Electrochemical Systems

Electricity from Chemistry

Electricity is the **flow of electrons**

Many **chemical reactions involve the transfer of electrons between atoms** or ions

  - electron transfer reactions

Chemical applications to yield electrons represent areas we investigate, to create new devices.

Electrochemistry: The area of chemistry concerned with the interconversion of chemical and electrical energy.
Electrochemical cells come in two varieties:

Galvanic (or Voltaic) Cell: A spontaneous chemical reaction which generates an electric current.

Electrolytic Cell: An electric current which drives a nonspontaneous reaction.

Luigi Galvani

Alessandro Volta

We'll come back to these later, …

Oxidation–Reduction

Reactions where electrons are transferred from one atom to another are called **oxidation–reduction reactions**

- **Often shortened to "redox"** reactions

In redox reactions, atoms Losing Electrons are being Oxidized, (LEO) atoms that Gaining Electrons are being Reduced (GER).

$2\,Na(s) + Cl_2(g) \rightarrow 2\,Na^+Cl^-(s)$ (Overall reaction)

The redox reaction can be separated into two pieces:

$Na \rightarrow Na^+ + 1\,e^-$ (the oxidation)

$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$ (the reduction)

Galvanic Cells

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

Oxidation half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

The **overall reaction** combines these half-reactions

In an **electrochemical cell**, the two half-reactions are physically separated, and the electrons are forced to travel in a circuit to do useful work.

Identifying Reduction / Oxidation Chemistry

Redox reactions involve **a change of oxidation state** for the chemicals in the reaction.

To **identify a redox reaction:**

We will need to be able to **assign oxidation states** (oxidation number) of species in reactions.

- **This is ALWAYS the first step** in ANY electrochemical reaction.
- A series of simple rules is available as an aid.
- Practice using the rules is the only way;

Rules for Assigning Oxidation States

Rules are in order of priority

1. **Standard elemental forms, oxidation state = 0**
   - $2\ Na_{(s)} + Cl_{2(g)}$; Na = 0 and Cl = 0

2. **monatomic ions** have **oxidation state equal to their charge**
   - NaCl → $Na^+\ Cl^-$; Na = +1 and Cl = −1
   - Some elements have very common oxidation numbers, learning these makes our approach simpler

Rules for Assigning Oxidation States

3. Common elements have oxidation states according to the table below (some exceptions apply)

Nonmetal	Example	Oxidation State
H	CH_4	Each H is +1, thus C is -4
O	CO_2	Each O is −2, thus C is +4
Group 7A (Halogens)	CCl_4	Each Cl is −1, thus C is +4

Exceptions:

- when H is bound to a metal, -1
- when O is in O-O, each is -1
- if halogen is the central atom, ???

Rules for Assigning Oxidation States

4. (a) the **sum of the oxidation states** of all the atoms **in a neutral molecule is 0**
   - in NaCl, Na = +1 and Cl = −1; (+1) + (−1) = 0

4. (b) the **sum of the oxidation states** of all the atoms **in a polyatomic ion equals the charge on the ion**
   - in NO_3^-, $O_{O.S.} = -2$, then $N_{O.S.} = +5$ as $(N_{O.S.}) + 3(-2) = -1$

5. (a) **Group I metals** have an **oxidation state of +1** in all their compounds
   - in NaCl, Na = +1, thus Cl = -1 (as expected!)

5. (b) **Group II metals** have an **oxidation state of +2** in all their compounds
   - in $MgCl_2$, Mg = +2 thus Cl = -1 (as expected!)

Example: Determine the oxidation states (O.S.) of all the atoms in a propanoate ion, $C_3H_5O_2^-$

There are no free elements or free ions in propanoate, so we use the sum of O.S. equals charge:

$$({}_{O.S.}C_3) + ({}_{O.S.}H_5) + ({}_{O.S.}O_2) = -1 \text{ (charge)}$$

$$3*({}_{O.S.}C_{each}) + 5*({}_{O.S.}H_{each}) + 2*({}_{O.S.}O_{each}) = -1 \text{ (charge)}$$

Note: unlike charges, oxidation states can be fractions!

Practice – Assign an oxidation state to each element in the following

Br_2

K^+

LiF

CO_2

SO_4^{2-}

Na_2O_2

Oxidation & Reduction

Oxidation is the process that occurs when

- the oxidation number of an element increases
- an element loses electrons
- a half-reaction has electrons as products

Reduction is the process that occurs when

- the oxidation number of an element decreases
- an element gains electrons
- a half-reaction has electrons as reactants

Most important biochemical reactions, responsible for supplying energy in the body, are redox processes

Reduced or Oxidized

Oxidation: a chemical process in which there is a loss of electrons

Reduction: a chemical process in which there is a gain of electrons by a species

Some helpful mnemonic devices:

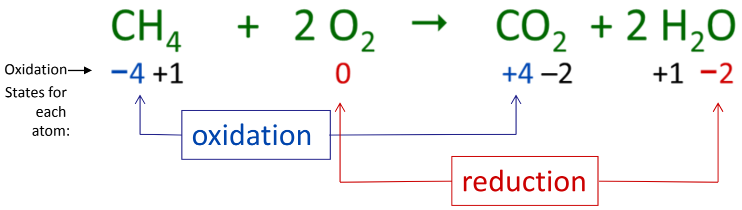
OIL RIG

LEO the lion says GER

Always two, there are.

Oxidation occurs when an atom’s oxidation state increases during a reaction

Reduction occurs when an atom’s oxidation state decreases during a reaction



$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

In a redox reaction, an oxidation and a reduction must **always occur as a pair.**

Oxidation–Reduction

Oxidation and reduction must occur simultaneously

- if an atom loses electrons another atom must take them

The reactant that reduces an element in another reactant is called the **reducing agent**

- the reducing agent contains the element that is oxidized

The reactant that oxidizes an element in another reactant is called the **oxidizing agent**

- the oxidizing agent contains the element that is reduced

$$2\ \text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\ \text{Na}^+\text{Cl}^-(s)$$

Na is oxidized, Cl is reduced

Na is the reducing agent, Cl_2 is the oxidizing agent

Practice – Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions

$$\text{Sn}^{4+} + \text{Ca} \rightarrow \text{Sn}^{2+} + \text{Ca}^{2+}$$

$$\text{F}_2 + 1/8\ \text{S}_8 \rightarrow \text{SF}_4$$

Balancing Equations and Redox Reactions

Previously: $Mg(OH)_2 + HCl \rightarrow MgCl_2 + H_2O$

Balancing Method: “trial and error balancing”

When a redox process occurs, **balancing the chemical reaction is typically not straightforward.**

In order to balance redox reactions, we recognize that electrons are transferred

- if we find a method to keep track of the electrons, we will be able to balance the equation

Visualizing electrons: Half-Reactions

To keep track of electrons, we need to SEE them.

We split a redox reaction into two **half-reactions** – each reaction involves either the oxidation or the reduction

- the oxidation half-reaction has electrons as products
- the reduction half-reaction has electrons as reactants

$$\mathbf{3\,Cl_2 + I^- + 3H_2O \rightarrow 6\,Cl^- + IO_3^- + 6\,H^+}$$

o.s. 0 −1 +1 −2 −1 +5 −2 +1

oxidation: $I^- \rightarrow IO_3^- + 6\,e^-$

reduction: $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$

Balancing Redox reactions: Acid or Base

As a complication, the method for balancing redox reactions is sensitive to the pH of the reaction.

Under **acidic conditions (H^+)**, a redox process can behave one way – and drastically change behaviour if the solution has **basic conditions (OH^-)!**

Solution: Develop ONE set of general rules:

1. We treat ALL reactions as if the conditions are acidic, 1st step.
2. If basic, then we correct our work.

General Balancing by the Half-Reaction Method

The overall reaction is separated into two parts, an oxidation reaction, and a reduction reaction.

*The separated reactions are called **"half-reactions"***

Each half-reaction includes electrons

- *electrons are products of the oxidation half-reaction*
  - *oxidation: loss of electrons (LEO, OIL)*
- *electrons are reactants in the reduction half-reaction*
  - *reduction: gain of electrons (GER, RIG)*

Each half-reaction is balanced for the atoms present.

The two half-reactions are adjusted so that the electrons transferred are equal when reactions are combined

Balancing Redox Reactions: Rules

1. assign all oxidation states of reaction species
    a) determine element oxidized and element reduced
2. write ox. & red. half-reactions, including electrons
    a) ox. electrons on right, red. electrons on left of arrow
3. balance half-reactions by mass
    a) first balance elements other than H and O
    b) add H_2O where need O
    c) add H^+ where need H
    d) if reaction done in Base, neutralize H^+ with OH^-
4. balance half-reactions by charge
    a) balance charge by adjusting electrons
5. balance electrons between half-reactions
6. add half-reactions together, to get FULL reaction.
7. check by counting atoms and total charge

Example: Balance $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$ in acidic solution

1. assign oxidation states and determine element oxidized and element reduced

$$\underset{+2}{Fe^{2+}} + \underset{+7\ \ -2}{MnO_4^-} \rightarrow \underset{+3}{Fe^{3+}} + \underset{+2}{Mn^{2+}}$$

2. separate into oxidation & reduction half-reactions

Example: Balance $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$ in acidic solution

3. balance half-reactions by mass

   a) first balance atoms other than O and H

   b) balance O by adding H_2O to side that lacks O

   c) balance H by adding H^+ to side that lacks H

$Fe^{2+} \rightarrow Fe^{3+}$

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

Example: Balance $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$ in acidic solution

4. balance each half-reaction with respect to charge by adjusting the numbers of electrons

   a) electrons on product side for oxidation

   b) electrons on reactant side for reduction

$Fe^{2+} \rightarrow Fe^{3+}$

+1e

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

+7 +5e +2

Example: Balance $Fe^{2+} + MnO_4^{-} \rightarrow Fe^{3+} + Mn^{2+}$ in acidic solution

5. balance electrons between half-reactions

$$\left.Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-}\right\} \times 5$$

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

6. add half-reactions, canceling electrons and common species

$$5\ Fe^{2+} + MnO_4^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_2O + 5\ Fe^{3+}$$

7. Check that numbers of atoms and total charge are equal

reactant side	Element	product side
5	Fe	5
1	Mn	1
4	O	4
8	H	8
+18 -1 = +17	charge	+17

Practice: Balance the reaction $I^{-} + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$ in basic solution

1. assign oxidation states and determine element oxidized and element reduced

$$\underset{-1}{I^{-}} + \underset{+6\ -2}{CrO_4^{2-}} \rightarrow \underset{0}{I_2} + \underset{+3}{Cr^{3+}}$$

2. separate into oxidation & reduction half-reactions

Practice: Balance the reaction $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$ in basic solution

3. balance half-reactions by mass
   a) first balance atoms other than O and H
   b) balance O by adding H_2O to side that lacks O
   c) balance H by adding H^+ to side that lacks H
   d) **if in basic solution, neutralize the H^+ with OH^-, to form H_2O**

ox: $I^- \rightarrow I_2$

red: $CrO_4^{2-} \rightarrow Cr^{3+}$

red: $CrO_4^{2-} \rightarrow Cr^{3+} + 4H_2O$

$CrO_4^{2-} + 8H^+ \rightarrow Cr^{3+} + 4H_2O$

Practice: Balance the reaction $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$ in basic solution

4. balance each half-reaction with respect to charge by adjusting the numbers of electrons
   a) Oxidation: electrons are products
   b) Reduction: electrons as reagents

$2\ I^- \rightarrow I_2$

$CrO_4^{2-} + 4H_2O \rightarrow Cr^{3+} + 8OH^-$

Practice: Balance the reaction $I^- + CrO_4^{2-} \rightarrow I_2 + Cr^{3+}$ in basic solution

5. balance electrons between half-reactions
6. add half-reactions, canceling electrons and common species
7. check

$$2\,I^- \rightarrow I_2 + 2e^-$$

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr^{3+} + 8OH^-$$

$$2CrO_4^{2-} + 8H_2O + 6\,I^- \rightarrow 2Cr^{3+} + 16OH^- + 3\,I_2$$

reactant side	Element	product side
2	Cr	2
6	I	6
16	O	16
16	H	16
−10	charge	−10

Redox Reactions & Electricity

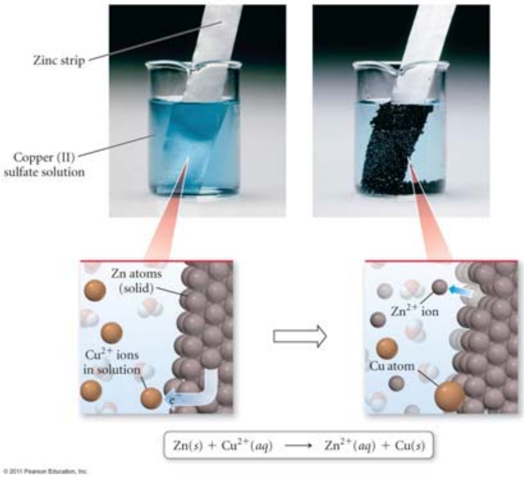
Redox reactions involve the **transfer of electrons** between substances. An electron flow is what we consider **'electricity'.**

Redox reactions can be used to generate electric current. We **can do useful work!**

HOWEVER: To use the electrical current:

- We must first **physically separate** the oxidation and reduction half-reactions

Chemical based electric current

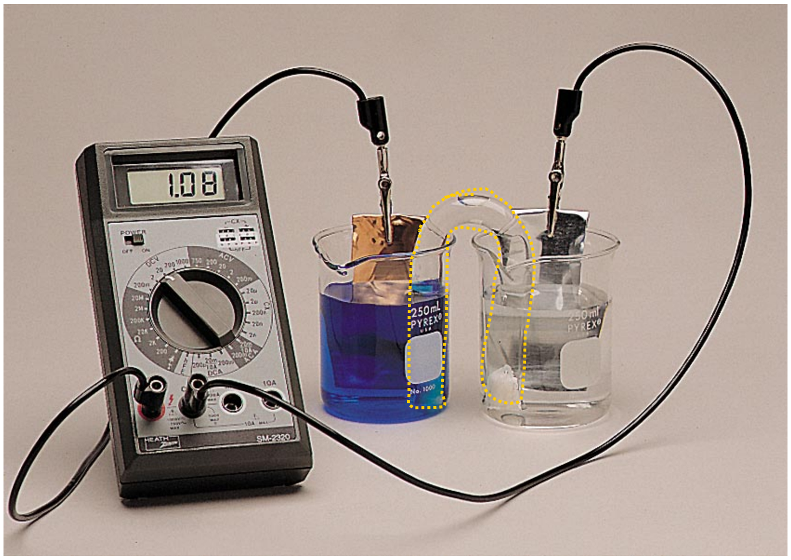


Net reaction involves the transfer of 2 moles of electrons, per mole of ion used.

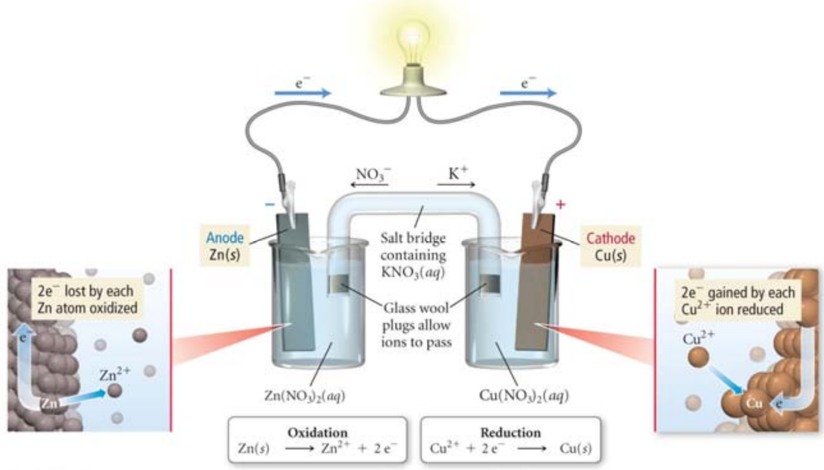
When the two half-reactions are **in close contact, reaction is VERY fast.**

If we **separate the two reactions, we could slow the electron flow**

Voltaic Cell: Zinc - Copper



Chemically generated electrical current



Electrochemical Cells: I told you we'd be back…

Electrochemical cell: *a setup which can take advantage of a chemical reaction that either uses or generates a flow of electrons*

Voltaic Cell

- –Also called galvanic cells, batteries
- –*An electrochemical cell in which a* ***spontaneous reaction produces a flow of electrons***

Electrolytic Cell

- –*An electrochemical cell in which* ***an electric current is used*** *to force an otherwise* ***non-spontaneous reaction*** *to occur*.

Voltaic Cells

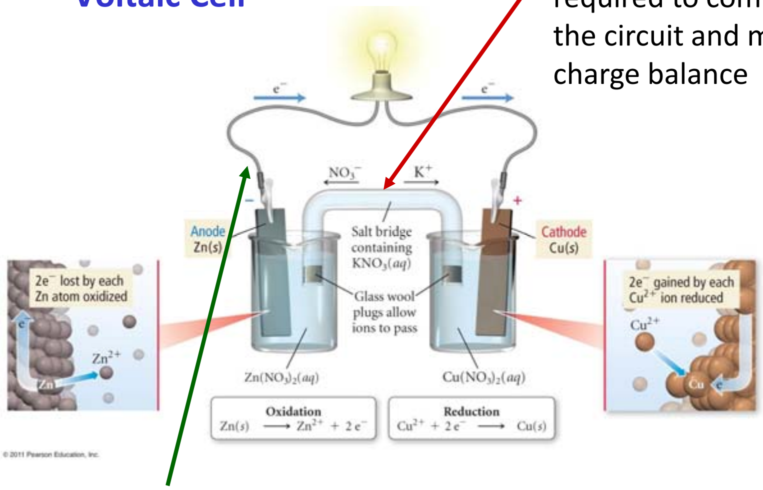
To take advantage of an electrochemical reaction, we **separate a redox reaction into its two half reactions,**

If we provide an easy path for electrons, the electron transfer reaction will proceed, **and we can use the electron flow to do work!**

Requires

- Pathways for electrons and ions
  - Use a wire for electrons
  - Use a salt bridge or other semi-permeable membrane for ions to move

Voltaic Cell



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the **salt bridge** is required to complete the circuit and maintain charge balance

The connecting wire allows the electrons to move between solutions, and the electron energy can be used.

Reaction surfaces: Electrodes

Reactions occur on a surface called an **electrode.**

Each half-reaction has its own electrode:

Anode (+)

- electrode where oxidation occurs
- anions are attracted to it

Cathode (-)

- electrode where reduction occurs
- cations are attracted to it

Galvanic Cells

Anode half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Electrochemical Cell Notation

We **simplify the cells,** for discussion, **using shorthand** to describe the cell

We summarize **the principal reagent and product** for each electrode separated with **vertical line (for change of phase of material),** otherwise by a comma

Write **anode (oxidation) first,** separated **with a double vertical line (represents salt bridge)**

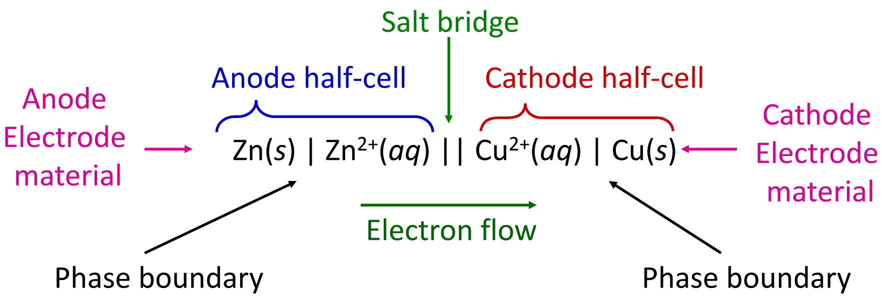
Electrodes for each cell should always be written on the **far left (anode)** and the **far right (cathode)** of the notation

Shorthand Notation for Galvanic Cells

Anode half-reaction: $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2e^{-}$

Cathode half-reaction: $\mathrm{Cu}^{2+}(aq) + 2e^{-} \longrightarrow \mathrm{Cu}(s)$

Overall cell reaction: $\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$



Salt bridge

Anode half-cell

Cathode half-cell

Anode Electrode material

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

Cathode Electrode material

Electron flow

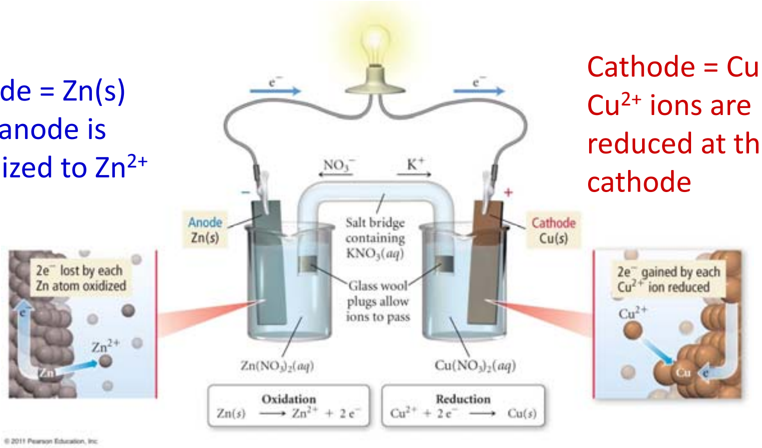
Phase boundary

Phase boundary

Voltaic Cell

Anode = Zn(s)
the anode is
oxidized to Zn^{2+}

Cathode = Cu(s)
Cu^{2+} ions are
reduced at the
cathode



Electrochemical cell notation:

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

Nonstandard concentrations

Concentrations are important for the operation of a Voltaic cell, particularly if non-standard.

Cell notation **indicates concentration of aqueous species in brackets**, in place of $_{(aq)}$

Thus:

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

would be:

$Zn(s)|Zn^{2+}(1.0\ M)\ ||\ Cu^{2+}(1.0\ M)|Cu(s)$

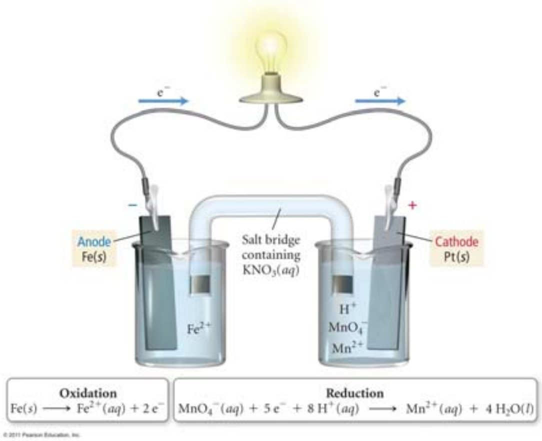
Electrodes: Some comments

Often the anode or cathode are made of the same metal that is reacting in the respective half-cell.

However, when reactions involve the oxidation or reduction between oxidation states, or the use of a gas, **inert electrodes are used.**

- an **inert electrode** does not chemically participate in the reaction.
- It only **provides a surface for the transfer of electrons**.

$\mathrm{Fe}(s)\ |\ \mathrm{Fe}^{2+}(aq)\ ||\ \mathrm{MnO_4}^{2-}(aq),\ \mathrm{Mn}^{2+}(aq),\ \mathrm{H}^{+}(aq)\ |\ \mathrm{Pt}(s)$



Because the half-reaction involves **reducing the Mn oxidation state from +7 to +2,** we use an **inert electrode.**

It provides a surface where electron transfer can easily occur, without side-reactions involving the MnO_4^-.

Platinum (also Pd or Ni) works well because it is very unreactive, but conducts electricity well.

Electrochemical Potential

In an electrochemical cell the electrons move from one electrode to the other

$$\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,e^{-}_{\text{(energy, }E_1\text{)}}$$

$$\mathrm{Cu^{2+}(aq)} + 2\,e^{-}_{\text{(energy, }E_2\text{)}} \longrightarrow \mathrm{Cu\,(s)}$$

Zn will lose 2 e^- and be oxidized at the anode

Cu^{2+} will gain 2 e^- and be reduced at the cathode

Energy released by the complete reaction depends on the **energy difference of the electrons in the half reactions** occurring between the electrodes

Potential difference: Voltage

The difference in potential energy between the reactants and products is the **potential difference**

- unit of potential difference is the **Volt, V**

1 V is the energy it takes to move 1 electron over a fixed distance.

When electrons move through a wire, they move from **high potential to low potential.**

The amount of force pushing the electrons through the wire is called the **electromotive force, emf**

Potential difference, emf, and Cell Potential, E

The value of the **cell potential, E_{cell},** depends on the specific oxidation and reduction reactions of the cell.

Under standard conditions, **the cell potential** is often called the **standard emf, $E°_{cell}$**

- Each paired set of half-reactions produces a different value.
- Deviation from standard conditions will change the value of E.

What is "Standard Condition"?

As with free energy, **the potential** of an electrochemical cell **depends on temperature and reagent concentration**

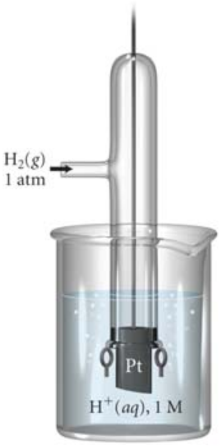
Standard Electrode Potentials are determined assuming:

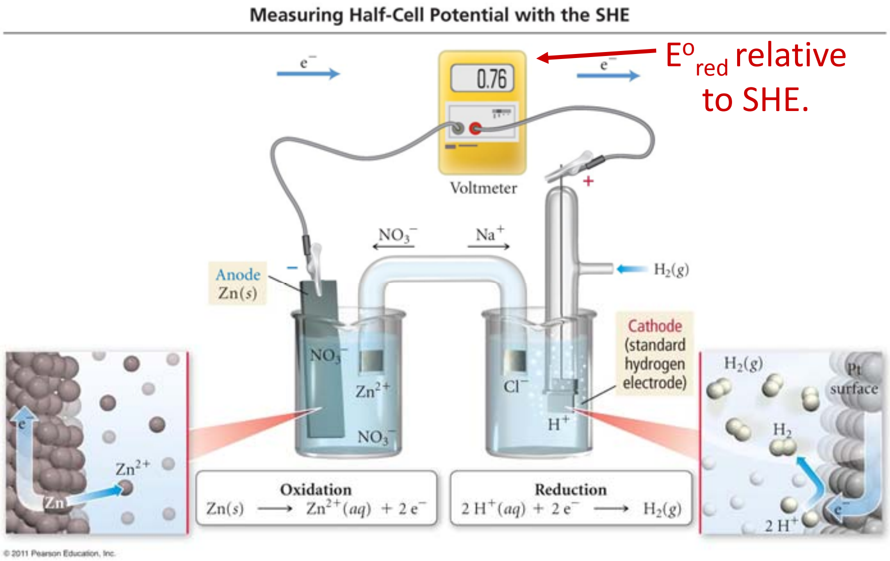
- T = 25º C = 298.15 K,
- concentration of dissolved ions is exactly 1 mol L^{-1}
- pressures of gases are all 1 atm.

Standard conditions are **indicated by the º**, *i.e.* Eº.

Standard Reduction Potential

- Like thermochemistry, we use **reference points to measure cell-potential.**
- We measure relative to a **STANDARD half-cell reaction**.
- The reduction of H^+ to H_2 under standard conditions, is assigned a potential difference = 0 v
  - **standard hydrogen electrode, SHE**





E^o_{red} relative to SHE.

$Zn(s) \mid Zn^{2+}(1\ M) \parallel H^+(1\ M) \mid H_2(g) \mid Pt(s)$

Half-Cell Potentials

Half-reactions with a **stronger tendency toward reduction than the SHE** have $E^\circ_{red} > 0$

Half-reactions with a **stronger tendency toward oxidation** than the SHE have $E^\circ_{red} < 0$

For simplicity, **ALL reactions are listed in tables as REDUCTION reactions.** Therefore, when you look up cell values for an oxidation half-reaction,

$$E^\circ_{\text{oxidation}} = -\,E^\circ_{\text{reduction (in table)}}$$

Standard Reduction Potentials

Anode half-reaction: $H_2(g) \longrightarrow 2H^{1+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^{1+}(aq) + Cu(s)$

The **standard potential of the TOTAL cell is the sum of the standard half-cell potentials** for oxidation at the anode and reduction at the cathode:

$$\boxed{E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}}$$

We can use this to measure E^o_{cell} for chemical reactions.

Standard Reduction Potentials

Anode half-reaction: $H_2(g) \longrightarrow 2H^{1+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^{1+}(aq) + Cu(s)$

The measured potential for this cell: $\mathbf{E°_{cell} = 0.34\ V}$

The anode is the Standard Hydrogen Electrode: $\mathbf{E°_{SHE,ox} = 0\ V}$

$$E°_{cell} = E°_{ox} + E°_{red}$$

$$0.34\ V = 0\ V + E°_{red}$$

A standard reduction potential can be defined:

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $\mathbf{E° = 0.34\ V}$

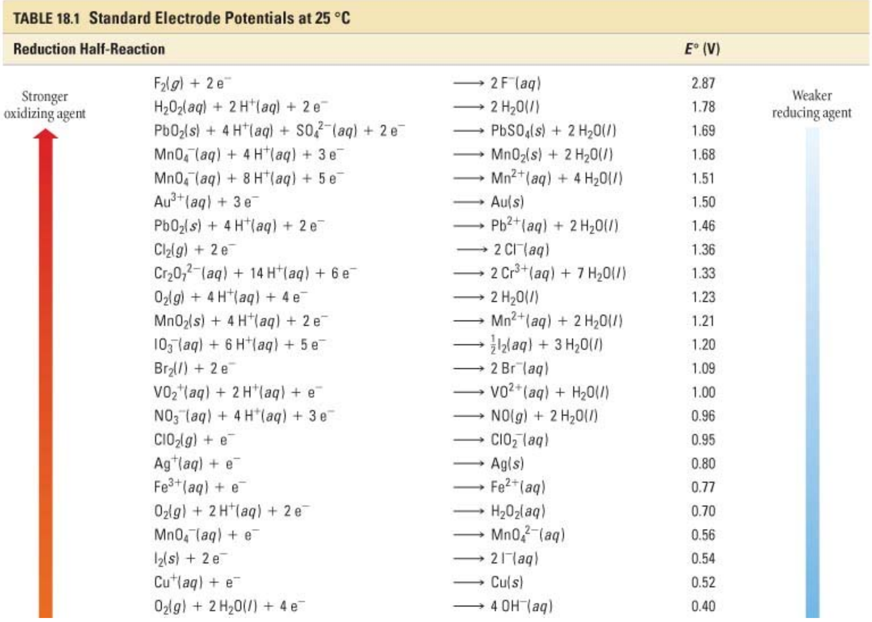
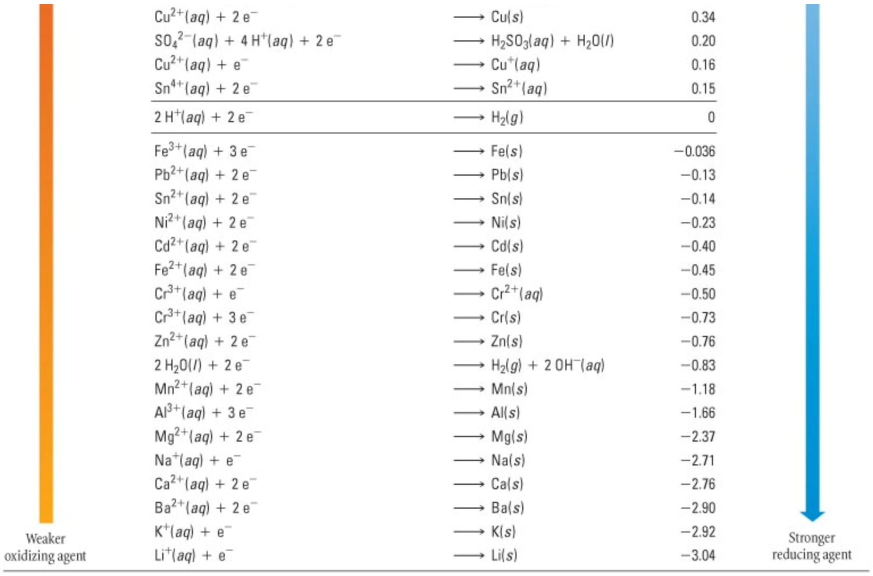


TABLE 18.1 Standard Electrode Potentials at 25 °C

	Reduction Half-Reaction		$E°$ (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow MnO_2(s) + 2H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	1.46	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.21	
	$IO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3H_2O(l)$	1.20	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(g) + 2H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	

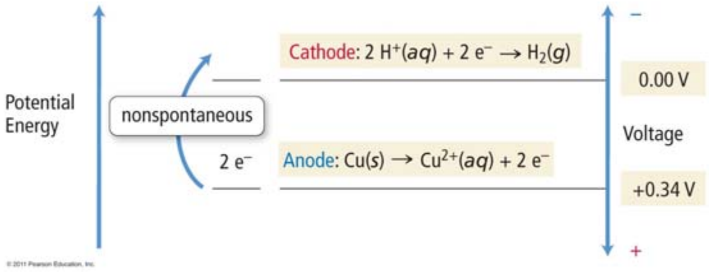


$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Fe^{3+}(aq) + 3e^-$	$\longrightarrow Fe(s)$	−0.036
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.23
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50
$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.73
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.76
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Cell Potential and Electron Flow

Half-reaction with **large cell potentials** are reactions that have a **strong tendency to occur**

When two half-cells are connected, electrons flow in the direction of the stronger reaction.



Tables of Reduction Potentials

Good oxidizing agents (easily reduced)

Species X + ne^- → products E° = positive

…

…

…

…

Species Y + k e^- →products E° = negative

Good reducing agents

(easily oxidized. If reaction flipped, E = positive)

Oxidizing Agents and Reducing Agents

H_2O_2 has a **E^o_{red} of +1.78 V** for the reaction

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$$

measured against SHE.

Therefore, H_2O_2 is a **potent oxidizing agent**

Zn^{2+} has a E^o_{red} of –0.76 V for the reaction

$Zn^{2+} + 2e^- \longrightarrow Zn$ thus $Zn \longrightarrow Zn^{2+} + 2e^-$ $E_{ox} = +0.76$

So, Zn releases electrons and is a **good reducing agent**

Calculating E_{cell} and Using E_{cell}

General properties of E_{cell} values:

When a reaction has a value of E_{cell} as written:

- **Reversing the reaction has the value of $-E_{cell}$**

HOWEVER: electrode potential is **an intensive property**

- *i.e.* independent of amount of electrons involved in the process
- Hills don't get higher if more water runs down them.

Thus, we **DO NOT EVER multiply an E_{cell} value when we multiply reactions by a constant.**

Note: this is quite different than thermochemistry, where thermochemical values are EXTENSIVE.

Standard Electrode Potentials: REDUCTIONS

With the tables, we can now calculate general reactions:

$$\mathbf{Zn_{(s)} + Cu^{2+}_{(aq,\ 1.0M)} \rightarrow Zn^{2+}_{(aq,\ 1.0M)} + Cu_{(s)}}$$

Potentials are tabulated for half cells **as reductions**

From table $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad E^o = 0.34\ V$

Remember: $E_{ox} = -(E_{red})$, thus **for Zn oxidation:**

From table $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad E^o = -0.76\ V$

Changed to oxidation $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad E^o = 0.76\ V$

Thus, the potential for the Zn/Cu cell (E_{cell}) is:

$$E_{cell} = E_{ox} + E_{red} = 0.76\ V + 0.34\ V = 1.10V$$

What Does the sign of E° mean?

The **sign of E^o_{cell}** for a reaction is important.

positive E^o_{cell} values indicate that the reaction will proceed as written, without any extra driving force

- It is a **spontaneous reaction**

negative E^o_{cell} values indicate that the reverse reaction will occur

- It is a **non-spontaneous reaction**

For non-spontaneous reactions, it is possible to change the conditions from standard conditions, to make the reaction occur.

Electrolysis and Electrolytic Cells

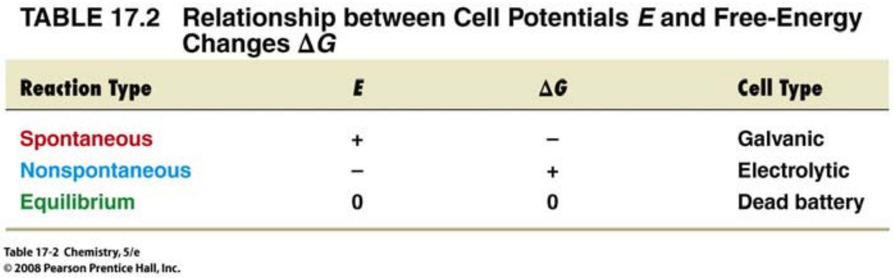


TABLE 17.2 Relationship between Cell Potentials E and Free-Energy Changes ΔG

Reaction Type	E	ΔG	Cell Type
Spontaneous	+	–	Galvanic
Nonspontaneous	–	+	Electrolytic
Equilibrium	0	0	Dead battery

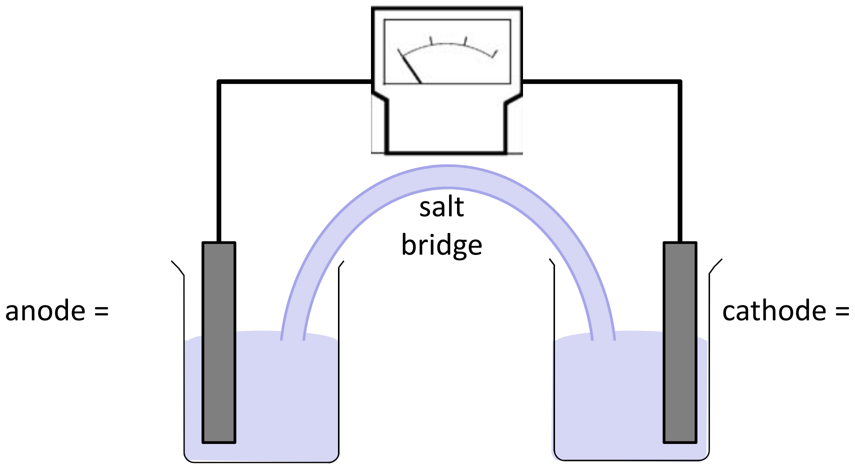
Table 17-2 Chemistry, 5/e

We are presently focusing on Galvanic cells…The processes occurring in galvanic cells have **a positive E_{cell}**

We will examine electrolysis later…

Practice – Sketch and label a voltaic cell in which one half-cell has Ag(*s*) immersed in 1 M $AgNO_3$, and the other half-cell has a Pt electrode immersed in 1 M $Cr(NO_3)_2$ and 1 M $Cr(NO_3)_3$ Write the half-reactions and overall reaction, and determine the cell potential under standard conditions.

Reduction Half-Reaction	E°_{red}, V
$F_2(g) + 2e^- \rightarrow 2\,F^-(aq)$	+2.87
$IO_3^-(aq) + 6\,H^+ + 5e^- \rightarrow \frac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	+0.80
$I_2(s) + 2e^- \rightarrow 2\,I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cr^{3+}(aq) + 1e^- \rightarrow Cr^{2+}(aq)$	−0.50
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37



ox: $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + 1\,e^-$ $E^\circ = +0.50$ V

red: $Ag^+(aq) + 1\,e^- \rightarrow Ag(s)$ $E^\circ = +0.80$ V

tot: $Cr^{2+}(aq) + Ag^+(aq) \rightarrow Cr^{3+}(aq) + Ag(s)$ $E^\circ = +1.30$ V

Practice – Calculate E°_{cell} for the following reaction at 25 °C

$$IO_3^-(aq) + 6\ H^+(aq) + 5\ I^-(aq) \rightarrow 3\ I_2(s) + 3\ H_2O(l)$$

Reduction Half-Reaction	E°_{red}, V
$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$	+2.87
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow \frac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	+0.80
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cr^{3+}(aq) + 1e^- \rightarrow Cr^{2+}(aq)$	−0.50
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37

Practice – Calculate E°_{cell} for the following reaction at 25 °C

$$IO_3^-(aq) + 6\ H^+(aq) + 5\ I^-(aq) \rightarrow 3\ I_2(s) + 3\ H_2O(l)$$

Identify which reactions we need; Oxidation states!
Remember, the tables **list REDUCTION reactions**

Reduction Half-Reaction	E°_{red}, V
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow \frac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	+0.54
As an oxidation: $I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	-0.54

Practice – Calculate $E°_{cell}$ for the reaction at 25 °C

$2\,IO_3^- + 12\,H^+ + 10\,I^- \rightarrow 6\,I_2 + 6\,H_2O$

separate the reaction into the oxidation and reduction half-reactions	red: $IO_3^-{}_{(aq)} + 6\,H^+{}_{(aq)} + 5\,e^- \rightarrow ½\,I_{2(s)} + 3\,H_2O_{(l)}$ ox (anode): $2\,I^-{}_{(s)} \rightarrow I_{2(aq)} + 2\,e^-$
find the $E°$ for each half-reaction and sum to get $E°_{cell}$	

Electrical Work and the E_{cell} (emf) value

Galvanic cells release energy.

If energy is released, work can be done by the system!

The maximum amount of work (in J) done by an electrochemical cell is:

work = charge x potential difference

We measure **potential difference in volts (V)**

We measure **the charge in coulombs (C)**

Electromotive Force (emf): The force or electrical potential that pushes the negatively charged electrons away from the anode (- electrode) and pulls them toward the cathode (+ electrode).

The **cell potential (*E*)** or the **cell voltage**.

1 J = 1 C x 1 V

joule
SI unit of energy

coulomb
Electric charge

volt
SI unit of electric potential

1 coulomb is the amount of charge transferred when a current (I) of 1 ampere (A) flows for 1 second.

Current, I

Current (I) is the number of electrons that flow through the system per second

- unit = Ampere, A.   1 A = 1 C/s

1 A of current = 1 Coulomb of charge flowing by in one second

- 1 A = 6.242 x 10^{18} electrons per second
- We can **use values of current to count the moles of electrons** used in electrochemistry
- This **allows stoichiometric calculations** within electrochemistry.

Faraday's Constant

Chemical measurements of amount of substance are made in units of moles (mol)

The charge on one electron is: **e** = 1.60×10^{-19} C

Thus, a mol of electrons has a charge of, **F**:

$$\mathbf{F} = N_A \times e$$

$$F = 6.022 \times 10^{23}\ \text{mol}^{-1} \times 1.60 \times 10^{-19}\ \text{C}$$

$$F = 9.65 \times 10^{4}\ \text{C mol}^{-1}$$

Faraday constant (F) : charge in coulombs of 1 mol of electrons = 9.65×10^4 C

E_{cell}: Maximum Potential Difference

The **maximum work supplied** by a cell:

$$w_{max} = -nFE_{cell}$$

Where

n: number of moles of e^- transferred in the reaction

F: the Faraday constant (on formula sheet)

E_{cell}: The potential of the chemical cell

As before: **the negative sign indicates work is being done by the reaction** of the electrochemical cell on the surroundings

Hold on a second here …. Free energy!

The **standard Gibbs (Free) energy (ΔG):**

$$\Delta G^o = work_{max} = w_{max}$$

That **was the maximum energy** that can be **given from the chemical system, to perform "work".**

THERE IS A DIRECT RELATIONSHIP BETWEEN THE GIBBS ENERGY AND ELECTROCHEMICAL CELLS!

Free-energy change, ΔG: the free energy was the maximum work the chemical system could do.

It is directly related to E^o_{cell}, **for redox processes:**

Faraday or **Faraday constant**

$$w_{max} = \Delta G = -nFE \quad \text{or} \quad \Delta G° = -nFE°$$

free-energy change

cell potential

number of moles of electrons transferred in the reaction

Properties of free energy relate to cell potential →

Spontanaeity!

Example: The standard cell potential at 25 °C is 0.92 V for the following reaction:

$$Al(s) + Cr^{3+}(aq) \longrightarrow Al^{3+}(aq) + Cr(s)$$

Calculate the standard free-energy change for this reaction at 25 °C.

$\Delta G° = -nFE°$

Redox Reactions: Predicting Spontaneity

A **spontaneous reaction** occurs when $\Delta G < 0$.

A **spontaneous reaction** occurs when $E_{cell} > 0$

$$\Delta G = -nFE_{cell}$$

Spontaneous when: a reduction half-reaction is paired with an oxidation half-reaction lower on the table.

Reverse reaction → reverse spontaneity

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $E^\circ_{red} = +0.34$ V
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$ $E^\circ_{red} = -0.76$ V

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

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

Practice – Decide whether each of the following will be spontaneous as written or in the reverse direction

$F_{2(g)} + 2\ I^-_{(aq)} \rightarrow I_{2(s)} + 2\ F^-_{(aq)}$

$Mg_{(s)} + 2\ Ag^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2\ Ag_{(s)}$

$Cu^{2+}_{(aq)} + 2\ I^-_{(aq)} \rightarrow I_{2(s)} + Cu_{(s)}$

$Cu^{2+}_{(aq)} + 2\ Cr^{2+}_{(aq)} \rightarrow Cu_{(s)} + 2\ Cr^{3+}_{(aq)}$

Reduction Half-Reaction
$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow I_2(s) + 3H_2O(l)$
$Ag^+(aq) + 1e^- \rightarrow Ag(s)$
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
$Cr^{3+}(aq) + 1e^- \rightarrow Cr^{2+}(aq)$
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

Practice – Calculate $\Delta G°$ for the reaction at 25°C
$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$

Reduction Half-Reaction	$E°_{red}$, **V**
$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$	+2.87
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow ½I_2(s) + 3H_2O(l)$	+1.20
$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	+0.80
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cr^{3+}(aq) + 1e^- \rightarrow Cr^{2+}(aq)$	−0.50
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37

Practice – Calculate $\Delta G°$ for the reaction at 25°C

$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$

Reduction Half-Reaction	$E°_{red}$, V
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow ½I_2(s) + 3H_2O(l)$	+1.20
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	+0.54
As an oxidation: $2\ I^-(aq) \rightarrow I_2(s) + 2e^-$	-0.54

		For e^- transfer
$2\ IO_3^-(aq) + 12\ H^+ + 10e^- \rightarrow I_2(s) + 6H_2O(l)$	+1.20	2 * Reduction
$10\ I^-(aq) \rightarrow 5\ I_2(s) + 10\ e^-$	-0.54	5 * Oxidation
$2\ IO_3^-{}_{(aq)} + 12\ H^+{}_{(aq)} + 10\ I^-{}_{(aq)} \rightarrow 6\ I_{2\ (s)} + 6\ H_2O_{(l)}$	+0.66	Overall; **n =10**

Practice – Calculate $\Delta G°$ for the reaction at 25 °C

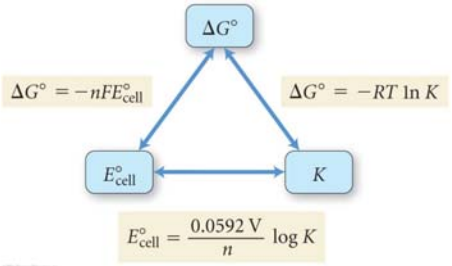
$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6\ I_2(s) + 6\ H_2O(l)$

Given: **Find:**	$2IO_3^-{}_{(aq)} + 12H^+{}_{(aq)} + 10I^-{}_{(aq)} \rightarrow 6\ I_{2(s)} + 6\ H_2O(l)$ $\Delta G°$, (J)
Conceptual Plan: **Relationships:**	$E°_{ox}, E°_{red} \Rightarrow E°_{cell} \Rightarrow \Delta G°$ $E°_{cell} = E°_{ox} + E°_{red}$ $\quad \Delta G° = -nFE°_{cell}$
Solve:	$\Delta G° = -nFE°_{cell}$
Answer:	**because $\Delta G°$ is –**, the reaction is **spontaneous** in the forward direction under standard conditions

$E^\circ_{\text{cell,}}$ ΔG° and K

We have many descriptors for spontaneous reactions

- one that proceeds in the forward direction with the chemicals in their standard states
- $\Delta G^\circ < 1$ (negative)
- $E^\circ > 1$ (positive)
- $K > 1$



$\Delta G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}}$

- n is the number of electrons
- F = Faraday's Constant = 96,485 C/mol e^-

Practice – Calculate K for the reaction at 25°C
$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$

Reduction Half-Reaction	E°_{red}, V
$F_2(g) + 2e^- \rightarrow 2\ F^-(aq)$	+2.87
$IO_3^-(aq) + 6\ H^+ + 5e^- \rightarrow \frac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$Ag^+(aq) + 1e^- \rightarrow Ag(s)$	+0.80
$I_2(s) + 2e^- \rightarrow 2\ I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cr^{3+}(aq) + 1e^- \rightarrow Cr^{2+}(aq)$	−0.50
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.37

Practice – Calculate *K* for the reaction at 25°C

$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$

Reduction Half-Reaction	$E°_{red}$, V
$IO_3^-(aq) + 6\ H^+ + 5e^- \longrightarrow ½I_2(s) + 3H_2O(l)$	+1.20
$I_2(s) + 2e^- \longrightarrow 2\ I^-(aq)$	+0.54
As an oxidation: $2\ I^-(aq) \longrightarrow I_2(s) + 2e^-$	-0.54

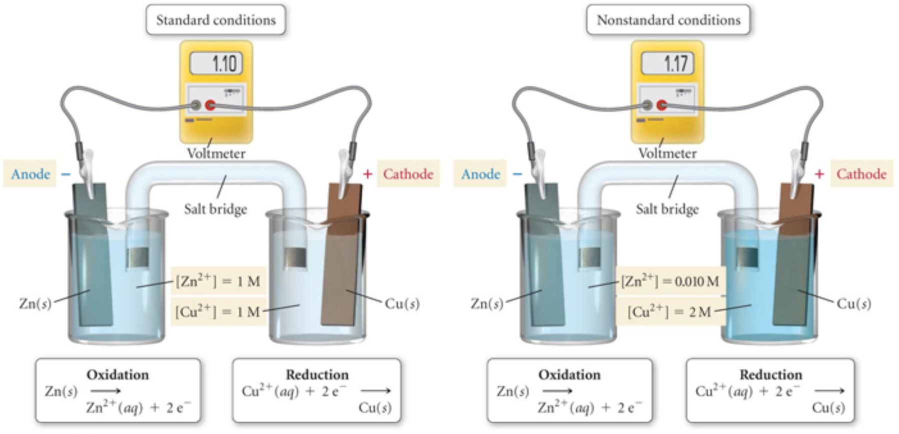
Recall, **we determined 10 total electrons transferred**

Practice – Calculate *K* for the reaction at 25 °C

$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$

Given: **Find:**	$2\ IO_{3\ (aq)}^- + 12\ H^+_{(aq)} + 10\ I^-_{(aq)} \rightarrow 6\ I_{2(s)} + 6\ H_2O_{(l)}$ K
Conceptual Plan: **Relationships:**	$E°_{ox}, E°_{red}$ → $E°_{cell}$ → K $E°_{cell} = E°_{ox} + E°_{red}$ $\quad E°_{cell} = \frac{0.0592\ V}{n} \log K$
Solve:	
Answer:	because *K* >> 1, the position of equilibrium lies far to the right under standard conditions

E_{cell} When Ion Concentrations are Not 1 M



Electrochemistry: Non Standard Conditions

In thermodynamics, we could relate solution conditions to the Gibb's Free Energy (ΔG), the equilibrium constant, K, and the reaction quotient, Q.

Now we also know that ΔG and E_{cell} are related.

The Nernst Equation relates E_{cell} to E^{o}_{cell} and the reaction quotient (Q)

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln Q \quad \text{or} \quad E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF}\log Q$$

Deriving the Nernst Equation

$$\Delta G = \Delta G^\circ + \mathrm{RT}\ln Q$$

$\Delta G^{(\circ)} = -nFE^{(\circ)}$

$$-nFE = -nFE^\circ + \mathrm{RT}\ln Q$$

Divide both sides by -nF

$$\frac{-nFE}{-nF} = \frac{-nFE^\circ}{-nF} + \frac{\mathrm{RT}\ln Q}{-nF}$$

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

Sub in for R, T (in K), F

when the temperature is 25°C

$$E = E^\circ - \frac{0.0592}{n}\log Q$$

Remember:

For: a A + b B ↔ c C + d D

$$Q = \frac{\Pi\left[product\right]^{n_{product}}}{\Pi\left[reac\tan t\right]^{n_{reactamt}}} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

(s) And (l) contribute [X] = 1.

Practice – Calculate E_{cell} for the reaction at 25°C if all ion concentrations are 0.10 M

$$2IO_3^-(aq) + 12H^+(aq) + 10\ I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$$

Reduction Half-Reaction	**E°_{red}, V**
$F_2(g) + 2e^- \longrightarrow 2\ F^-(aq)$	+2.87
$IO_3^-(aq) + 6\ H^+ + 5e^- \longrightarrow \tfrac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$Ag^+(aq) + 1e^- \longrightarrow Ag(s)$	+0.80
$I_2(s) + 2e^- \longrightarrow 2\ I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Cr^{3+}(aq) + 1e^- \longrightarrow Cr^{2+}(aq)$	−0.50
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37

Practice – Calculate E_{cell} for the reaction at 25°C if all ion concentrations are 0.10 M

$$2IO_3^-(aq) + 12H^+(aq) + 10\,I^-(aq) \rightarrow 6I_2(s) + 6H_2O(l)$$

Reduction Half-Reaction	$E°_{red}$, V
$IO_3^-(aq) + 6\,H^+ + 5e^- \rightarrow ½I_2(s) + 3H_2O(l)$	+1.20
$I_2(s) + 2e^- \rightarrow 2\,I^-(aq)$	+0.54
As an oxidation: $2\,I^-(aq) \rightarrow I_2(s) + 2e^-$	-0.54

The reaction transfers 10 electrons overall (shown earlier in the notes).

Recall: The above tables summarizes E° values, **for STANDARD CONDITIONS:** 1.0 M for each ionic species

Practice – Calculate E_{cell} at 25 °C for the reaction $2\,IO_3^-(aq)+12\,H^+(aq)+10\,I^-(aq) \rightarrow 6\,I_2(s) + 6\,H_2O(l)$ if all ion concentrations are 0.10 M.

Given:	$2\,IO_3^-(aq)+12\,H^+(aq)+10\,I^-(aq) \rightarrow 6\,I_2(s) + 6\,H_2O(l)$ $[H^+] = 0.10$ M, $[IO_3^-] = 0.10$ M, $[I^-] = 0.10$ M
Find:	E_{cell}
Conceptual Plan: **Relationships:**	$E°_{ox}, E°_{red} \rightarrow E°_{cell} \rightarrow E_{cell}$ $E°_{cell} = E°_{ox} + E°_{red}$ $\quad E_{cell} = E°_{cell} - \frac{0.0592\text{ V}}{n}\log Q$
Solve:	
Check:	units are correct, $E_{cell} < E°_{cell}$ as expected because all the ions are reactants and < 1M

Calculating Equilibrium Constants (K_c)

Recall: equilibrium was no net direction for a reaction.

For redox process, this means no net electron transfer, thus $E_{cell} = 0 = (-\Delta G/nF)$

For a cell **at equilibrium Q = K** and **E_{cell} must be 0,** so the **Nernst Equation becomes:**

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log Q \longrightarrow 0 = E^o_{cell} - \frac{0.0592}{n}\log K$$

and

$$E^o_{cell} = \frac{0.0592}{n}\log K_c \quad \text{or} \quad K_c = 10^{\left(\frac{nE^o_{cell}}{0.0592}\right)}$$

Things You Can Do With Nernst

Calculate E_{cell}

- knowing E^o_{cell}, predict E_{cell} under any conditions
- use the equilibrium constant for a reaction, and determine E_{cell}

Calculate K_c

- determine standard E, relate to K

Calculate a concentration (*eg* [H^+])

- this is how a pH meter works!

Three methods to determine equilibrium constants:

1. *K* from **concentration** data: $$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

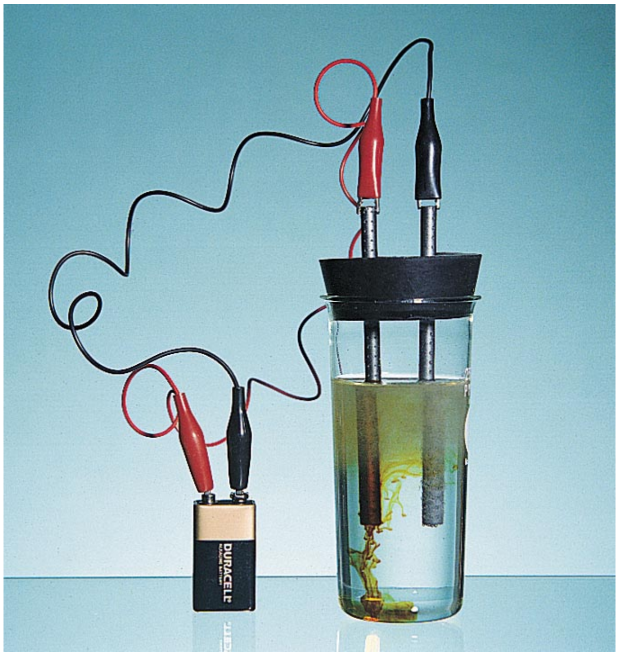
2. *K* from **thermochemical** data: $$\ln K = \frac{-\Delta G°}{RT}$$

3. *K* from **electrochemical** data: $$E° = \frac{RT}{nF} \ln K$$

or

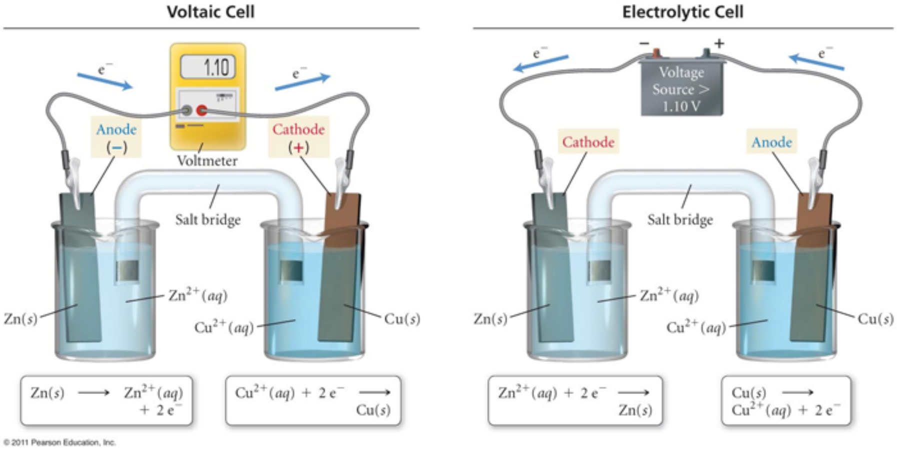
$$\ln K = \frac{nFE°}{RT}$$

Using Electricity in Redox Reactions



Electrons force their own way through…

Electrons are forced through…



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Electrolysis

We can use electricity from a battery (power supply) to FORCE a chemical reaction using **“electrolysis”**

Electrolysis is done in an electrolytic cell

Electrolytic cells are often used to separate elements from within their compounds

e.g. $2\ H_2O \rightarrow 2\ H_2 + O_2$

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Electrolytic Cells

The source of energy is a battery or DC power supply

The **+ terminal of the source** is attached **to the anode**

The **– terminal of the source** is attached **to the cathode**

Any processes with $E_{rxn} < E_{battery}$ can be forced to occur using the high energy of the electrons, supplied by the battery.

Electrolysis

Electrolysis uses electrical energy to overcome the energy barrier of a non-spontaneous reaction, forcing it to occur

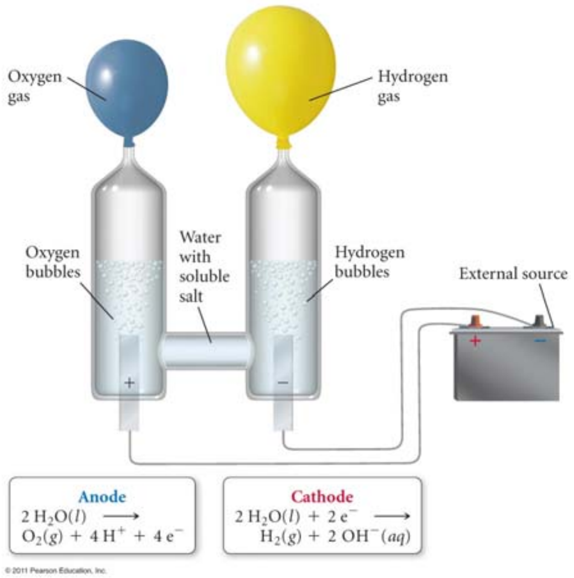
$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ spontaneous

$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ electrolysis

Often, electrolysis is use for: purification, element separation from compounds, controlled forcing of a reaction

Industrially and Biochemically significant!

Electrolysis of Water



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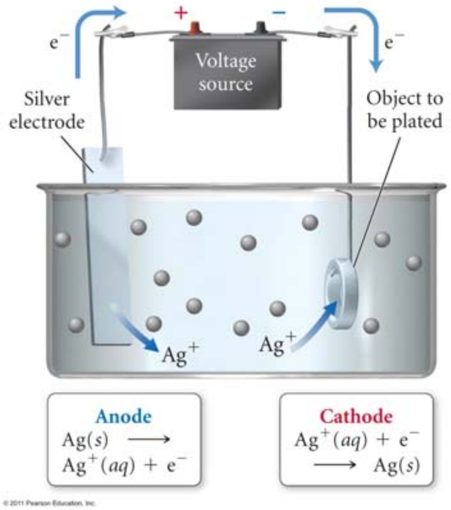
Electroplating

In electroplating, the work piece is the cathode

Cations are reduced at cathode and plate to the surface of the work piece

The anode is made of the plate metal. The anode oxidizes and replaces the metal cations in the solution.



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Mixtures of Ions

When several cations are present, the easiest cation to reduce will be selectively plated out at the cathode

1st to plate out is least negative or **most positive $E°_{red}$**

When several anions are, the anion that is easiest to oxidize will be selectively oxidized at the anode

1st to oxidize is least negative or most positive $E°_{ox}$

1st to oxidize is most negative or least positive $E°_{red}$

Example: Predict the half-reaction occurring at the anode and cathode for the electrolysis of a mixture of molten $AlBr_{3(l)}$ and $MgBr_{2(l)}$

in the electrolysis of a molten salt, the anion is oxidized and the cation is reduced	ox: $2\,Br^-_{(l)} \rightarrow Br_{2\,(g)} + 2\,e^-$ red: $Al^{3+}_{(aq)} + 3\,e^- \rightarrow Al_{(s)}$ $Mg^{2+}_{(aq)} + 2\,e^- \rightarrow Mg_{(s)}$
use the values of $E°$ of the half-reactions as a guide to determine which half-reaction is easiest	
oxidation occurs at the anode and reduction at the cathode	

Stoichiometry of Electrolysis

In an electrolytic cell, **the amount (moles) of product made is related to the number of electrons transferred**

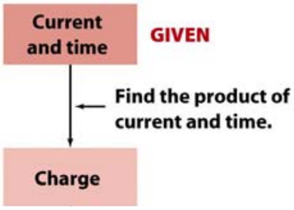
- the electrons are a reactant, we can use stoichiometry

The **number of moles of electrons** that flow through the electrolytic cell **depends on the current (I, A) and length of time (t, s)**

1 Amp = 1 Coulomb of charge/second

1 mole of e^- = 96,485 Coulombs of charge (Faraday's constant)

Quantitative Aspects of Electrolysis



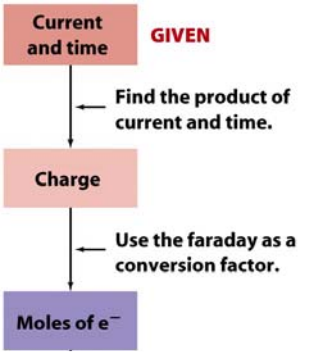
How many kilos of Al(l) can be produced in 8.00 h with a constant current of 1.00×10^5 A through a mixture of aluminum oxide and cryolite?

Charge(C) = Current(A) x Time(s)

$= (1.00 \times 10^5 \text{ C/s}) \times 8.00 \text{ h} \times 3600 \text{ s/h}$

$= 2.88 \times 10^9$ C

Quantitative Aspects of Electrolysis



Current and time GIVEN

Find the product of current and time.

Charge

Use the faraday as a conversion factor.

Moles of e⁻

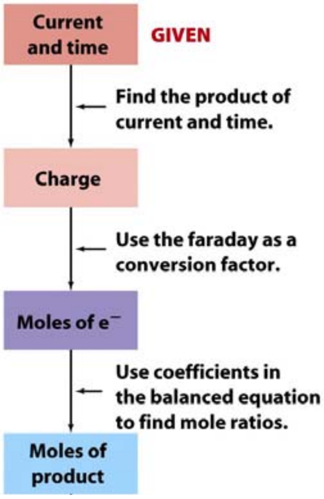
How many kilos of Al(l) can be produced in 8.00 h with a constant current of 1.00×10^5 A through a mixture of aluminum oxide and cryolite?

$$\text{Moles of } e^- = \text{Charge(A)} \times \frac{1 \text{ mol } e^-}{96{,}500 \text{ C}}$$

$$= 2.88 \times 10^9 \text{ C} \; \frac{1 \text{ mol } e^-}{96{,}500 \text{ C}}$$

$$= 2.98 \times 10^4 \text{ mol } e^-$$

Quantitative Aspects of Electrolysis



Current and time GIVEN

Find the product of current and time.

Charge

Use the faraday as a conversion factor.

Moles of e⁻

Use coefficients in the balanced equation to find mole ratios.

Moles of product

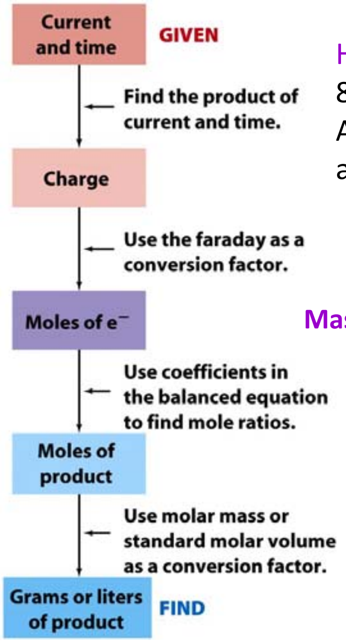
How many kilos of Al(l) can be produced in 8.00 h with a constant current of 1.00×10^5 A through a mixture of aluminum oxide and cryolite?

$$Al^{3+}(l) + 3e- \longrightarrow Al(l)$$

$$\text{Moles of Al(l)} = 2.98 \times 10^4 \text{ mol } e^- \; \frac{1 \text{ mol Al(l)}}{3 \text{ mol } e^-}$$

$$= 9.95 \times 10^3 \text{ mol Al(l)}$$

Quantitative Aspects of Electrolysis



How many kilos of Al(l) can be produced in 8.00 h with a constant current of 1.00×10^5 A through a mixture of aluminum oxide and cryolite?

$$\textbf{Mass of Al(l)} = 9.95 \times 10^3 \text{ mol Al(l)} \quad \frac{27.0 \text{ g}}{\text{mol Al(l)}}$$

$$= 2.69 \times 10^5 \text{ g Al(l)}$$

$$\mathbf{= 269 \text{ kg Al(l)}}$$

Example: Calculate the mass of Au that can be plated in 25 min using 5.5 A for the half-reaction $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$

Given:	3 mol e^- : 1 mol Au, current = 5.5 amps, time = 25 min
Find:	mass Au, g
Conceptual Plan:	t(s), amp ⟹ charge (C) ⟹ mol e^- ⟹ mol Au ⟹ g Au
Relationships:	$\frac{5.5 \text{ C}}{1 \text{ s}}$ $\frac{1 \text{ mol } e^-}{96{,}485 \text{ C}}$ $\frac{1 \text{ mol Au}}{3 \text{ mol } e^-}$ $\frac{196.97 \text{ g}}{1 \text{ mol Au}}$
Solve:	
Check:	units are correct, answer is reasonable because 10 A running for 1 hr ~ 1/3 mol e^-

Practice – Calculate the amperage required to plate 2.5 g of Au in 1 hour (3600 sec)
$Au^{3+}(aq) + 3\ e^{-} \rightarrow Au(s)$

Given:	3 mol e^{-} : 1 mol Au, mass = 2.5 g, time = 3600 s
Find:	current, A
Conceptual Plan:	g Au ⇒ mol Au ⇒ mol e^{-} ⇒ charge ⇒ amps
Relationships:	$\frac{1\text{ mol Au}}{196.97\text{ g}}$ $\frac{3\text{ mol }e^{-}}{1\text{ mol Au}}$ $\frac{96{,}485\text{ C}}{1\text{ mol }e^{-}}$ $\text{amps} = \frac{\text{Coulombs}}{\text{seconds}}$
Solve:	
Check:	units are correct, answer is reasonable because 10 A running for 1 hr ~ 1/3 mol e^{-}