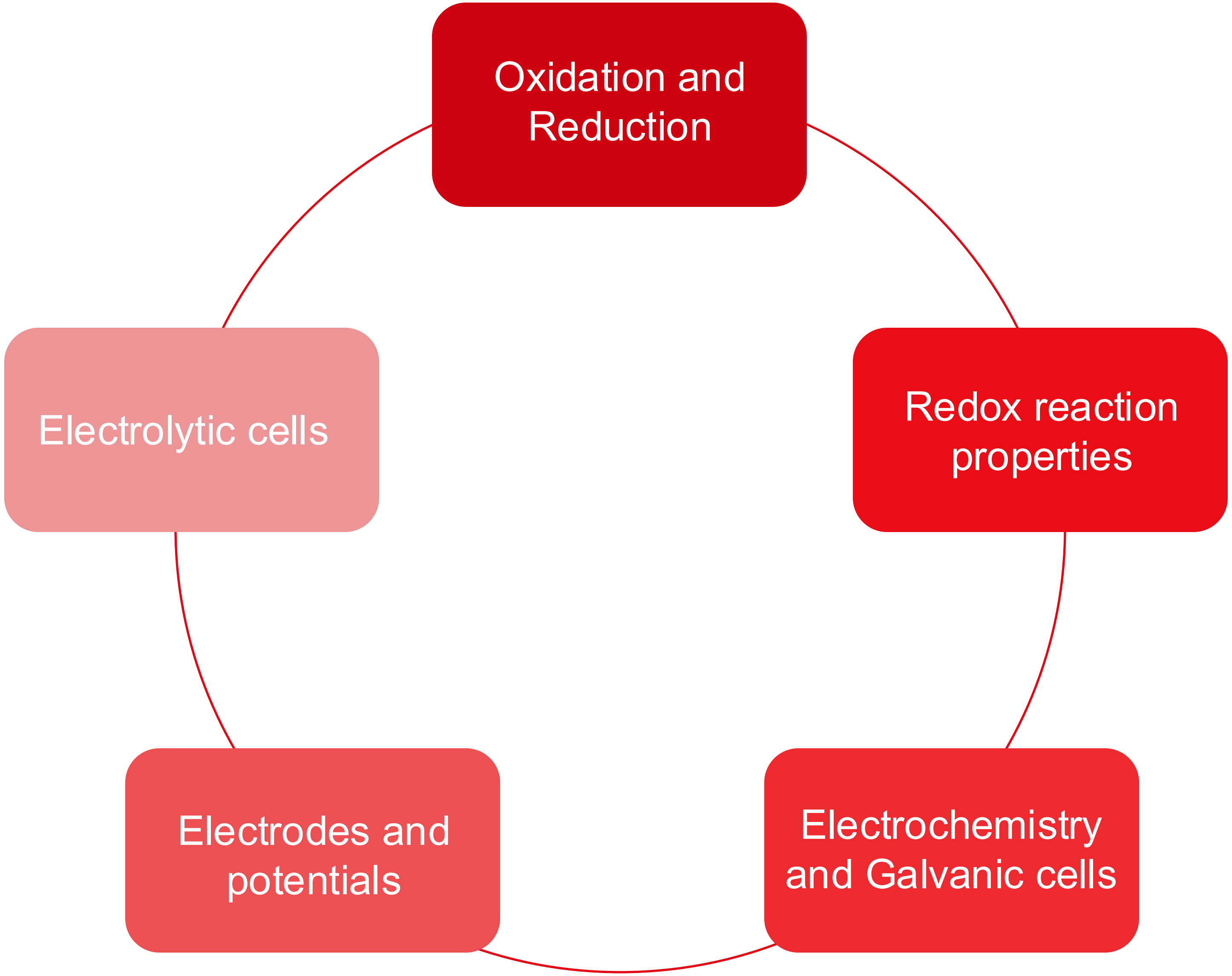


Oxidation and Reduction

Redox reaction properties

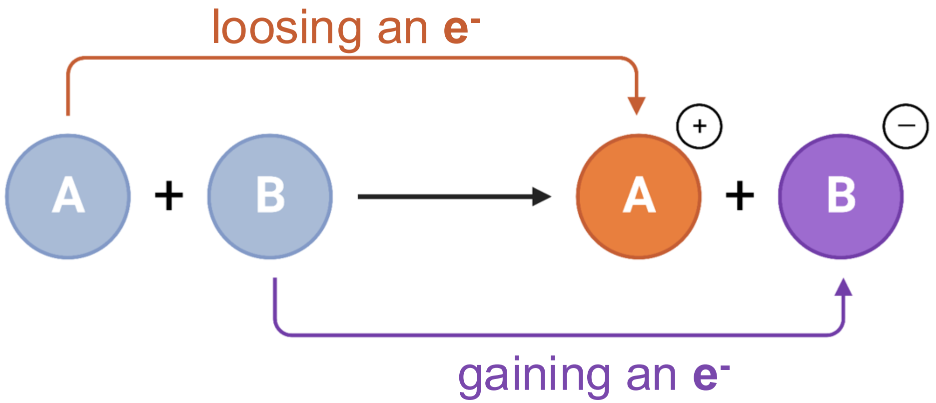
Electrochemistry and Galvanic cells

Electrodes and potentials

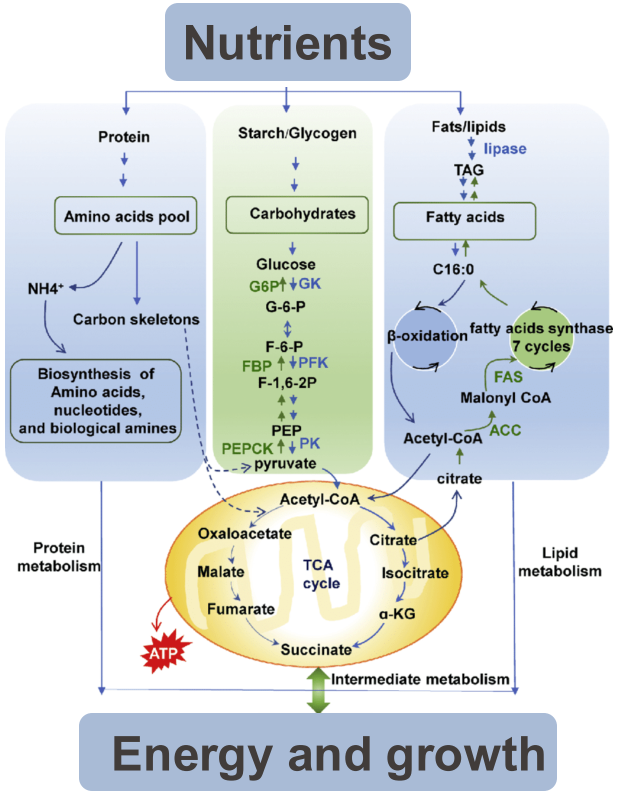
Electrolytic cells

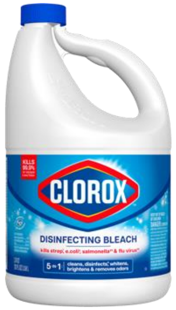
Oxidation and Reduction

- **Redox chemistry** (oxidation–reduction chemistry) is the broad area of chemistry that deals with **how electrons are transferred between chemical species** and how these transfers change the **composition, energy,** and **reactivity** of matter.



- Some common examples of redox reactions:
  - Combustion
  - Battery reactions
  - Metal corrosion
  - Bleaching and disinfection
  - Metabolic processes (e.g., photosynthesis)





Oxidation and Reduction

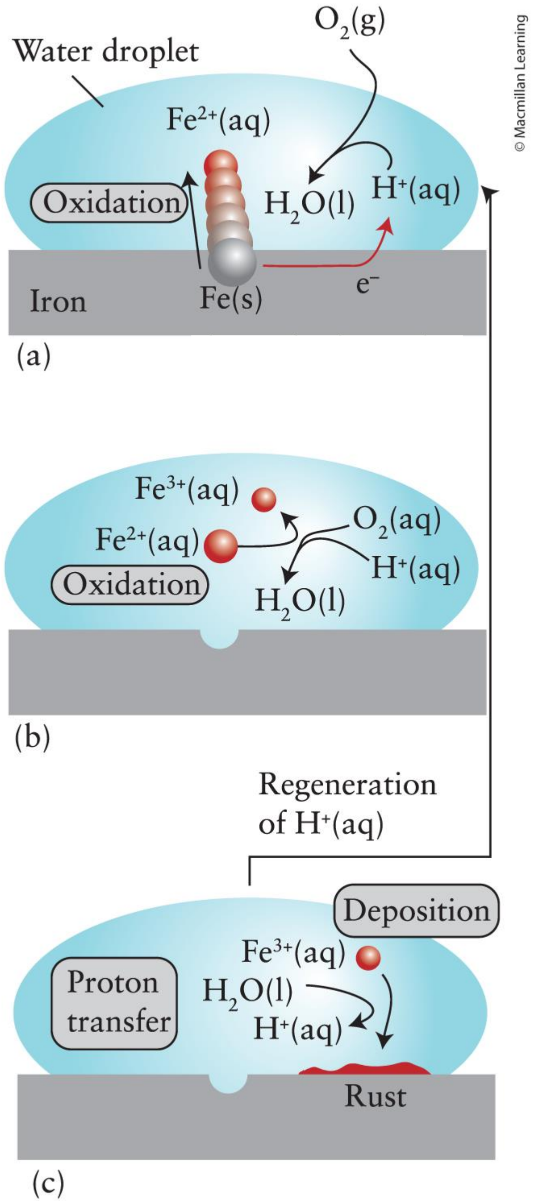
- Example: The corrosion of iron (Fe):

$$2\ Fe(s) + 3/2\ O_2(g) + 3\ H_2O(l) \rightarrow 2\ Fe(OH)_3(s)$$

- Antoine Lavoisier was the first to characterize these reactions and coined the term **oxidation** (= binding oxygen)
- Later work showed that such reactions actually involve an electron transfer while oxygen is not always essential

$$2\ Fe(s) \rightarrow 2\ Fe^{3+} + 6\ e^-$$

$$3/2\ O_2(g) + 3\ H_2O(l) + 6\ e^- \rightarrow 6\ OH^-(aq)$$



Adapted from Lecture 2

Oxidation

- **Oxidation** is a chemical process in which a substance **loses electrons**, or more generally, undergoes an **increase in oxidation state**.

- Example: Reaction **involving** oxygen

$$2\,\mathbf{Mg(s)} + \mathbf{O_2(g)} \rightarrow 2\,\mathbf{MgO(s)}$$

$$2\,Mg^0 \xrightarrow{-4\,e^-} 2\,Mg^{2+}$$

Oxidation state of Mg changes from **0** to **+2**

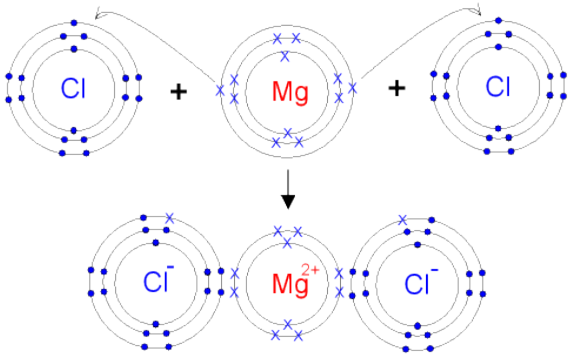
Fun fact: This reaction is used to make fireworks

- Example: Reaction **not involving** oxygen

$$\mathbf{Mg(s)} + \mathbf{Cl_2(g)} \rightarrow \mathbf{MgCl_2(s)}$$

$$Mg^0 \xrightarrow{-2\,e^-} Mg^{2+}$$

Oxidation state of Mg changes from **0** to **+2**



Magnesium uses 2 valent electrons to make bond(s)

Reduction

- **Reduction** is a chemical process in which a substance **gains electrons**, or more generally, undergoes a **decrease in oxidation state**.

- Example: Reaction **involving** oxygen

$$2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$$

$$O_2^{0} \xrightarrow{+\,4\,e^-} 2\,O^{2-}$$

Oxidation state of O changes from **0** to **-2**

- Example: Reaction **not involving** oxygen

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

$$Cl_2^{0} \xrightarrow{+\,2\,e^-} 2\,Cl^-$$

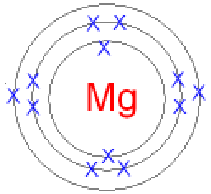
Oxidation state of Cl changes from **0** to **-1**

- The two processes, oxidation and reduction, are coupled to each other.
- The number of electrons given by one atom/group during a reaction equals the number of electrons received by the other atom/group.

Oxidation state

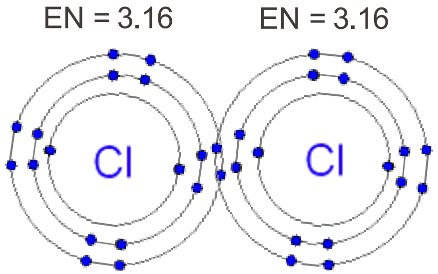
- The **oxidation state** or **oxidation number** (N_{ox}) indicates the number of electrons each atom would have given or received relative to the neutral state if the bonds in which these atoms are involved were purely ionic.
- The more electronegative atom is assigned the negative oxidation state and the less electronegative atom the positive one.
- If the electronegativity of the two bonded atoms is the same (e.g., if the bonded atoms are the same element), then the oxidation state for both is 0.

Atomic magnesium



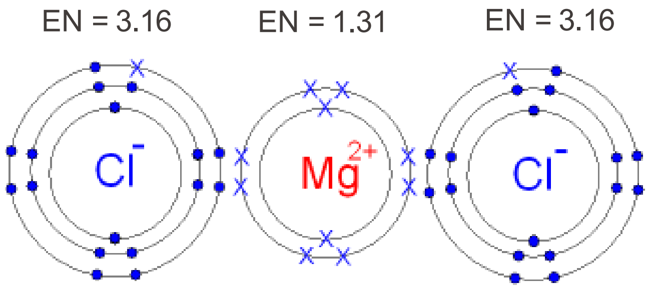
N_{ox} (Mg) = 0

Equal electronegativity



N_{ox} (Cl) = 0

Different electronegativity



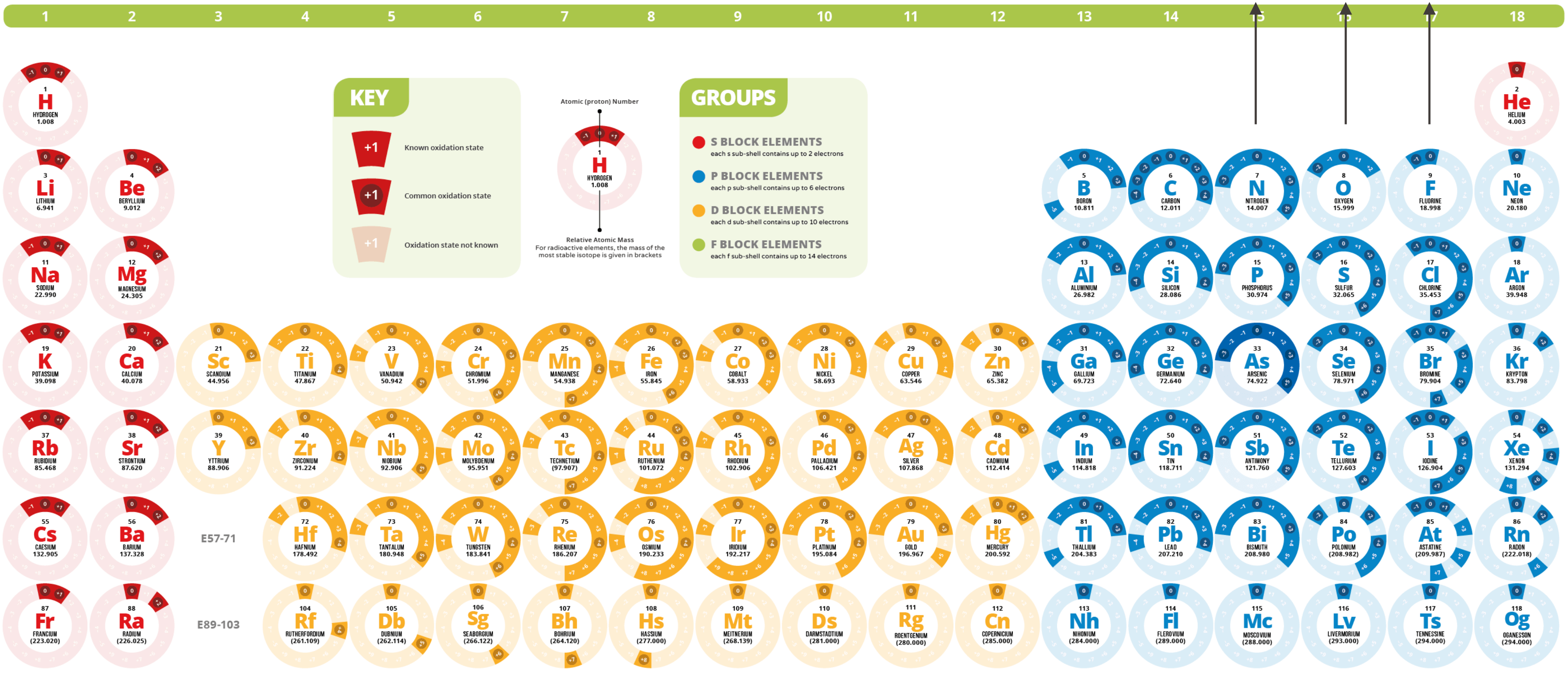
N_{ox} (Mg) = +2

N_{ox} (Cl) = -1

Rules for assigning the oxidation states

- The rules for assigning the oxidation state follow the electronegativity trends.

Oxydation state table



Negative N_{ox} → More prone to reduction

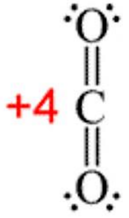
Positive N_{ox} → More prone to oxidation

See Lecture 2 for more rules

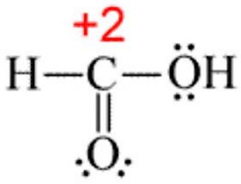
Rules for assigning the oxidation states

- Some general rules to know and follow:
  - All **elemental forms of atoms** have the N_{ox} = **0**
  - All **molecules made from atoms of a single element** have N_{ox} = **0**
  - When bound to other atoms **Halogens** (F, Cl, Br etc.) have N_{ox} = **-1** unless combined with oxygen or halogen
  - When bound to other atoms **Fluorine (F)** always has the N_{ox} = **-1**.
  - When bound to other atoms **alkali metals (Li, Na, etc.)** always have N_{ox} = **+1**.
  - When bound to other atoms **alkaline earth metals (Be, Mg, etc.)** have N_{ox} = **+2**.
  - **Hydrogen (H)** almost always has an N_{ox} = **+1**, except in metal hydrides where N_{ox} = **-1**.
  - **Oxygen (O)** most often has an N_{ox} **= -2**, unless it is bonded to itself or to fluorine.

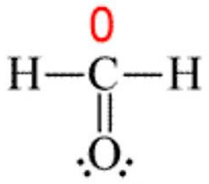
- The oxidation state can change, and it depends on the context of atoms around it:



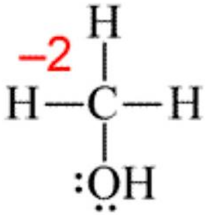
carbon dioxide



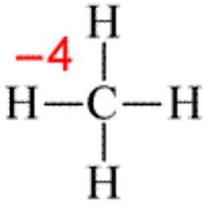
formic acid



formaldehyde



methanol



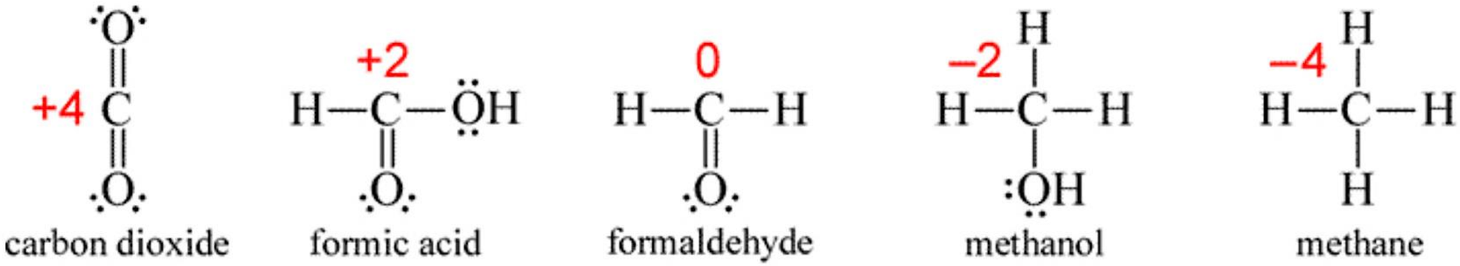
methane

Most oxidized

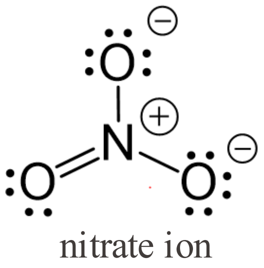
Most reduced

Relationship to valence and acid-base chemistry

- Oxidation state assignment is an “electron bookkeeping” system related to valence; but valence refers to the number of bonds created by an atom, and it cannot be negative.
- Further, N_{ox} can also exceed the possible number of bonds:

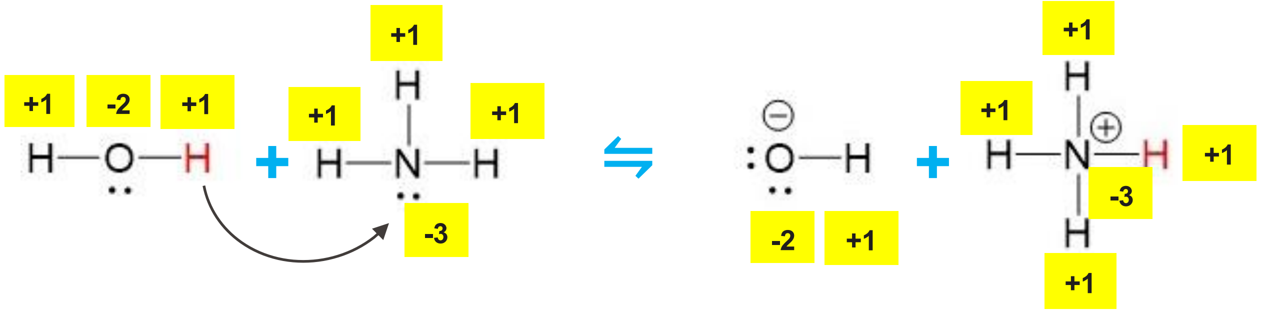


Same valence (4), but different N_{ox}.



Valence = 4; N_{ox} = +5

- Lewis acid–base reactions move electron pairs into bonds, but not between species. Therefore, electrons do not change “ownership” and oxidation states do not change.

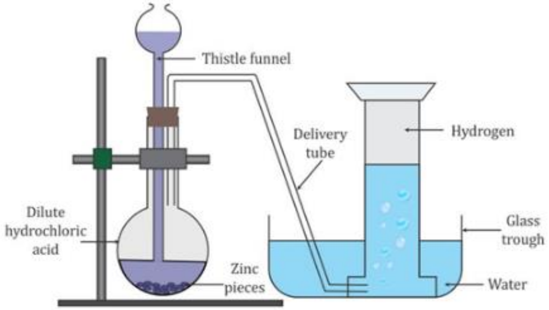


No change in oxidation state of any atoms

The uniqueness of redox chemistry

- This system based on ionic bond approximation and electronegativity, allows to explain reactions and processes that would otherwise be “invisible”.
  - It identifies when electrons move between species

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

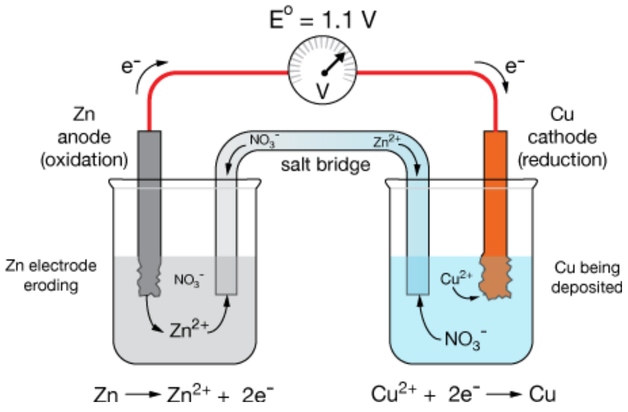


  - It allows to track the flow of chemical energy driven by electron transfer

Battery example: Daniell cell (Zn / Cu):

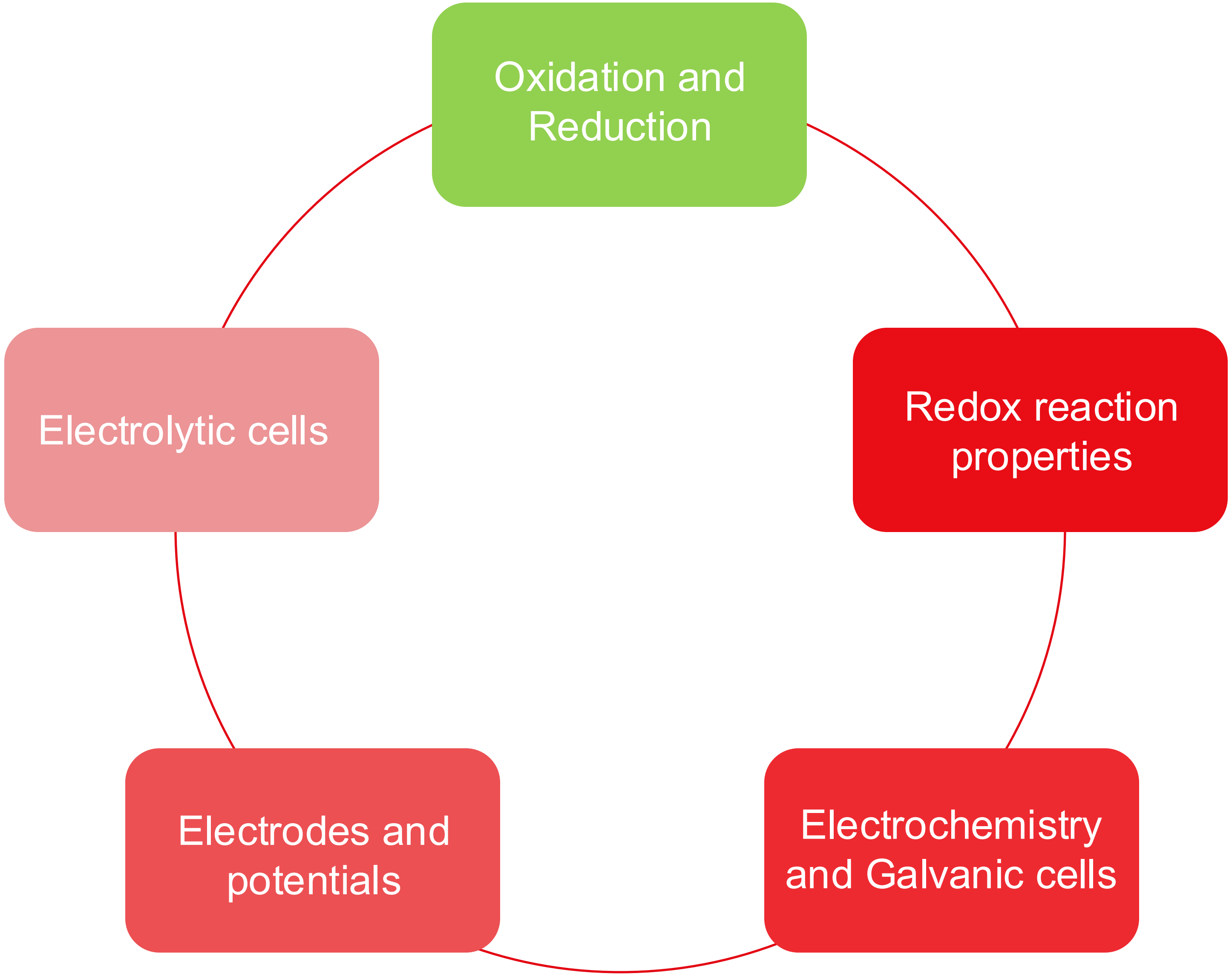
$$Zn\,(s) \;\rightarrow\; Zn^{2+}\,(aq) \;+\; 2\,e^{-} \qquad \text{(Anode)}$$

$$Cu^{2+}\,(aq) \;+\; 2\,e^{-} \;\rightarrow\; Cu(s) \qquad \text{(Cathode)}$$



  - It correlates to experimentally measurable properties (electric, optical, magnetic)

Plan



Oxidation and Reduction

Redox reaction properties

Electrochemistry and Galvanic cells

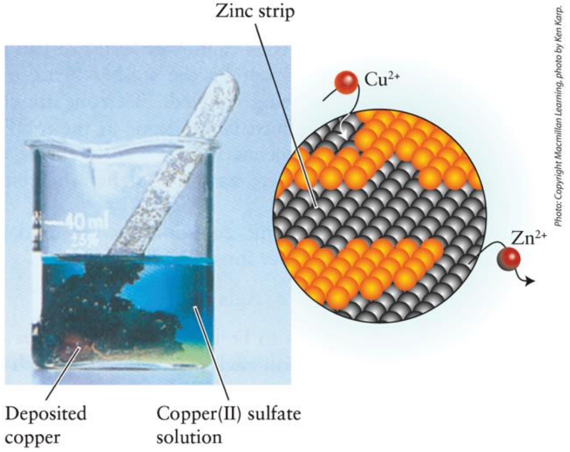
Electrodes and potentials

Electrolytic cells

Oxidants and reductants

- Given the coupling between oxidation and reduction processes the roles of chemical reactants can be defined based on their redox properties

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



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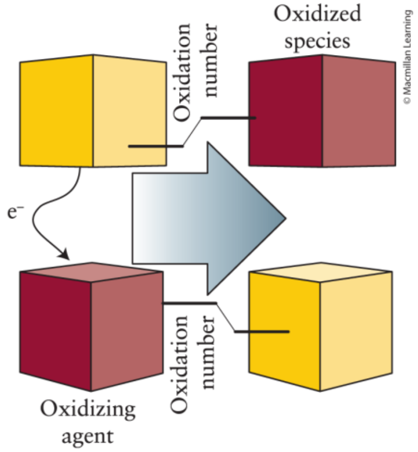
- Oxidant (oxidizing agent)
    - The species that causes oxidation and gets reduced in the process (Cu^{2+})

- Reductant (reducing agent)
    - The species that causes reduction and gets oxidized in the process (Zn)



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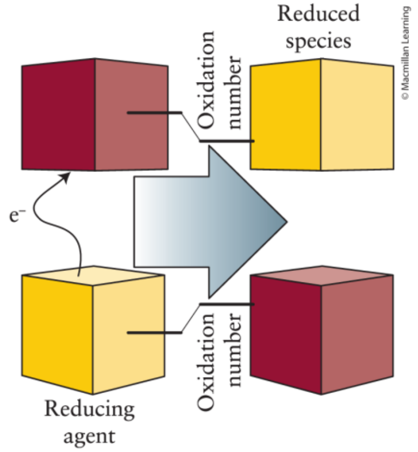

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Oxidants and reductants

- A few examples of half-reactions (oxidation or reduction):

$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	**Reduction**, Mn^{7+} is an oxidizing agent.
$Au(s) \rightarrow Au^{3+} + 3\,e^-$	**Oxidation**, Au(s) is the reducing agent.
$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-$	**Reduction**, $Cl_2(g)$ is the oxidizing agent.

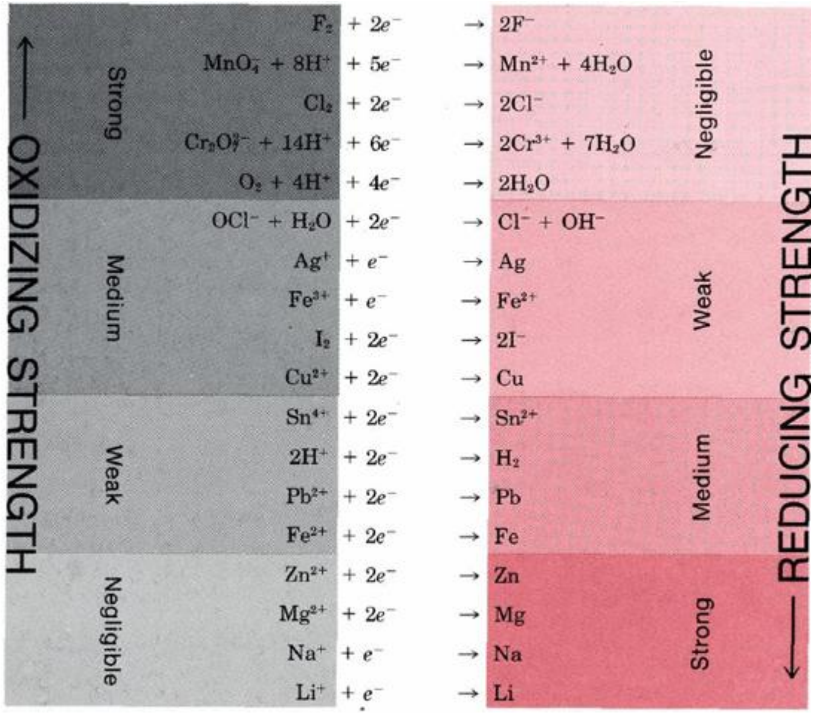
- A redox couple is the set of two species that can be interconverted by gaining or losing electrons. Always written as oxidized form/reduced form
  - Examples: Au^{3+}/Au, Cl_2/Cl^-, O_2/H_2O

Factors contributing to redox properties

- Similar to acid-base chemistry, oxidants and reductants can be classified by their relative strength.

- Molecular factors contributing to **reducing** properties:
  - Low electronegativity (more likely to donate e^-)
  - Low ionization energy (e.g., Na,K)
  - Formation of stable ionic products after oxidation
  - Large atomic size and electron number (e.g., I^- versus F^-)

- Molecular factors contributing to **oxidizing** properties:
  - High electronegativity (more likely to take e^-)
  - High stability of the reduced form in solution (e.g., $Cl^- > Cl_2$)
  - High oxidation state / electron deficiency (e.g., nitric and sulfuric acid)



← OXIDIZING STRENGTH					REDUCING STRENGTH ←
Strong	F_2	$+ 2e^-$	→	$2F^-$	Negligible
	$MnO_4^- + 8H^+$	$+ 5e^-$	→	$Mn^{2+} + 4H_2O$	
	Cl_2	$+ 2e^-$	→	$2Cl^-$	
	$Cr_2O_7^{2-} + 14H^+$	$+ 6e^-$	→	$2Cr^{3+} + 7H_2O$	
	$O_2 + 4H^+$	$+ 4e^-$	→	$2H_2O$	
Medium	$OCl^- + H_2O$	$+ 2e^-$	→	$Cl^- + OH^-$	Weak
	Ag^+	$+ e^-$	→	Ag	
	Fe^{3+}	$+ e^-$	→	Fe^{2+}	
	I_2	$+ 2e^-$	→	$2I^-$	
	Cu^{2+}	$+ 2e^-$	→	Cu	
Weak	Sn^{4+}	$+ 2e^-$	→	Sn^{2+}	Medium
	$2H^+$	$+ 2e^-$	→	H_2	
	Pb^{2+}	$+ 2e^-$	→	Pb	
	Fe^{2+}	$+ 2e^-$	→	Fe	
Negligible	Zn^{2+}	$+ 2e^-$	→	Zn	Strong
	Mg^{2+}	$+ 2e^-$	→	Mg	
	Na^+	$+ e^-$	→	Na	
	Li^+	$+ e^-$	→	Li	

- Other important factors impacting redox properties: pH of the solution, solvation energy of reactants/products, relative bond strength in reactants/products etc.

How redox reagents drive reactions in solutions

- Every chemical species can, in principle, **gain** or **lose** electrons, but the conditions depend on its redox capacity relative to the redox capacity of the other reactant.
- The most favorable conditions occur when a strong oxidant meets a strong reductant (e.g., alkali metals and fluorine)

$$2\,Na(s) + F_2(g) \rightarrow 2NaF(s)$$

Very exothermic reaction. Not done in standard lab practice as it is dangerous.

- Even an oxidizing reagent can itself be oxidized — if a stronger oxidant is present:

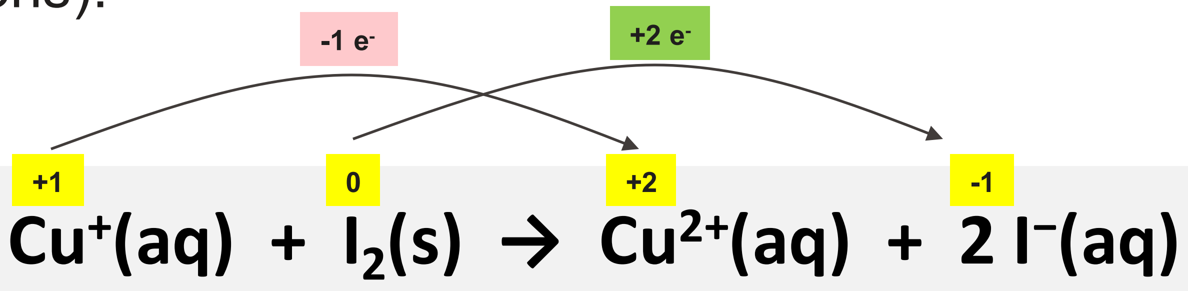
Iodine $\xrightarrow{\text{Oxidation}}$ Iodate

$$2\,MnO_4^-(aq) + 5\,I_2(s) + 6\,H_2O(l) \rightarrow 2\,Mn^{2+}(aq) + 10\,IO_3^-(aq) + 12\,H^+(aq)$$

- Choosing the correct redox reagent requires considering relative redox strengths, stability of the products, reaction conditions (pH, solvent), side reactions and selectivity.

Balancing the equations of redox reactions

- When writing the redox reactions, one additional factor is the need to balance the charge (electrons):



$$Cu^+(aq) + I_2(s) \rightarrow Cu^{2+}(aq) + 2\,I^-(aq)$$

Non-balanced

$$2\,Cu^+(aq) + I_2(s) \rightarrow 2\,Cu^{2+}(aq) + 2\,I^-(aq)$$

Balanced

- Quick guidelines:
  - Identify the elements whose oxidation state (N_{ox}) changes during the reaction.
  - The number of electrons lost by the reducing agent must equal the number of electrons gained by the oxidizing agent; this allows us to find the appropriate coefficients.
  - If other substances whose N_{ox} is not affected appear in the equation, their coefficients must be determined by calculating their mass balance.
  - If any reactants and/or products are ions, the calculation must be verified by calculating their charge balance.

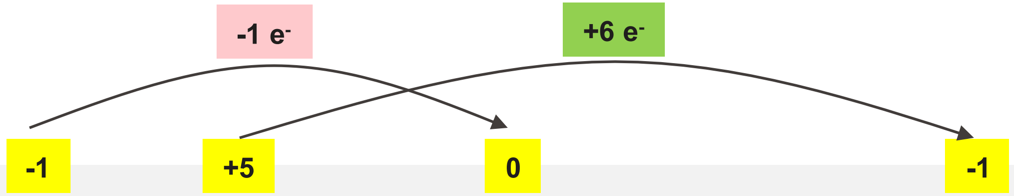
Balancing the equations of redox reactions

- Now let's try it on a more complex example:

$$HBr + KClO_3 \rightarrow Br_2 + H_2O + KCl$$

Non-balanced

- Now let's see which elements changed the N_{ox}, while keeping in mind the mass balance:



$$\overset{-1}{H\,Br} + K\overset{+5}{Cl}O_3 \rightarrow \overset{0}{Br_2} + H_2O + K\overset{-1}{Cl}$$

Minimally 6 e^- got exchanged

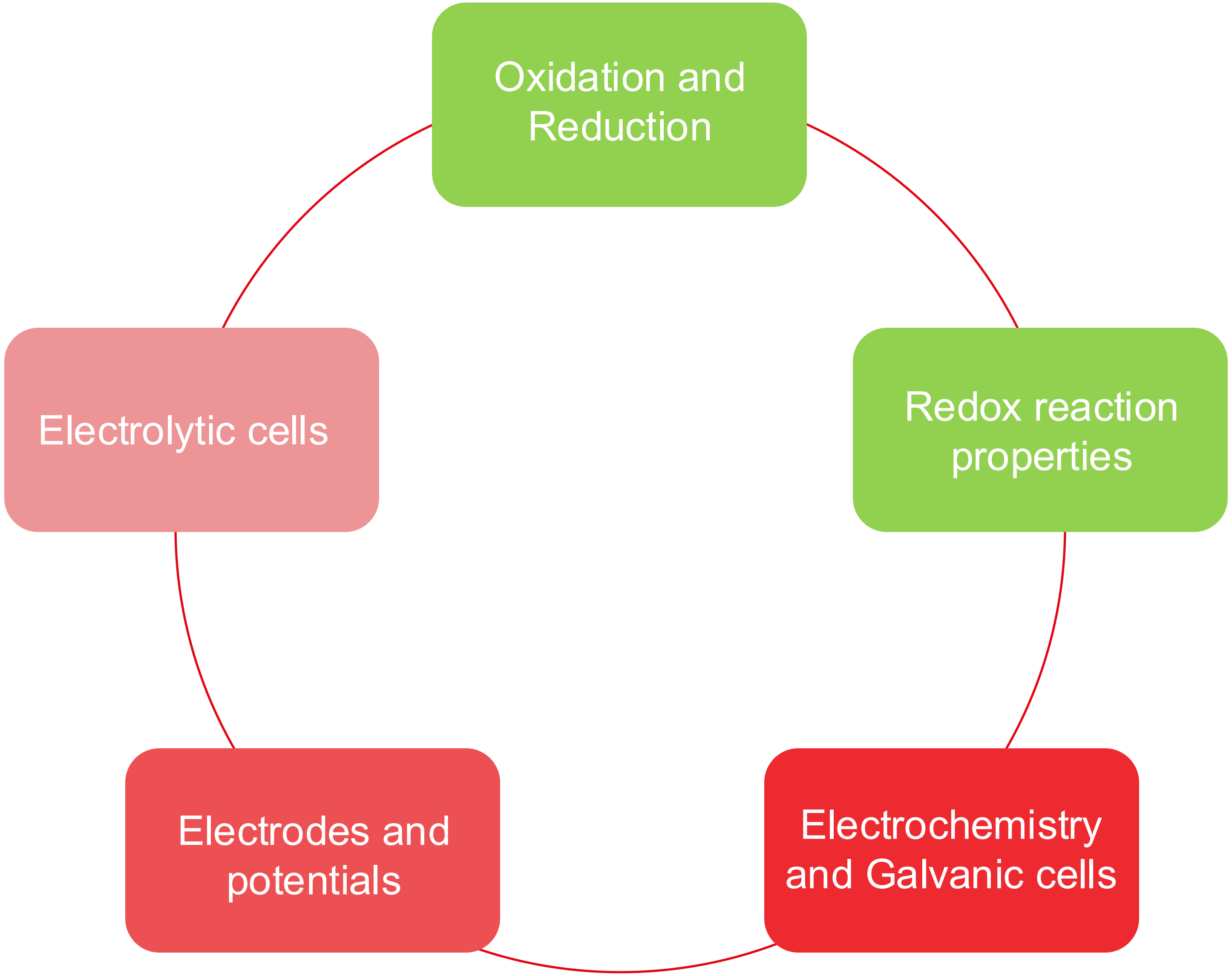
- Let's try starting with the minimal relative amount of reactants (in this case, 6 x Br):

$$6\,HBr + 1\,KClO_3 \rightarrow 3\,Br_2 + 3\,H_2O + 1\,KCl$$

Balanced

* This chemical equation balances quite easily without considering the number of electrons transferred, which is not always the case.

Plan


Oxidation and Reduction

Redox reaction properties

Electrochemistry and Galvanic cells

Electrodes and potentials

Electrolytic cells

Electrochemistry

- Electrochemistry is the study of chemical reactions that involve the transfer of electrons and the conversion between chemical energy and electrical energy.
- It explains how redox processes can generate electricity or be driven by electricity in both natural and technological systems.

Batteries & power sources

Industrial chemistry

Sensors and analysis

Corrosion and metal protection

Electrochemical reactions

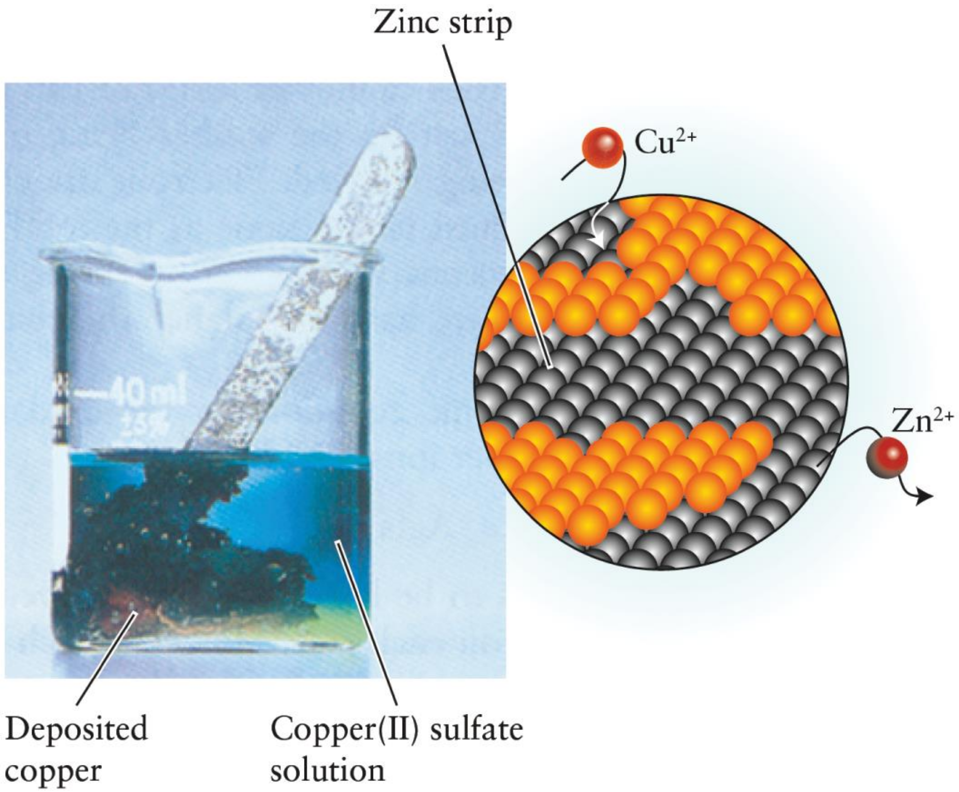
- Consider the same reaction involving Cu and Zn, as shown on previous slides:

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

Individual half-reactions:

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

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



- The reaction typically involves using $CuSO_4$ in solution and a solid zinc strip, leading to the deposition of copper on the surface of zinc strip and release of Zn^{2+} in solution

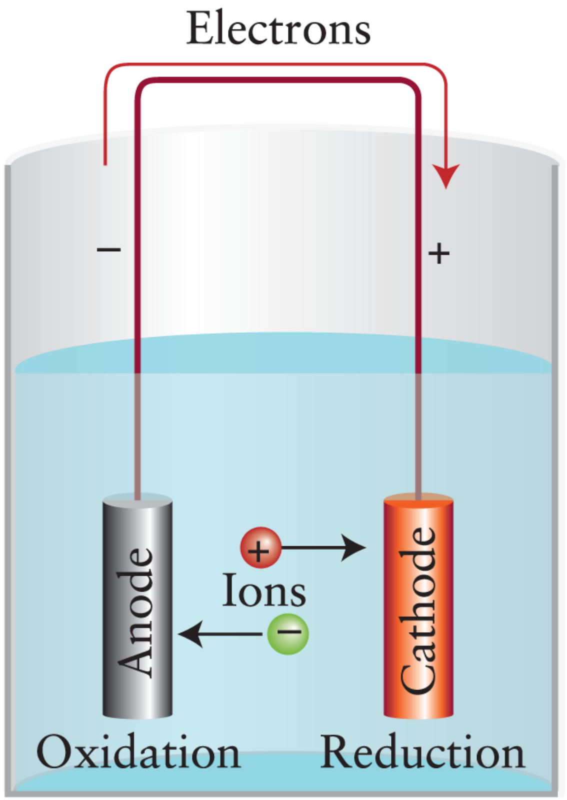
Electrochemical reactions

- But what if we separate the two processes and have them take place on 2 metal strips, one made of zinc and the other made of copper, and we connect them with a wire.

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

Oxidation

Zinc side accumulates electrons:
= **Anode**



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

Reduction

Copper side uses electrons:
= **Cathode**

- The difference in electron content generates a **potential difference** pulling electrons towards the cathode, thereby creating **electric current**.

Galvanic cells

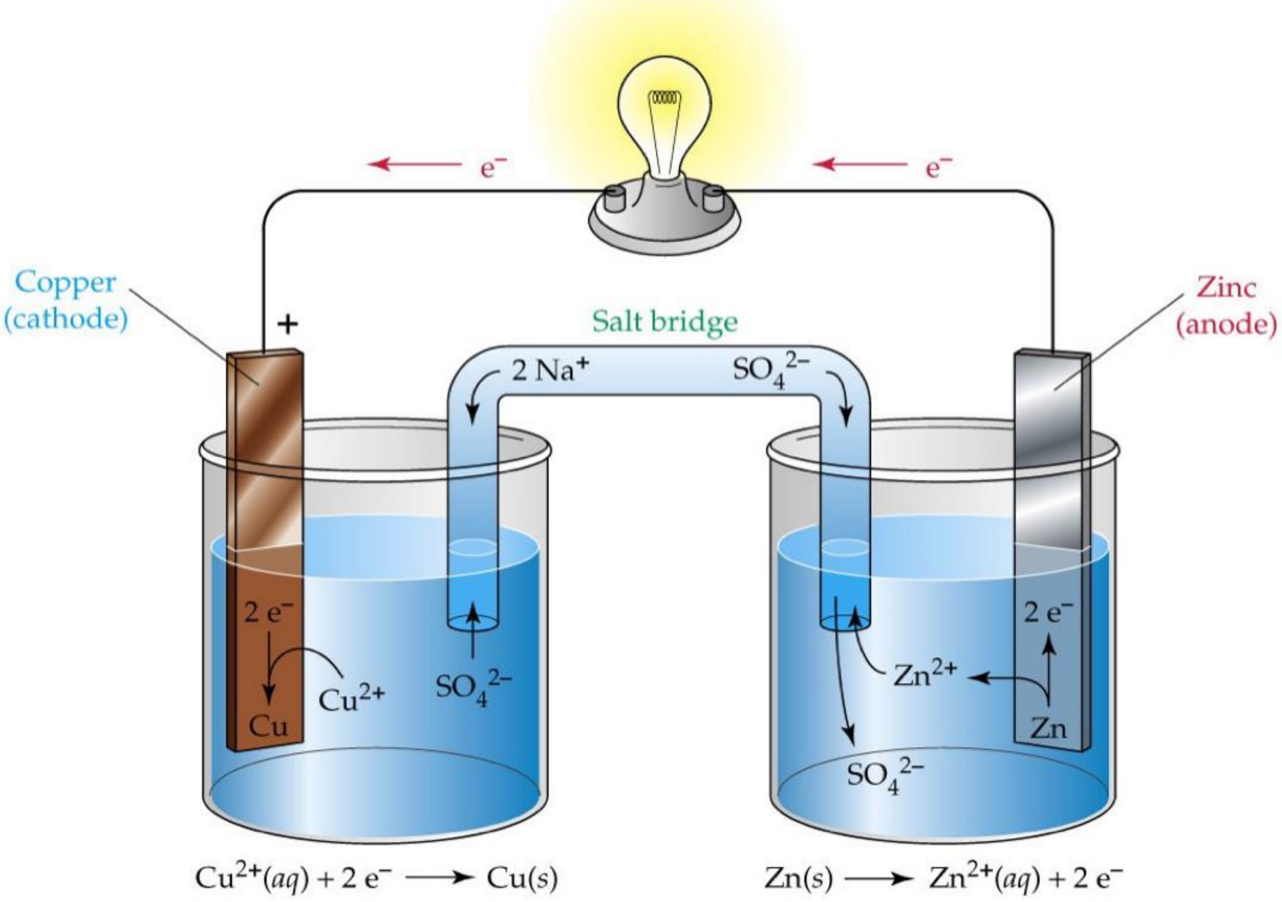
John Frederic Daniell
(1788-1866)

- The two half-reactions are separated such that:
  - The easiest route for electrons via the wire (as opposed to via the liquid)
  - Also, prevents the Cu and Zn from accumulating on opposite electrodes

- The ionic solution (Na^+ and SO_4^{2-}) assures electroneutrality of solution.

- It is also called a **salt bridge** and its components are **electrolytes**

- This design is called the **Daniell cell**



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

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

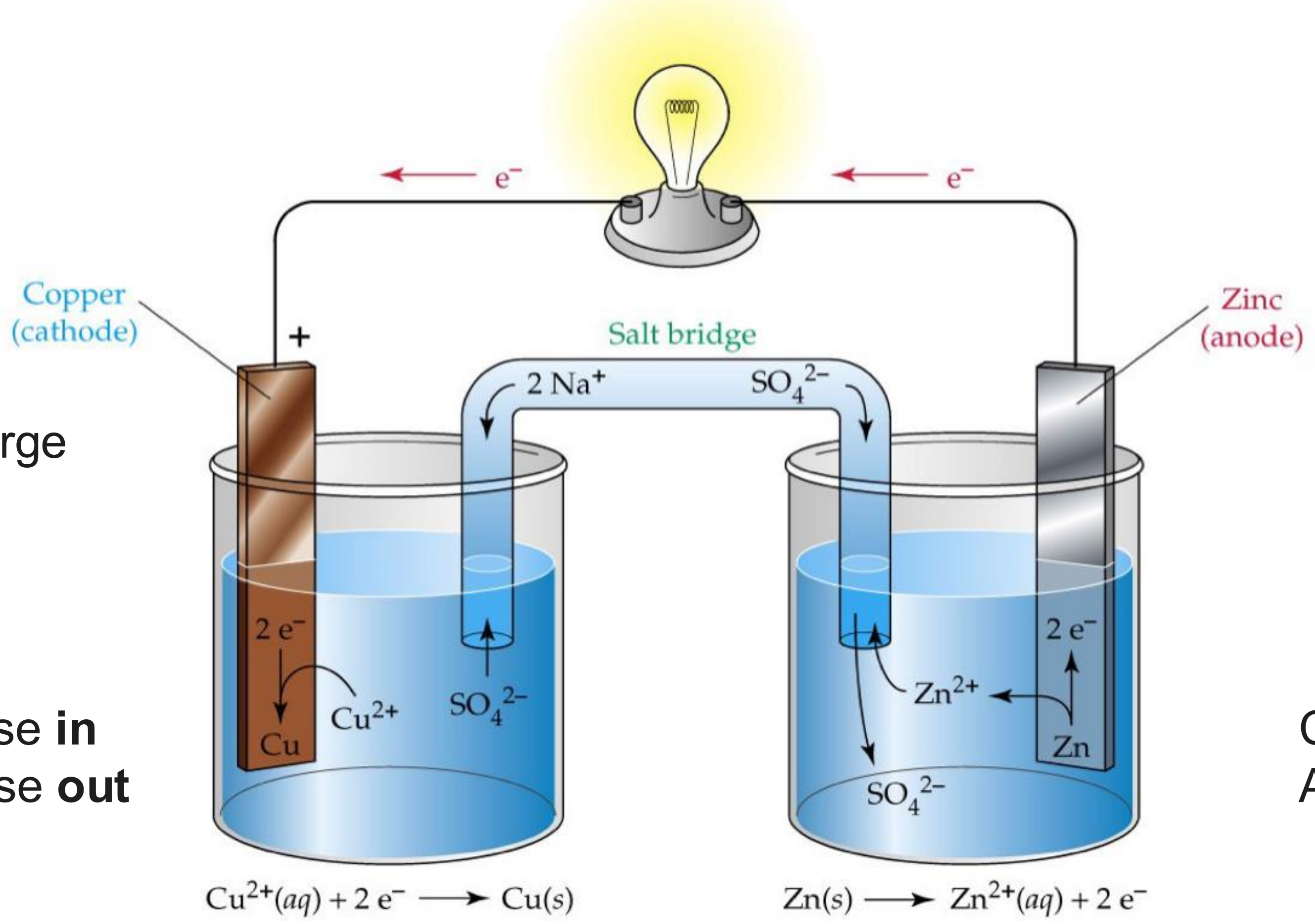
Galvanic cells

- The electrolytes ensure the electroneutrality of both solutions that constantly undergo removal of Cu^{2+} in cathode solution and generation of Zn^{2+} in anode solution

Excess **negative** charge due to Cu^{2+} removal

↓

Cations (Na^{2+}) - Diffuse **in**
Anions (SO_4^{2-}) - Diffuse **out**



Excess **positive** charge due to Zn^{2+} generation

↓

Cations (Na^{2+}) - Diffuse **out**
Anions (SO_4^{2-}) - Diffuse **in**

Reduction (cathode)

Oxidation (anode)

Galvanic cells - Brief history

- **Galvanic cells** are cells where *spontaneous* redox reactions generate electric current.
- Named after **Luigi Galvani** who first described a bioelectric phenomenon on a frog muscle
- **Alessandro Volta** created a stack of alternating metals which could provide sustained current
- **Batteries** are a collection of galvanic cells joined in a series.
- The unit of potential difference, is named after Alessandro Volta: $\mathbf{1\ V = J{\cdot}C^{-1}}$

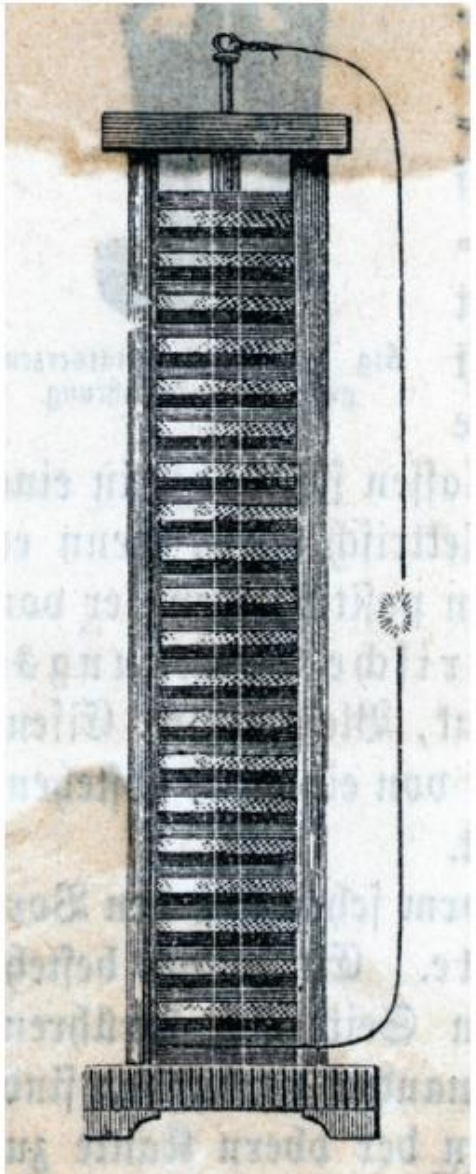


Fig. 330. Die Volta'ſche Säule.

Bettmann/Getty Images.

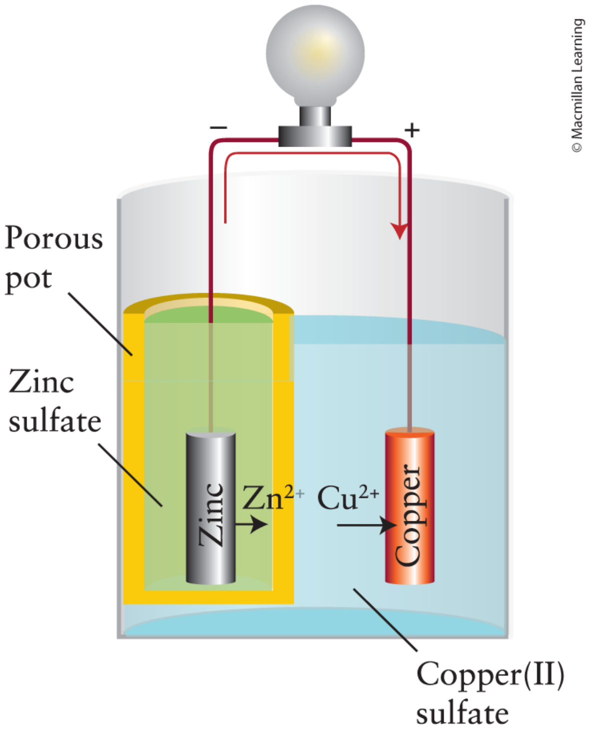
Alessandro Volta
(1745-1827)

From Daniell Cells to Modern Batteries

- Modern cells are upgraded Daniell cells with better energy density, reversibility, and safety.

Daniell Cell (1836)

- **Zn | Zn²⁺** = anode (oxidation)
- **Cu²⁺ | Cu** = cathode (reduction)
- Salt bridge to maintain charge balance



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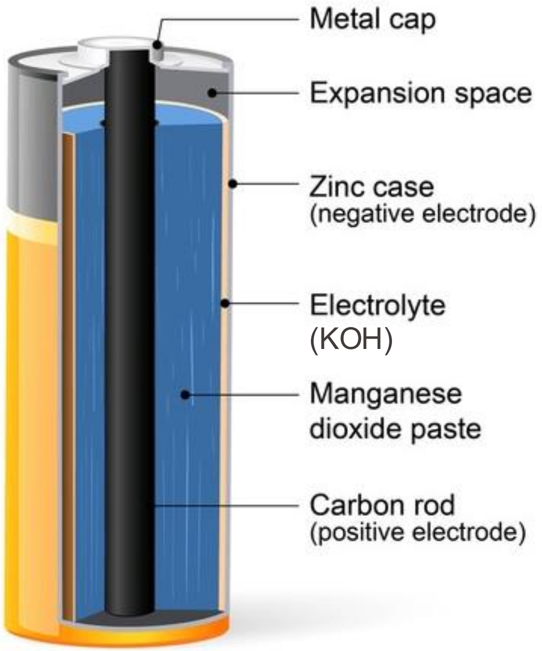
Modern Alkaline Batteries (1957)

- **Zn | Zn²⁺** = anode (oxidation)
- **MnO_2 | Mn_2O_3** = cathode (reduction)
- Paste-based contents (“dry cell”)



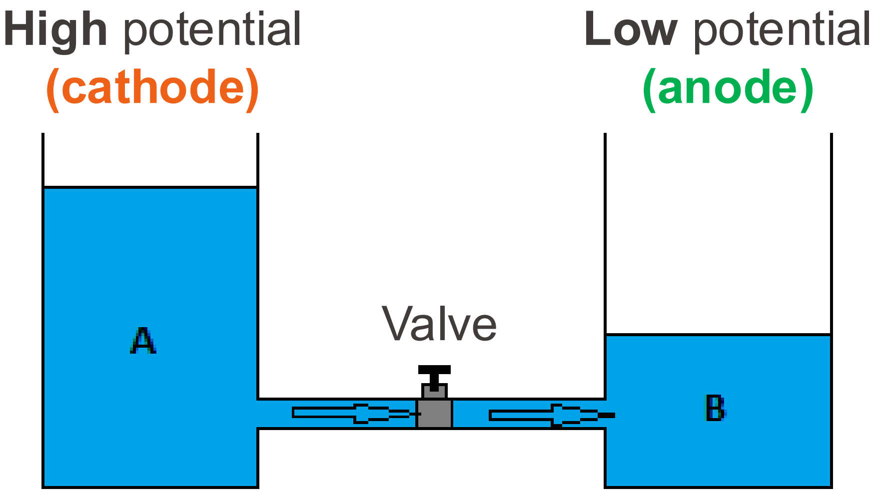
= Anode

Origin of “Alkaline”

= Cathode

Electromotive force of an electrochemical system

- The **electromotive force (∆E)** of a galvanic cell measures the capacity of electrons to flow through the circuit in the absence of current (the unit is **V**)
- As such it corresponds to "electron potential energy” and is a thermodynamic quantity



- The electromotive force is measured with a high-impendance voltmeter creating the absence of current (“closing” the valve)

Electromotive force and cell potential

- Standard EMF (ΔE^0) is measured with 1 M ions in solution, 1 bar gas pressure, and 25 °C, assuming ideal electrolyte activity.
- Under these conditions, the voltage measured is the true thermodynamic driving force for the redox reaction.

Going back to our Zn - Cu cell

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

$$\Delta E^0 = 1.1\ \mathrm{V} = 1.1\ \mathrm{J/C}$$

Meaning: When 1 coulomb of electric charge flows through the circuit, the cell can provide 1.10 joules of electrical energy, under ideal conditions.

- Cell potential is a related but not identical quantity pertaining to the measurement of voltage under any conditions (including while the current is flowing)

Standard electromotive force and Gibbs free energy

- Galvanic cells convert chemical into electrical energy. Another important parameter that is used to characterize this process is the Gibbs free energy of the reaction (**ΔG_r^0**)

$$\Delta G_r° = - z \bullet F \bullet \Delta E^0$$

ΔE^0 - Standard EMF (in V)
z - Number of transferred electrons
F - Faraday constant (= 96485 C/mol)
Faraday constant = charge of one mole of electrons

$$\Delta G_r° = - R \bullet T \bullet \ln(K)$$

K - Equilibrium constant of the reaction
R - Universal gas constant (=8.314 $Jmol^{-1}K^{-1}$)
T - Temperature (in K)

- **ΔG_r^0** (units: J/mol) provides a quantitative readout for reaction properties:
  - It measures the maximum *useful* work a reaction can perform (=electrical work)
  - It determines the direction of the redox reaction ($\Delta G_r° < 0$ → spontaneous reaction).
  - It is connected to the equilibrium constant of the redox reaction (K)

Standard electromotive force and Gibbs free energy

- If we go back to the Daniell cell reaction (ΔE^0 = 1.1 V)

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

$$K_{eq} = K = \frac{[Zn^{2+}] \bullet \boxed{[Cu]}}{[Cu^{2+}] \bullet \boxed{[Zn]}} \quad \begin{matrix} = 1 \\ = 1 \end{matrix}$$

$$K_{eq} = K = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Delta G_r° = -\, z \bullet F \bullet \Delta E^0$$

$$\Delta G_r° = -\, R \bullet T \bullet \ln(K)$$

$$\ln(K) = \frac{z \bullet F \bullet \Delta E^0}{R \bullet T}$$

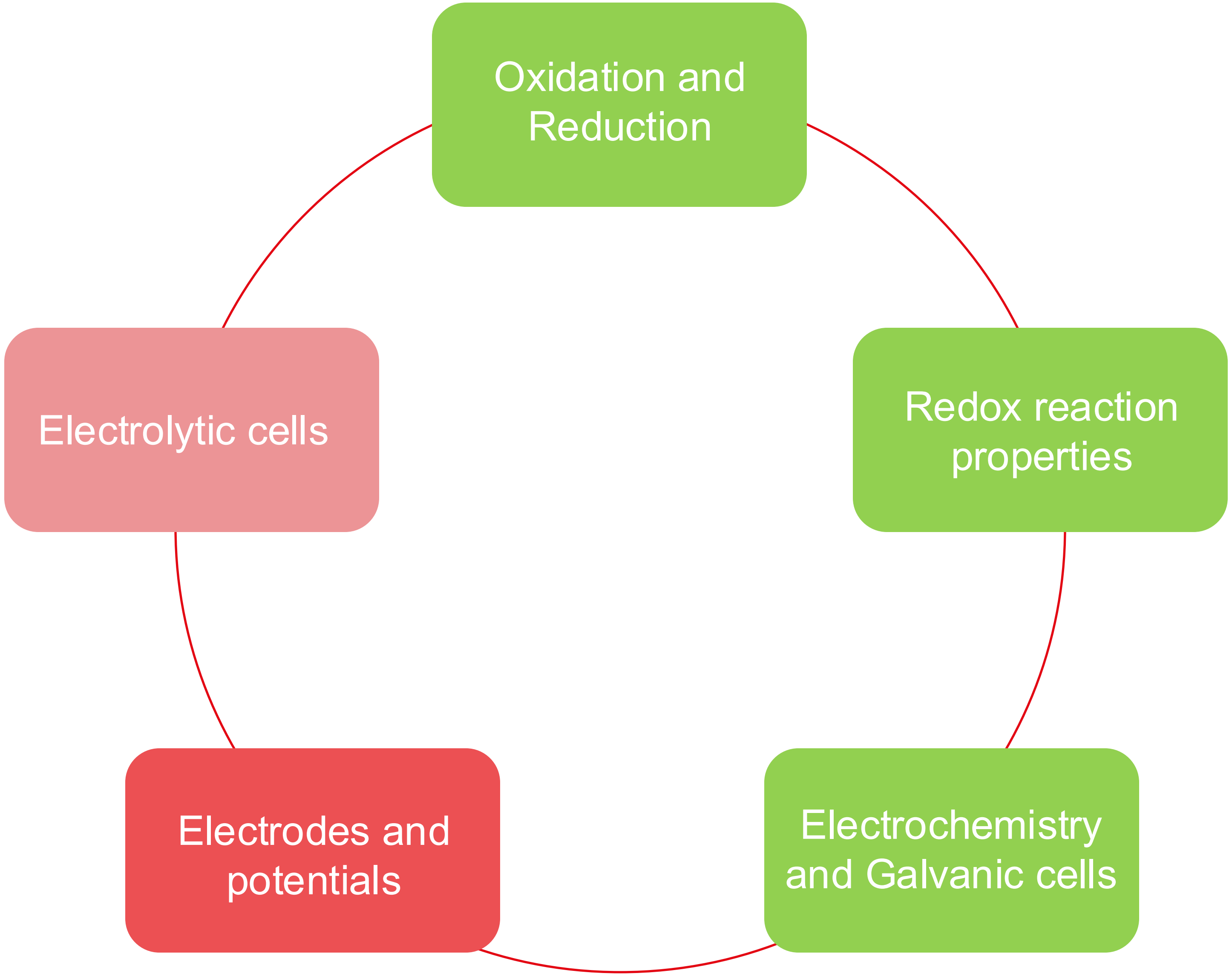
- By applying the ΔE^0 and other reaction parameters to these equations we get:

$\Delta G_r°$ = - 212.3 kJ/mol

ln (K) = 85.6 → $K = [Zn^{2+}] / [Cu^{2+}] = 1.6 \bullet 10^{37}$

Reaction heavily favors the products (Zn^{2+})

Plan



Oxidation and Reduction

Redox reaction properties

Electrochemistry and Galvanic cells

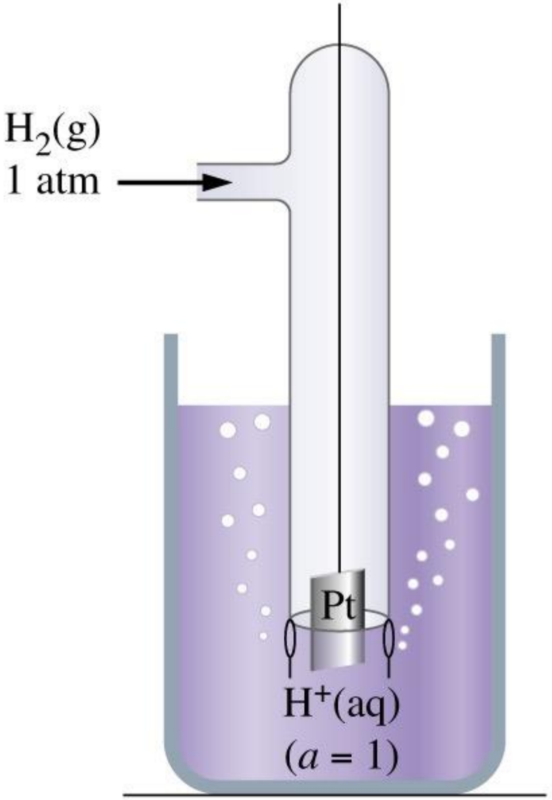
Electrodes and potentials

Electrolytic cells

Standard hydrogen electrode (SHE)

- For detailed analyses of electrochemical systems, it is often important to determine the potential of each individual electrode (comprising the entire half-cell)
- This is usually performed relative to the **standard hydrogen electrode** (SHE), which uses measure the hydrogen reaction on platinum surface:

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

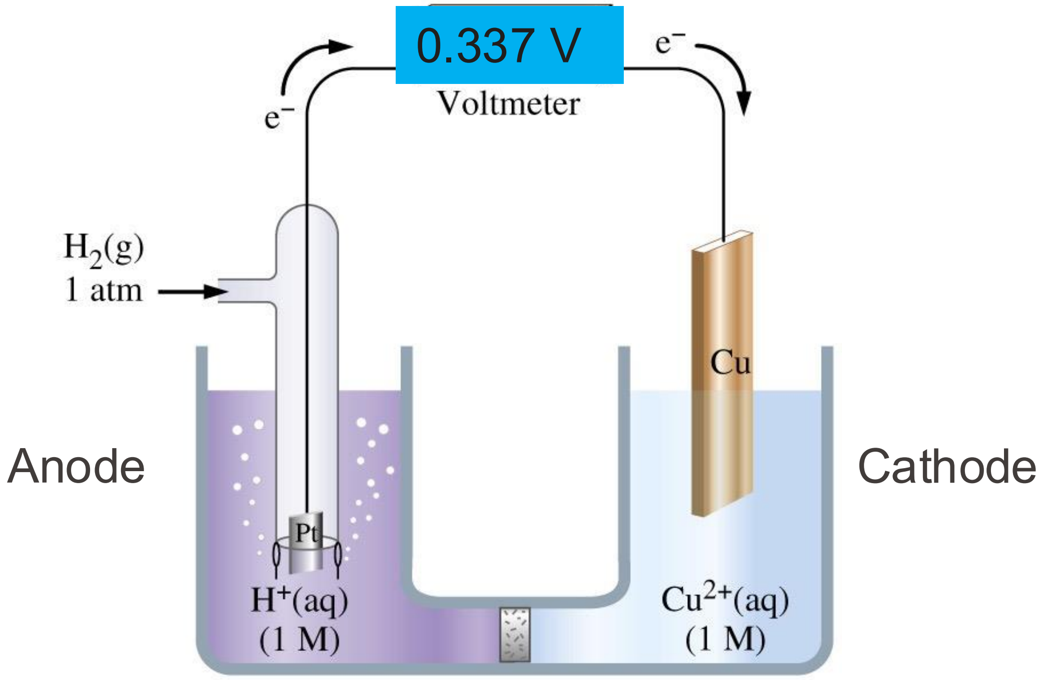


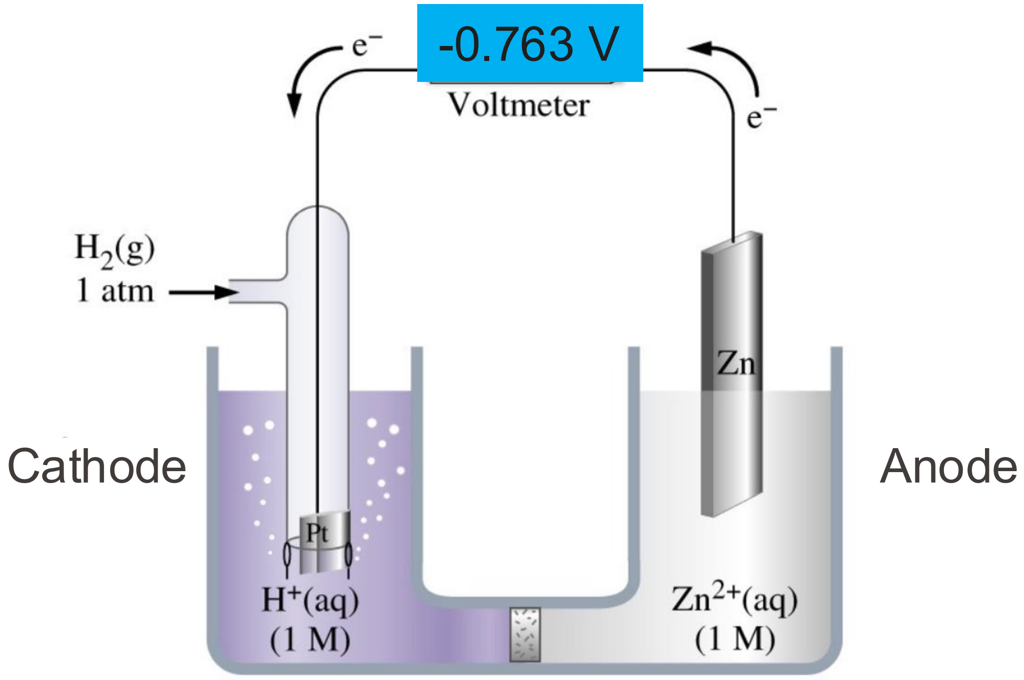
- By convention, the standard potential of this electrode is $E^0 = 0.00$ V, at all temperatures
- In electrode systems it is labelled as:

$$Pt(s)|H_2(g)|H^+(aq)||\{\text{Other electrode}\}$$

Standard electrode potential

- Standard electrode potentials of the Cu^{2+} / Cu and Zn^{2+} / Zn reactions





$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

$$Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

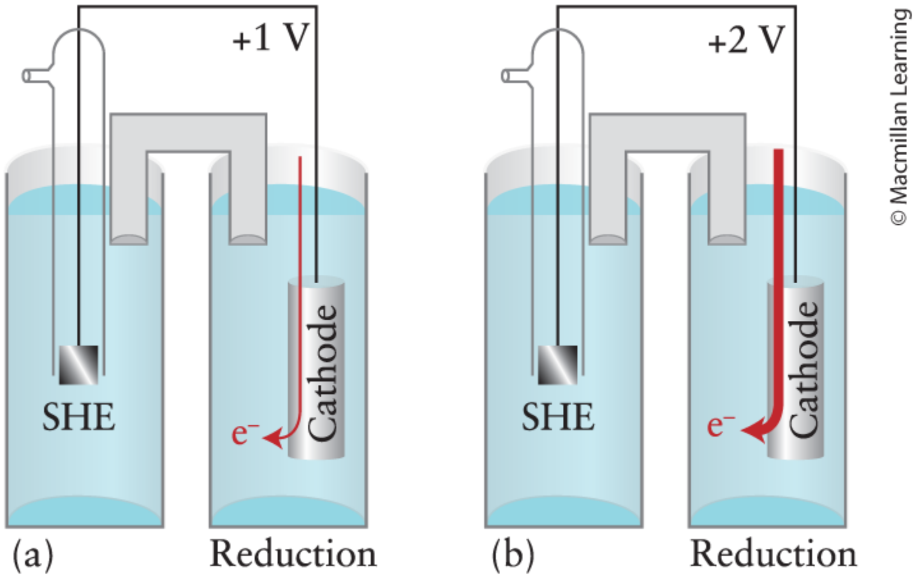
$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(s) + H_2(g)$$

$$Zn(s) \mid Zn^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$$

$$\Delta E^0 = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} = 0.337V - (-0.763V) = 1.10V$$

Standard electrode potential

- Each electrode makes its own characteristic contribution to the standard cell potential, called the standard potential of the electrode E^0.
- The measurement relative to SHE allows to study the thermodynamic properties of redox reactions on individual electrodes.



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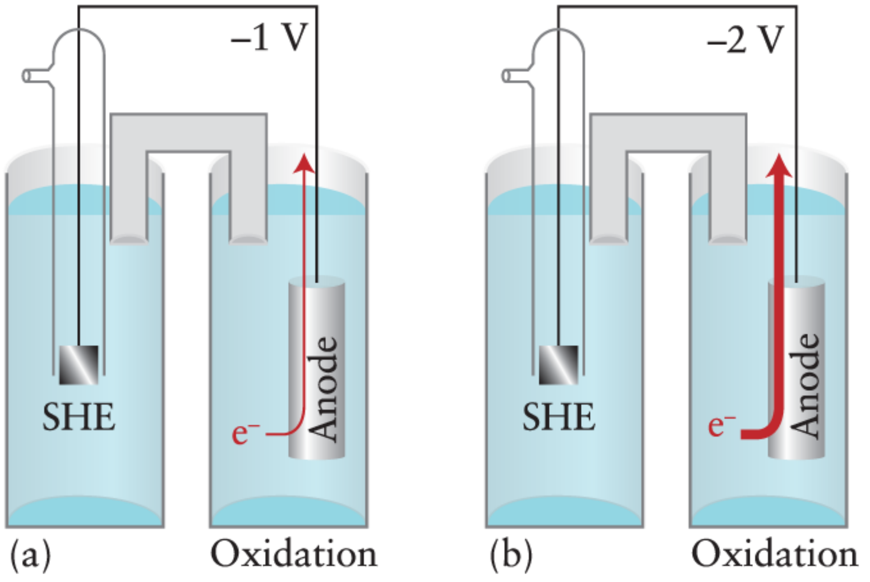
Lower reduction tendency

Higher reduction tendency

Comparing 2 cathodes to SHE



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Lower oxidation tendency

Higher oxidation tendency

Comparing 2 anodes to SHE

Standard Potentials of Main Group Elements

Species	Reduction half-reaction	E°/V
F_2/F^-	$F_2(g) + 2\,e^- \rightarrow 2\,F^-(aq)$	+2.87
Au^+/Au	$Au^+(aq) + e^- \rightarrow Au(s)$	+1.69
Fe^{3+}/Fe^{2+}	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
H^+/H_2	$2H^+(aq) + 2\,e^- \rightarrow H_2(g)$	0
Fe^{3+}/Fe	$Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s)$	−0.04
Pb^{2+}/Pb	$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$	−0.13
Zn^{2+}/Zn	$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76

Oxidants

Reductants

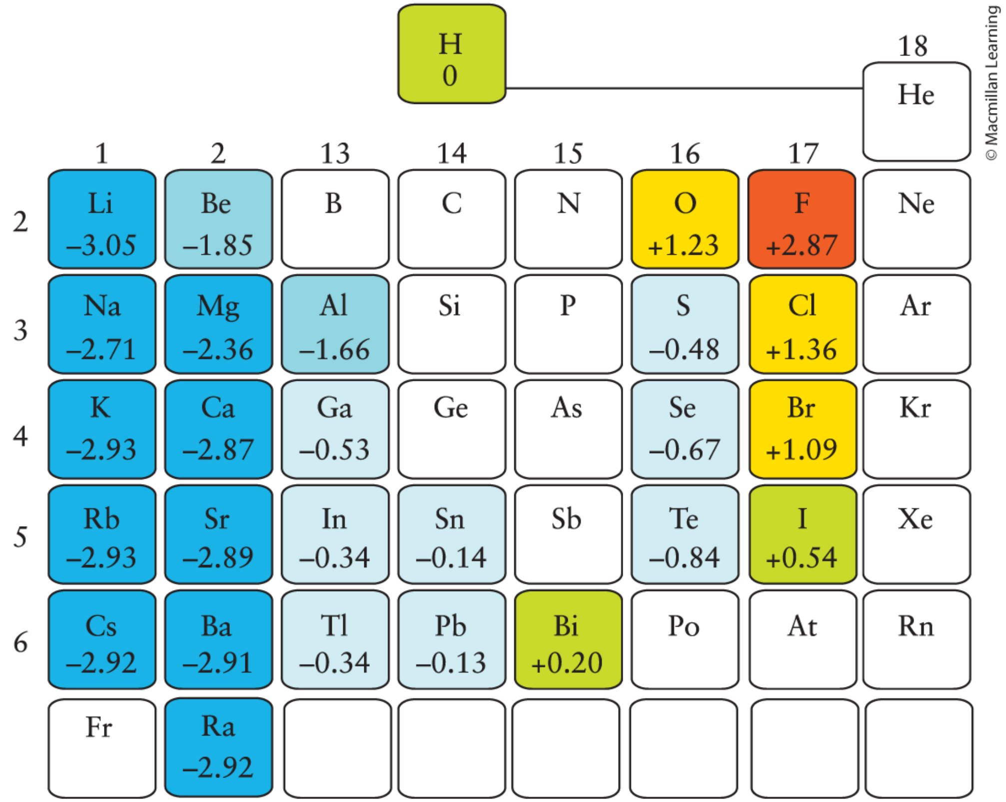
- The more positive the standard potential, the greater the power of the reactants to act as oxidizing agents (= undergo reduction).
- The more negative the standard potential, the greater the power of the products to act as reducing agents (= undergo oxidation).

Standard Potentials of Main Group Elements

- The most **negative** standard potentials are usually found toward the left of the periodic table while the most **positive** standard potentials are found toward the upper right of the periodic table.

Positive standard potential
→ **Oxidant** tendency
→ Likely to be a **cathode**

Negative standard potential
→ **Reductant** tendency
→ Likely to be an **anode**



	1	2	13	14	15	16	17	18
				H 0				He
2	Li −3.05	Be −1.85	B	C	N	O +1.23	F +2.87	Ne
3	Na −2.71	Mg −2.36	Al −1.66	Si	P	S −0.48	Cl +1.36	Ar
4	K −2.93	Ca −2.87	Ga −0.53	Ge	As	Se −0.67	Br +1.09	Kr
5	Rb −2.93	Sr −2.89	In −0.34	Sn −0.14	Sb	Te −0.84	I +0.54	Xe
6	Cs −2.92	Ba −2.91	Tl −0.34	Pb −0.13	Bi +0.20	Po	At	Rn
	Fr	Ra −2.92						

- Note the excellent reducing properties of lithium; hence the application in batteries

Reactions under non-standard conditions

- In realistic cases, the cell or battery will operate under non-standard conditions and have finite lifetime due to reactant depletion (= the battery dies)
- The ΔG_r in those cases approaches zero, reaching equilibrium

$$\Delta G_r = \Delta G_r^\circ + R \bullet T \bullet \ln(Q)$$

$$\Delta G_r = -zF\Delta E$$

$$\Delta G_r^0 = -zF\Delta E^0$$

Q - Reaction quotient (=K in equilibrium)

$$\boxed{\Delta E = \Delta E^0 - \frac{R \bullet T}{z \bullet F} \bullet \ln(Q)}$$

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

- The **Nernst equation** is a quantitative measure of a cell potential in terms of the concentrations of the reagents taking part in the cell reaction.

Reactions under non-standard conditions

- Let's go back to Nernst equation and assume standard cell conditions

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

$$\Delta E = \Delta E^0 - \frac{R \cdot T}{z \cdot F} \cdot \ln(Q)$$

Standard conditions:
$\Delta E^0 = 1.1$ V
T = 298K
$[Cu^{2+}] = [Zn^{2+}] = 1$ mol/L

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1 \rightarrow \Delta E = \Delta E^0 = 1.1\ \text{V}$$

- However, non-standard conditions yield $\Delta E \neq \Delta E^0$ due to differing concentrations

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

$$\Delta E = \Delta E^0 - \frac{R \cdot T}{z \cdot F} \cdot \ln(Q)$$

Non-standard conditions:
$\Delta E^0 = 1.1$ V
T = 298K
$[Cu^{2+}] = 0.001$ mol/L
$[Zn^{2+}] = 0.1$ mol/L

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = 100 \rightarrow \Delta E = 1.04\ \text{V}$$

Nernst equation and quantification of ions

- Quantification of ions can be performed electrochemically if there is a suitable redox reaction
- To measure the concentration of H_3O^+ ions (pH), we select an electrode based on H^+/H_2 redox process
- The measurement of potential difference against a 2nd electrode immersed in $[H^+]$ = 1 mol/L standard solution

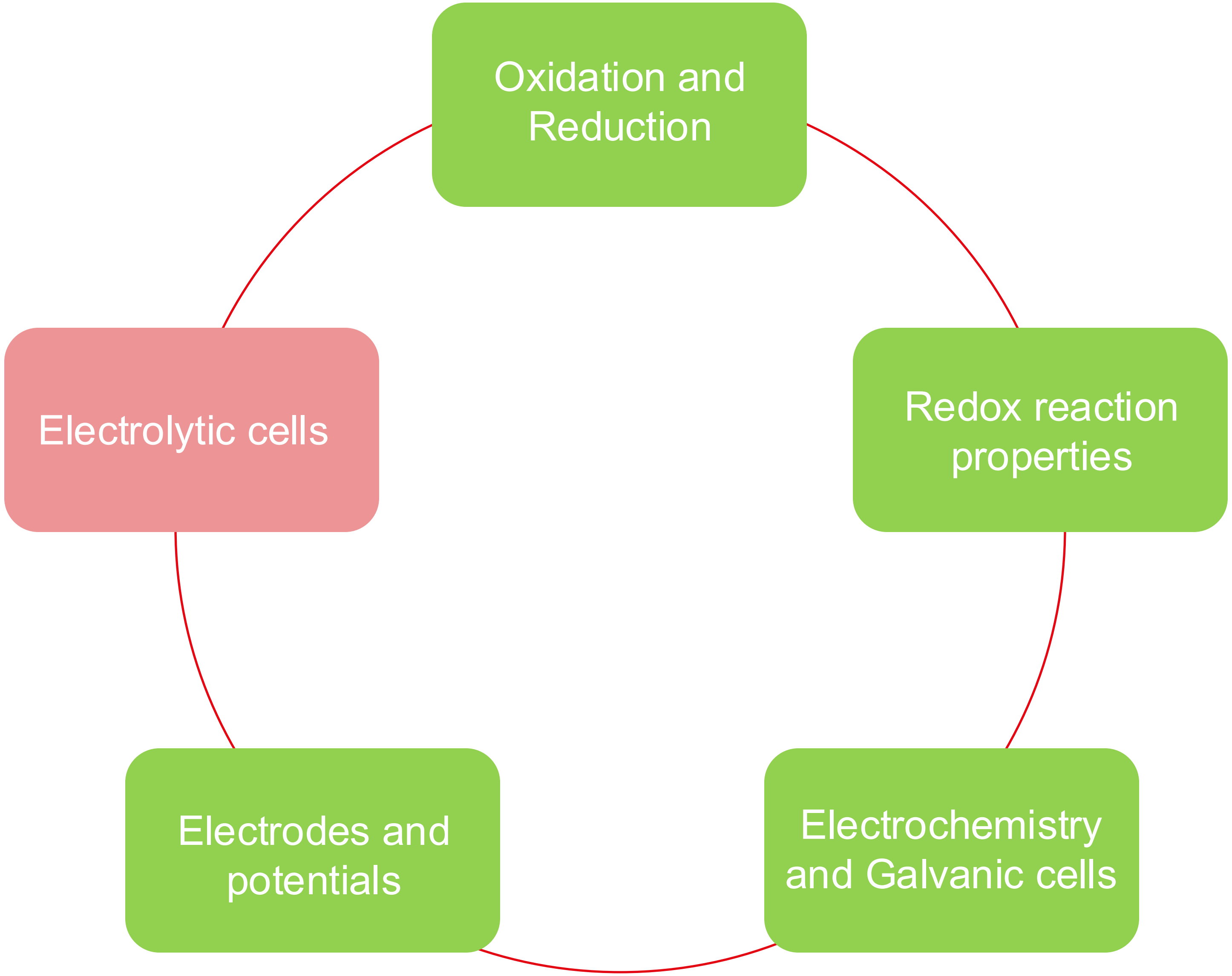
$$\Delta E = E_{ref} - E_x = 0.059\ V \bullet pH$$

E_{ref} - Potential of the electrode in reference solution
E_x - Potential of the electrode in tested solution

Charles D. Winters/Science Source.

- In practice, there is a more sophisticated and simpler system based on surface ion-exchange equilibrium

Plan



Oxidation and Reduction

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Electrolytic cells

Electrolytic cells - The opposite of Galvanic cells

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

- Whereas electrons flow spontaneously in a Galvanic cell from the anode to cathode, electrolytic cells apply an external EMF, making the cathode “−” and the anode “+.”

Anode

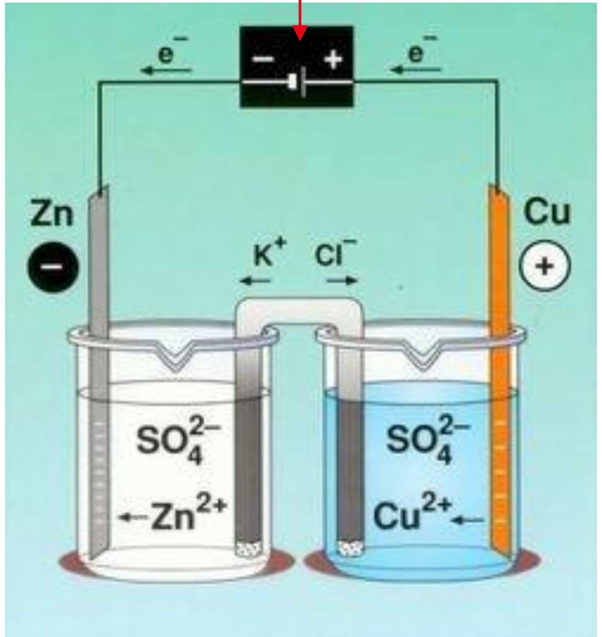
Cathode

Galvanic cell

Condition to switch:
$\Delta E^0_{(applied)} > \Delta E^0_{(cell)}$

Cathode

External voltage source



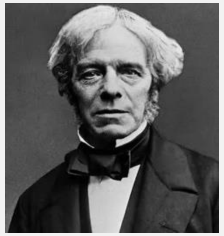
Anode

Electrolytic cell

Electrolysis - Faraday's First Law

- The number of moles (n) of product formed by an electric current at an electrode is stoichiometrically equivalent to the number of moles of electrons supplied.

$$n = \frac{I \bullet T}{z \bullet F}$$



Michael Faraday
(1791-1867)

n - number of moles of product
I - Current (A)
z - Number of transferred electrons per reaction
F - Faraday constant (= 96485 C/mol)

Example: Calculate the amount of Cu deposited at the cathode, by electrolysis of a 1M $CuSO_4$ solution for 10 min with a current of 2 A.

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

$$n = \frac{I \bullet T}{z \bullet F} = \frac{2A \bullet 10 \bullet 60s}{2 \bullet 96485\ C/mol} = 6.22 \bullet 10\text{-}3\ \text{mol}$$

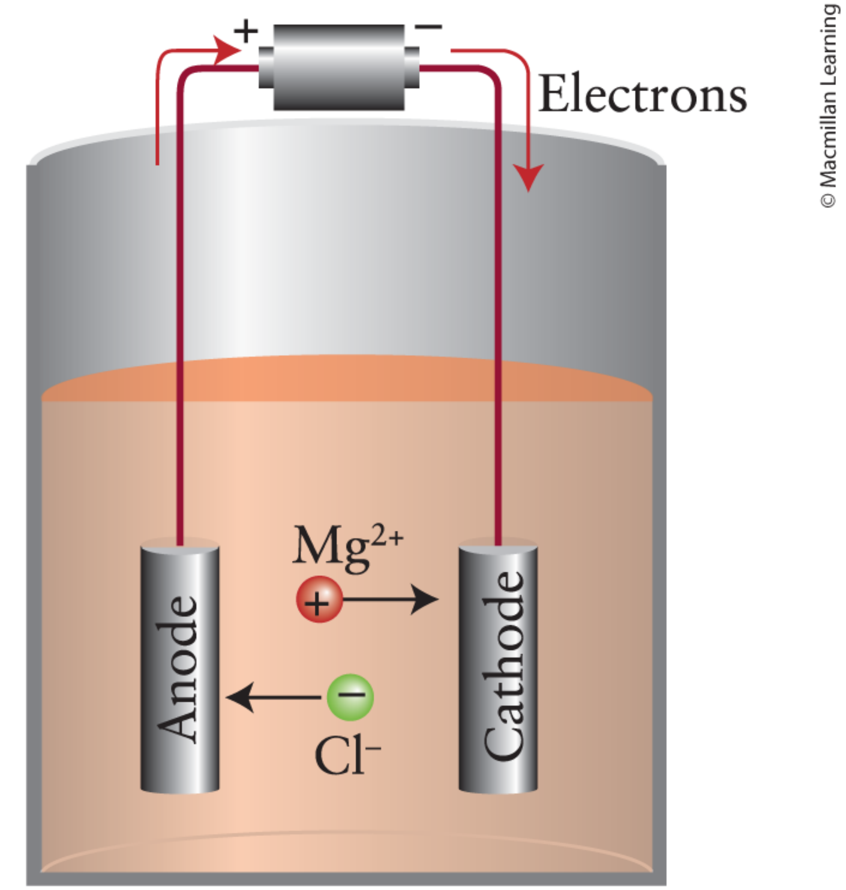
- Original definition based on the accumulated mass as oppose to moles
- More **current** and/or more **time** → More **substance** deposited

Example: Dow process

- Industrial process for production or magnesium as a metal

Anode: $2Cl^{-}$ (melt) → $Cl_2(g) + 2\ e^{-}$
Cathode: Mg^{2+} (melt) + $2\ e^{-}$ → Mg(l)

- Electrons are "forced" towards the cathode, instead of a higher potential anode.
- Notice the lack of a salt bridge (due to the absence of aqueous component)
- Done at high temperatures ~700-800˚C



Oxidation:
$2\ Cl^{-}(melt) \rightarrow Cl_2(g) + 2\ e^{-}$

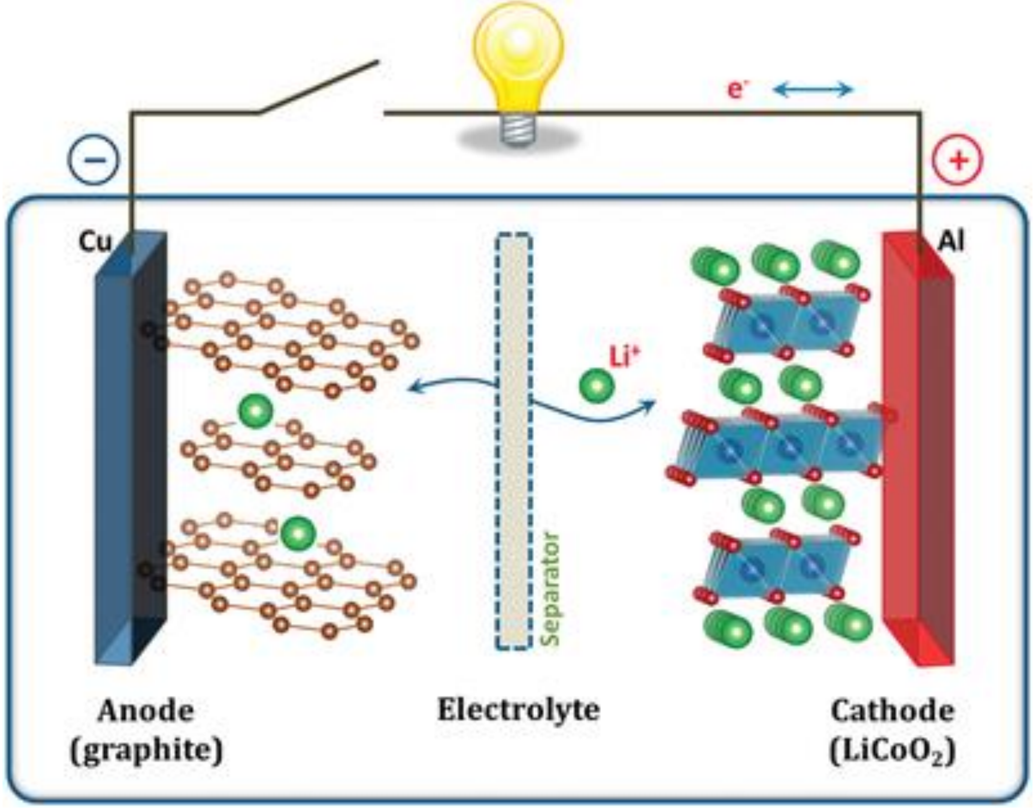
Reduction:
$Mg^{2+}(melt) + 2\ e^{-} \rightarrow Mg(l)$

* The "melt" signifies molten salt.

Example: Rechargeable batteries

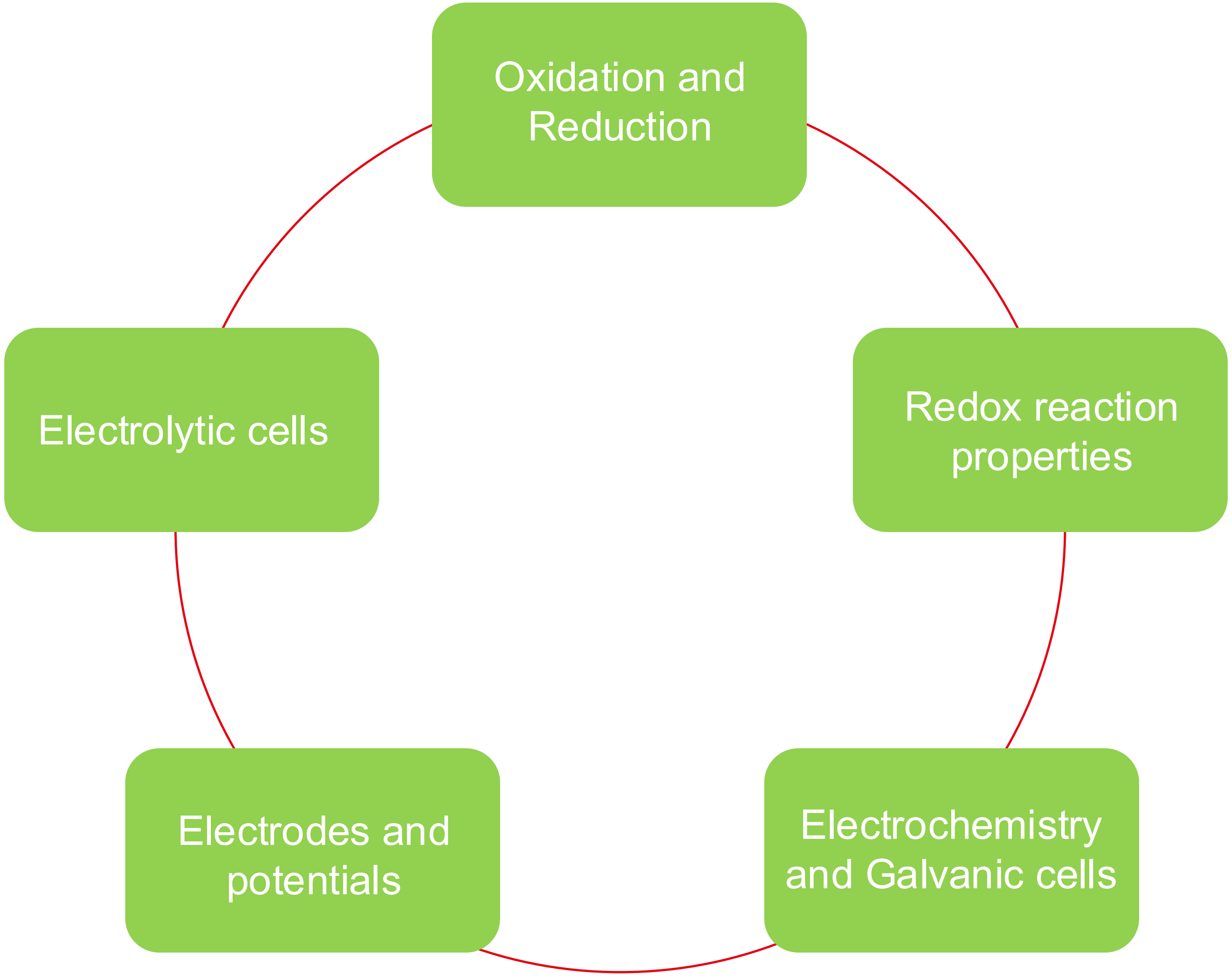
- **Discharge** = Galvanic mode:
  - Lithium ions move from the anode to the cathode while electrons flow through the circuit, delivering power.
- **Charge** = Electrolytic mode:
  - An external voltage forces electrons back to the former anode and drives lithium ions to re-intercalate, reversing the chemistry.

Anode: $LiC_6 \rightarrow C_6 + Li^+ + e^-$
Cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$



- Layered or porous electrode materials (e.g., graphite, $LiCoO_2$) can repeatedly accept and release lithium ions without major structural damage; this makes the reaction reversible over many cycles.

Plan



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