Electrochemistry

- Electrochemistry deals with the relationship between chemical change and electricity

- **Electrochemical cells** (two types)
  - **Galvanic cells** – use a spontaneous ($\Delta G < 0$) reaction to produce electricity (batteries)
  - **Electrolytic cells** – use a source of electricity to drive a non-spontaneous ($\Delta G > 0$) reaction (electrolysis)
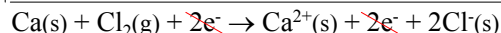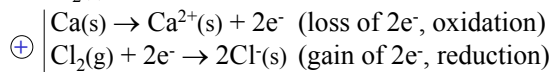
21.1 Redox Half-Reactions

- Redox reactions involve e^- transfer
  - **Oxidation** – loss of e^- (oxidation state $\uparrow$)
  - **Reduction** – gain of e^- (oxidation state $\downarrow$)

- **Half-reactions** – focus on oxidation and reduction separately

Example: $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$

$\rightarrow CaCl_2(s)$ consists of Ca^{2+} and Cl^- ions

$\oplus \left| \begin{array}{l} Ca(s) \rightarrow Ca^{2+}(s) + 2e^- \text{ (loss of 2e}^-\text{, oxidation)} \\ Cl_2(g) + 2e^- \rightarrow 2Cl^-(s) \text{ (gain of 2e}^-\text{, reduction)} \end{array} \right.$

$Ca(s) + Cl_2(g) + 2e^- \rightarrow Ca^{2+}(s) + 2e^- + 2Cl^-(s)$

$\rightarrow$ Adding the half-reactions gives the overall reaction
  - $\rightarrow$ Ca is oxidized (Ca is the reducing agent)
  - $\rightarrow Cl_2$ is reduced (Cl_2 is the oxidizing agent)

➤ Generalized expressions for half reactions:
  - ➤ **Red $\rightarrow$ Ox + ne^-** or **Ox + $ne^- \rightarrow$ Red**
  - ➤ **Ox/Red** form a **redox couple** (Ex: Ca^{2+}/Ca; Cl_2/Cl^-)

Balancing Redox Reactions

- **Half-reaction method** – divides the overall reaction into two half-reactions

- **Balancing in acidic solutions**
  1. Identify the redox couples and write the half-reactions
  2. Balance each half-reaction separately:
     - ➤ 1st, balance all elements other than O and H
     - ➤ 2nd, balance **O** by adding **H_2O**
     - ➤ 3rd, balance **H** by adding **H^+**
     - ➤ 4th, balance the **charge** by adding **e^-**
  3. Multiply the half-reactions by integers to equal the # of e^- in them
  4. Add the half-reactions and cancel the e^-

Example: Balance the following skeleton equation in acidic solution: $V^{3+} + Ce^{4+} \rightarrow VO_2^+ + Ce^{3+}$

1. Redox couples: VO_2^+/V^{3+} and Ce^{4+}/Ce^{3+}
   Half-reactions: $V^{3+} \rightarrow VO_2^+$ and $Ce^{4+} \rightarrow Ce^{3+}$

2. $V^{3+} \rightarrow VO_2^+$ (V is balanced)
   $V^{3+} + 2H_2O \rightarrow VO_2^+$ (balance O)
   $V^{3+} + 2H_2O \rightarrow VO_2^+ + 4H^+$ (balance H)
   $\rightarrow V^{3+} + 2H_2O \rightarrow VO_2^+ + 4H^+ + 2e^-$ (balance charge)

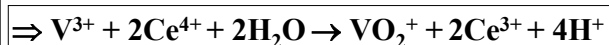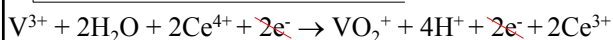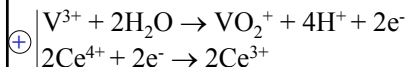 $Ce^{4+} \rightarrow Ce^{3+}$ (Ce, O and H are balanced)
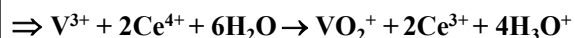 $\rightarrow Ce^{4+} + 1e^- \rightarrow Ce^{3+}$ (balance charge)

3. Multiply the 2nd half-reaction by 2 to get $2e^-$
   $2Ce^{4+} + 2e^- \rightarrow 2Ce^{3+}$

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4. Add the half-reactions

$\oplus \left| \begin{array}{l} V^{3+} + 2H_2O \rightarrow VO_2^+ + 4H^+ + 2e^- \\ 2Ce^{4+} + 2e^- \rightarrow 2Ce^{3+} \end{array} \right.$

$V^{3+} + 2H_2O + 2Ce^{4+} + 2e^- \rightarrow VO_2^+ + 4H^+ + 2e^- + 2Ce^{3+}$

$\boxed{\Rightarrow V^{3+} + 2Ce^{4+} + 2H_2O \rightarrow VO_2^+ + 2Ce^{3+} + 4H^+}$

Note: If H_3O^+ is required in the equation instead of H^+, add as many water molecules on both sides as the # of H^+ ions

$\Rightarrow V^{3+} + 2Ce^{4+} + 6H_2O \rightarrow VO_2^+ + 2Ce^{3+} + 4H_3O^+$

- **Balancing in basic solutions**
  - The same four steps are used plus a fifth step:
  5. Add OH^- on both sides of the equation in order to neutralize the H^+, and cancel the water molecules if necessary

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Example: Balance the following skeleton equation in basic solution: $CrO_2^- + BrO_4^- \rightarrow CrO_4^{2-} + BrO_3^-$

1. Redox couples: CrO_4^{2-}/CrO_2^- and BrO_4^-/BrO_3^-
   Half-reactions: $CrO_2^- \rightarrow CrO_4^{2-}$ and $BrO_4^- \rightarrow BrO_3^-$

2. $CrO_2^- \rightarrow CrO_4^{2-}$ (Cr is balanced)
   $CrO_2^- + 2H_2O \rightarrow CrO_4^{2-}$ (balance O)
   $CrO_2^- + 2H_2O \rightarrow CrO_4^{2-} + 4H^+$ (balance H)
   $\rightarrow CrO_2^- + 2H_2O \rightarrow CrO_4^{2-} + 4H^+ + 3e^-$ (balance charge)

   $BrO_4^- \rightarrow BrO_3^-$ (Br is balanced)
   $BrO_4^- \rightarrow BrO_3^- + H_2O$ (balance O)
   $BrO_4^- + 2H^+ \rightarrow BrO_3^- + H_2O$ (balance H)
   $\rightarrow BrO_4^- + 2H^+ + 2e^- \rightarrow BrO_3^- + H_2O$ (balance charge)

3. Multiply the 1st half-reaction by 2 and the 2nd by 3 to get 6e$^-$ in both half-reactions

$\oplus$ $\begin{array}{l} 2CrO_2^- + 4H_2O \rightarrow 2CrO_4^{2-} + 8H^+ + 6e^- \\ 3BrO_4^- + 6H^+ + 6e^- \rightarrow 3BrO_3^- + 3H_2O \end{array}$

4. Add the half-reactions

$2CrO_2^- + 4H_2O + 3BrO_4^- + 6H^+ + 6e^- \rightarrow$
$\rightarrow 2CrO_4^{2-} + 8H^+ + 6e^- + 3BrO_3^- + 3H_2O$

$\Rightarrow \mathbf{2CrO_2^- + 3BrO_4^- + H_2O \rightarrow 2CrO_4^{2-} + 3BrO_3^- + 2H^+}$

5. Add 2OH$^-$ on both sides of the equation

$2CrO_2^- + 3BrO_4^- + H_2O + 2OH^- \rightarrow$ $\overbrace{}^{2H_2O}$
$\rightarrow 2CrO_4^{2-} + 3BrO_3^- + 2H^+ + 2OH^-$

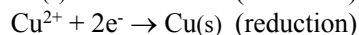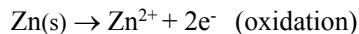$\boxed{\mathbf{2CrO_2^- + 3BrO_4^- + 2OH^- \rightarrow 2CrO_4^{2-} + 3BrO_3^- + H_2O}}$
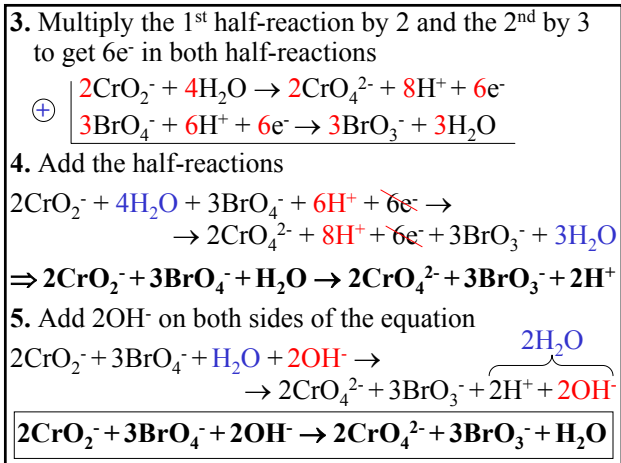
21.2 Galvanic (Voltaic) Cells

- Produce electricity from a spontaneous chemical reaction

  Example: Zn metal reacts spontaneously with Cu^{2+} solutions to yield metallic Cu and Zn^{2+} ions

  $Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$ (SO_4^{2-} counter ions)

  $\rightarrow$ The two half-reactions are:

  $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$ (oxidation)

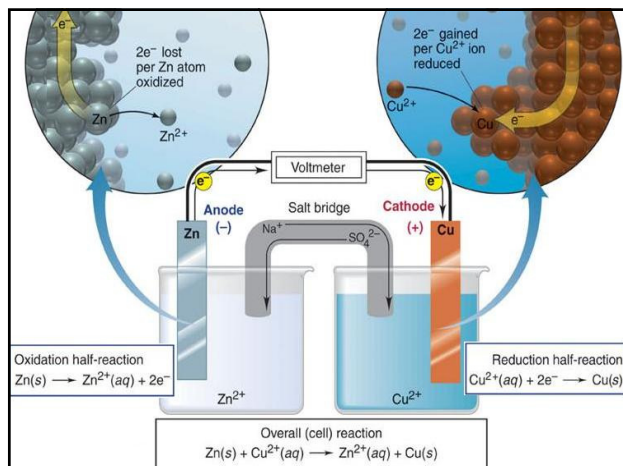 $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ (reduction)
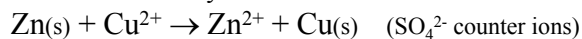
  $\rightarrow$ The two half-reactions can be **physically separated** by placing them in separate containers (half-cells)

  $\rightarrow$ **Half-cells** $\rightarrow$ where the half-reactions occur

  $\rightarrow$ **Anode** half-cell $\rightarrow$ where **oxidation** occurs

  $\rightarrow$ **Cathode** half-cell $\rightarrow$ where **reduction** occurs

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

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

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

- **Electrodes** – in contact with the electrolyte solutions and the external electrical circuit
  - **Anode** (oxidation)
  - **Cathode** (reduction)
  - In voltaic cells, the **anode** is **(-)** and the **cathode** is **(+)**
  - The e$^-$s **flow** from the anode toward the cathode
- **Salt bridge** – completes the electrical circuit and maintains electrical neutrality of the half-cells (porous material soaked in a concentrated electrolyte solution)
  - **Anions** in the salt bridge flow toward the **anode**
  - **Cations** in the salt bridge flow toward the **cathode**
- By convention, the **anode half-cell** appears on the **left**

Galvanic Cell Notation

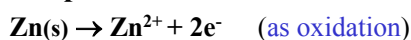- **Half-cell notation**
  - Different phases are separated by vertical lines
  - Species in the same phase are separated by commas
- **Types of electrodes**
  - ➢ **Active** electrodes – involved in the electrode half-reaction (most metal electrodes)

  Example: Zn^{2+}/Zn metal electrode

  $\mathbf{Zn_{(s)} \rightarrow Zn^{2+} + 2e^-}$ (as oxidation)
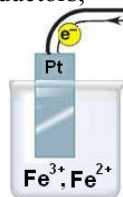
  Notation: $\mathbf{Zn_{(s)} | Zn^{2+}}$

➢ **Inactive (inert) electrodes** – not involved in the electrode half-reaction (inert solid conductors; serve as a contact between the solution and the external el. circuit)

Example: Pt electrode in Fe^{3+}/Fe^{2+} soln.
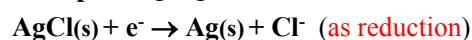
$\mathbf{Fe^{3+} + e^- \rightarrow Fe^{2+}}$ (as reduction)

Notation: $\mathbf{Fe^{3+}, Fe^{2+} | Pt_{(s)}}$

➢ Electrodes involving **metals** and their **slightly soluble salts**
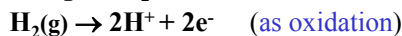
Example: Ag/AgCl electrode

$\mathbf{AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-}$ (as reduction)

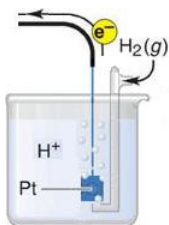Notation: $\mathbf{Cl^- | AgCl_{(s)} | Ag_{(s)}}$
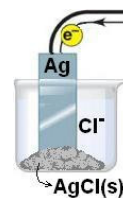
> Electrodes involving **gases** – a gas is bubbled over an inert electrode
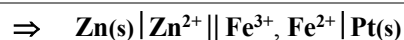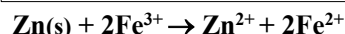
Example: H_2 gas over Pt electrode

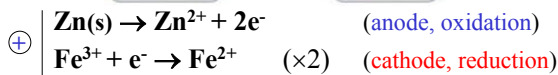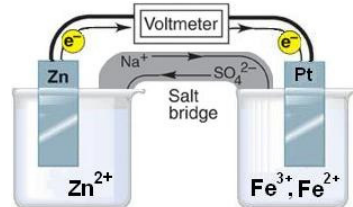$H_2(g) \rightarrow 2H^+ + 2e^-$ (as oxidation)

Notation: $Pt(s)|H_2(g)|H^+$

- **Cell notation**
  - The anode half-cell is written on the left of the cathode half-cell
  - The electrodes appear on the far left (anode) and far right (cathode) of the notation
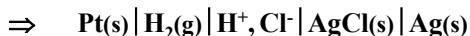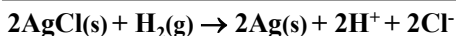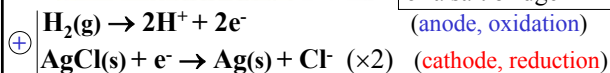 - Salt bridges are represented by double vertical lines

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Example: A combination of the $Zn(s)|Zn^{2+}$ and $Fe^{3+}, Fe^{2+}|Pt(s)$ half-cells leads to:

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

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (×2)   (cathode, reduction)

$Zn(s) + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+}$

$\Rightarrow$ $Zn(s)|Zn^{2+}||Fe^{3+}, Fe^{2+}|Pt(s)$

Example: A combination of the $Pt(s)|H_2(g)|H^+$ and $Cl^-|AgCl(s)|Ag(s)$ half-cells leads to:
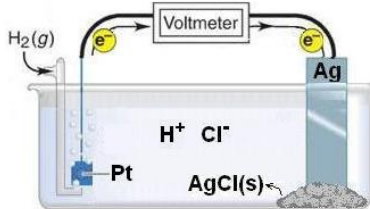
Note: The reactants in the overall reaction are in different phases (no physical contact) $\Rightarrow$ no need of a salt bridge

$H_2(g) \rightarrow 2H^+ + 2e^-$ (anode, oxidation)

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ (×2)   (cathode, reduction)

$2AgCl(s) + H_2(g) \rightarrow 2Ag(s) + 2H^+ + 2Cl^-$

$\Rightarrow$ $Pt(s)|H_2(g)|H^+, Cl^-|AgCl(s)|Ag(s)$
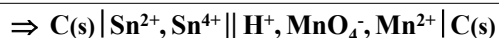

Example: Write the cell reaction and the cell notation for a cell consisting of a graphite cathode immersed in an acidic solution of MnO_4^- and Mn^{2+} and a graphite anode immersed in a solution of Sn^{4+} and Sn^{2+}.

→ Write the half reactions (a list of the most common half-reactions is given in **Appendix D**)

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ ×5 (oxidation)

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O(l)$ ×2 (reduction)

$5Sn^{2+} + 2MnO_4^- + 16H^+ + \cancel{10e^-} \rightarrow 5Sn^{4+} + \cancel{10e^-} +$
$+ 2Mn^{2+} + 8H_2O(l)$
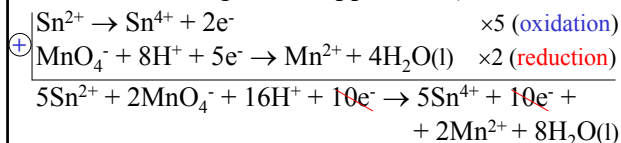
→ The graphite (C) electrodes are inactive

$\Rightarrow C(s)|Sn^{2+}, Sn^{4+}||H^+, MnO_4^-, Mn^{2+}|C(s)$

Why Do Galvanic Cells Work?

- Consider a cell made of two active metal electrodes, M_1 and M_2, and their ions.
  - If the cell circuit is open, the two metals are in equilibrium with their ions
  1) $M_1 \leftrightarrow M_1^+ + e^-$ 2) $M_2 \leftrightarrow M_2^+ + e^-$
  - The produced electrons accumulate in the metal electrodes and produce **electrical potentials**
  - If M_1 has a greater tendency to give out its electrons, the 1st equilibrium is shifted further to the right and the potential of M_1 is more negative
  - When the circuit is closed, electrons flow from the more negative M_1 (anode) toward the less negative M_2 (cathode)

21.3 Cell Potentials

- **Electromotive force (*emf*)** – drives the electrons in the el. circuit
  - *emf* is the difference between the electrical potentials of the two electrodes (voltage)
- **Cell potential (E_{cell})** $\rightarrow E_{cell} = emf$
  - Units $\rightarrow$ volts (V) $\rightarrow$ (1 V = 1 J/C since the electrical work is equal to the applied voltage times the charge moving between the electrodes)
- **Standard cell potential (E^o_{cell})** – the cell potential at standard-state conditions (gases $\rightarrow$ 1 atm, solutions $\rightarrow$ 1 M, liquids & solids $\rightarrow$ pure)

- E_{cell} is measured with a voltmeter
  - If the (+) terminal of the voltmeter is connected to the (+) electrode (cathode), the voltmeter shows a positive reading
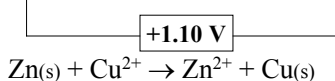- E_{cell} characterizes the overall cell reaction
  - If $E_{cell} > 0$, the cell reaction is spontaneous
  - If $E_{cell} < 0$, the cell reaction is non-spontaneous
  - If $E_{cell} = 0$, the cell reaction is at equilibrium

Example: $Zn(s) | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s)$

$$+1.10\ V$$

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

$E^o_{cell} = 1.10\ V > 0 \rightarrow$ spontaneous reaction

- **Electrode potentials** (E) – characterize the individual electrodes (half-reactions)
  - The cell potential is the difference between the electrode potentials of the cathode and anode

$$E_{cell} = E_{cathode} - E_{anode}$$

- **Standard electrode potentials** (E^o) – electrode potentials at the standard-state

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

  - E^o values are reported for the half-reaction written as reduction (**standard reduction potentials**) $\rightarrow$ listed in **Appendix D**

- Absolute values for E and E^o can't be measured
  - $\Rightarrow$ A **reference electrode** (half-cell) is needed
    - The potentials of all electrodes are measured relative to the reference electrode
- **Standard hydrogen electrode** – used as a reference electrode $\rightarrow E^o_{ref} = 0\ V$ (assumed)

$$H^+(1M) | H_2(g,\ 1atm) | Pt(s)$$

$$2H^+(1M) + 2e^- \rightarrow H_2(g,\ 1atm)$$
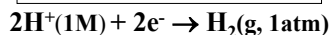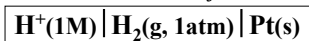
  - To find the potential of any electrode, a cell is constructed between the unknown electrode and the reference electrode
  - The cell potential is directly related to the unknown electrode potential

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  - If the unknown electrode is the cathode of the cell
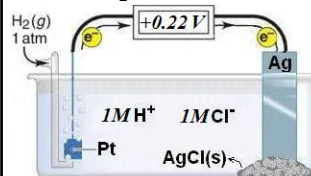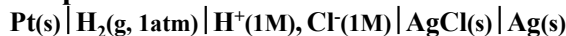$\rightarrow E^o_{cell} = E^o_{unkn} - E^o_{ref}$
$\rightarrow E^o_{unkn} = E^o_{cell} + E^o_{ref} = E^o_{cell} + 0 = E^o_{cell} > 0$
  - If the unknown electrode is the anode of the cell
$\rightarrow E^o_{cell} = E^o_{ref} - E^o_{unkn}$
$\rightarrow E^o_{unkn} = E^o_{ref} - E^o_{cell} = 0 - E^o_{cell} = -E^o_{cell} < 0$

Example:
$Pt(s) | H_2(g,\ 1atm) | H^+(1M),\ Cl^-(1M) | AgCl(s) | Ag(s)$

$H^+/H_2 \rightarrow$ anode
$Ag/AgCl \rightarrow$ cathode
$E^o_{cell} = E^o_{Ag/AgCl} - E_{ref}$
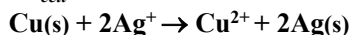$\qquad = E^o_{Ag/AgCl}$
$E^o_{Ag/AgCl} = +0.22\ V$

Determination of Electrode Potentials
- Electrode potentials can be determined by measurements versus the standard H-electrode or other electrodes with known potentials

Example: $E^o_{cell} = +0.46\ V$ for the reaction:
$$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)$$
If $E^o = +0.34\ V$ for the Cu^{2+}/Cu redox couple, what is E^o for the Ag^+/Ag redox couple?
$\rightarrow$ Split into half-reactions:
$Cu(s) \rightarrow Cu^{2+} + 2e^-$ $\qquad E^o_{Cu} = +0.34\ V$ (anode, ox)
$Ag^+ + e^- \rightarrow Ag(s)$ $\qquad E^o_{Ag} = ???\ V$ (cathode, red)
$E^o_{cell} = E^o_{Ag} - E^o_{Cu} = E^o_{Ag} - (+0.34) = +0.46$
$\qquad \Rightarrow E^o_{Ag} = +0.46 + (+0.34) = $ **+0.80 V**

Using Cell Potentials in Calculations
- Cell potentials are **additive**
  - If two reactions are added, their potentials are added too
- Cell potentials are **intensive properties** – remain independent of the system size
  - If a reaction (or a half-reaction) is multiplied by a number, its potential remains the same

Example:
$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)$ ($\times 3$) $\quad E^o_{cell} = +0.46\ V$
$3Ag(s) + Au^{3+} \rightarrow 3Ag^+ + Au(s)$ ($\times 2$) $\quad E^o_{cell} = +0.70\ V$

$3Cu(s) + 2Au^{3+} \rightarrow 3Cu^{2+} + 2Au(s)$
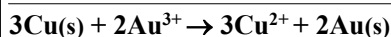
$\qquad\qquad\qquad E^o_{cell} = +0.46 + 0.70 = $ **+1.16 V**

Strengths of Oxidizing and Reducing Agents

- E^o values are always tabulated for **reduction**

$$Ox + ne^- \rightarrow Red \qquad (E^o)$$

  - **Ox** is an oxidizing agent; **Red** is a reducing agent
- E^o is a measure for the tendency of the half-reaction to undergo reduction
$\Rightarrow$ **Higher** (more positive) E^o means
  - Greater tendency for reduction
  - Lower tendency for oxidation
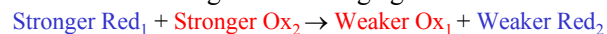$\Rightarrow$ **Higher** (more positive) E^o means
  - **Stronger oxidizing agent** (Ox) $\leftarrow$ Ox is reduced
  - **Weaker reducing agent** (Red) $\leftarrow$ Red is oxidized

---

- **Electrochemical series** – an arrangement of the redox couples in order of decreasing reduction potentials (E^o) $\rightarrow$ Appendix D
  - The most positive E^os are at the top of the table
  - The most negative E^os are at the bottom of the table
$\Rightarrow$ The **strongest oxidizing agents** (Ox) are **at the top** of the table **as reactants**
$\Rightarrow$ The **strongest reducing agents** (Red) are **at the bottom** of the table **as products**
- Every redox reaction is a sum of two half-reactions, one occurring as oxidation and another as reduction
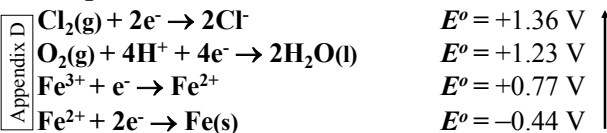
$$Red_1 \rightarrow Ox_1 + ne^- \qquad Ox_2 + ne^- \rightarrow Red_2$$
$$Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$$

- In a **spontaneous redox reaction**, the stronger oxidizing and reducing agents react to produce the weaker oxidizing and reducing agents

Stronger Red_1 + Stronger $Ox_2 \rightarrow$ Weaker Ox_1 + Weaker Red_2

Example: Given the following half-reactions:

$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	$E^o = +1.36$ V
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$	$E^o = +1.23$ V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$E^o = +0.77$ V
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	$E^o = -0.44$ V

(Appendix D)

a) Rank the oxidizing and reducing agents by strength
$\rightarrow$ Ox agents on the left; Red agents on the right
Oxidizing $\rightarrow$ (Top) $Cl_2 > O_2 > Fe^{3+} > Fe^{2+}$ (Bottom)
Reducing $\rightarrow$ (Bottom) $Fe > Fe^{2+} > H_2O > Cl^-$ (Top)

---

b) Can Cl_2 oxidize H_2O to O_2 in acidic solution?
$\rightarrow Cl_2/Cl^-$ has higher E^o (Cl_2/Cl^- is above $O_2, H^+/H_2O$)
$\Rightarrow Cl_2$ is a stronger oxidizing agent than O_2
$\Rightarrow Cl_2$ can oxidize H_2O to O_2 at standard conditions

c) Write the spontaneous reaction between the Cl_2/Cl^- and Fe^{3+}/Fe^{2+} redox couples and calculate its E^o_{cell}
$\rightarrow Cl_2/Cl^-$ has the higher reduction potential (E^o)
$\Rightarrow Cl_2/Cl^-$ undergoes **reduction**
$\Rightarrow Fe^{3+}/Fe^{2+}$ undergoes **oxidation** (reverse equation)

$\oplus$
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ (reduction) $E^o = +1.36$ V
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ ×2 (oxidation) $E^o = +0.77$ V
$Cl_2(g) + 2e^- + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+} + 2e^-$
$E^o_{cell} = E^o_{cath} - E^o_{anod} = +1.36 - (+0.77) = $ **+0.59 V**

---

d) Is the reaction of disproportionation (simultaneous oxidation and reduction) of Fe^{2+} to Fe^{3+} and $Fe(s)$ spontaneous at standard conditions?
$\rightarrow$ Need the sign of E^o_{cell}
$\Rightarrow Fe^{2+}/Fe(s)$ undergoes **reduction**
$\Rightarrow Fe^{3+}/Fe^{2+}$ undergoes **oxidation** (reverse equation)
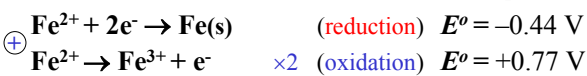
$\oplus$
$Fe^{2+} + 2e^- \rightarrow Fe(s)$ (reduction) $E^o = -0.44$ V
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ ×2 (oxidation) $E^o = +0.77$ V
$3Fe^{2+} + 2e^- \rightarrow Fe(s) + 2Fe^{3+} + 2e^-$
$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.44 - (+0.77) = $ **−1.21 V**
$\Rightarrow E^o_{cell} < 0 \rightarrow$ the reaction is **non-spontaneous** at standard conditions

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Relative Reactivity of Metals

- The **activity series** of metals – ranks metals based on their ability to displace H_2 from acids or water or displace each other's ions in solution
- **Metals that can displace H_2 from acids**
  - The reduction of H^+ from acids to H_2 is given by the standard hydrogen half-reaction

$$2H^+ + 2e^- \rightarrow H_2(g) \qquad E^o = 0 \text{ V}$$

  - In order for this half-reaction to proceed as written, the metal must have lower reduction potential (**the metal must be below H_2/H^+ in Appendix D**)
$\Rightarrow$ If $E^o_{metal} < 0$, the metal **can** displace H_2 from acids
$\Rightarrow$ If $E^o_{metal} > 0$, the metal **cannot** displace H_2

Example: Can **Fe** and **Cu** be dissolved in HCl(aq)?
→ **Fe^{2+}/Fe** is below and **Cu^{2+}/Cu** is above **H_2/H^+**

⊕ $2H^+ + 2e^- \to H_2(g)$ (reduction) $E^o = 0.00$ V
   $Fe(s) \to Fe^{2+} + 2e^-$ (oxidation) $E^o = -0.44$ V
————————————————————————
$2H^+ + 2\not{e^-} + Fe(s) \to H_2(g) + Fe^{2+} + 2\not{e^-}$
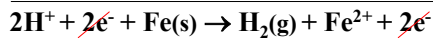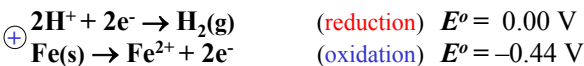
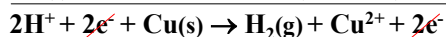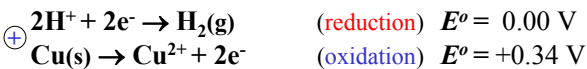$E^o{}_{cell} = E^o{}_{cath} - E^o{}_{anod} = 0.00 - (-0.44) = +\textbf{0.44 V}$
⇒ $E^o{}_{cell} > 0 \to$ spontaneous (Fe dissolves in HCl)

⊕ $2H^+ + 2e^- \to H_2(g)$ (reduction) $E^o = 0.00$ V
   $Cu(s) \to Cu^{2+} + 2e^-$ (oxidation) $E^o = +0.34$ V
————————————————————————
$2H^+ + 2\not{e^-} + Cu(s) \to H_2(g) + Cu^{2+} + 2\not{e^-}$

$E^o{}_{cell} = E^o{}_{cath} - E^o{}_{anod} = 0.00 - (+0.34) = -\textbf{0.34 V}$
⇒ $E^o{}_{cell} < 0 \to$ non-spontaneous (Cu doesn't dissolve)

- **Metals that can displace H_2 from water**
  – The reduction of H_2O to H_2 is given by:
  $$2H_2O(l) + 2e^- \to H_2(g) + 2OH^- \qquad E = -0.42 \text{ V}$$
  – The value of E is for $pH = 7$ (nonstandard state)
⇒ Metals that are **below H_2O/H_2,OH$^-$** in Appendix D can displace H_2 from water at standard conditions
⇒ Metals that have $E^o{}_{metal} < \textbf{-0.42}$ can displace H_2 from water at $pH = 7$
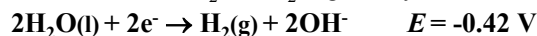
Example: Potassium, **K**, dissolves readily in water
$2H_2O(l) + 2e^- \to H_2(g) + 2OH^-$ (reduction) $E = -0.42$ V
$K(s) \to K^+ + e^-$ ×2   (oxidation) $E^o = -2.93$ V
————————————————————————
$2H_2O(l) + 2\not{e^-} + 2K(s) \to H_2(g) + 2OH^- + 2K^+ + 2\not{e^-}$
$E^o{}_{cell} = -0.42 - (-2.93) = +\textbf{2.51 V} > 0$ **(spontaneous)**

21.4 Free Energy and Electrical Work

Relationship Between E_{cell} and ΔG_r

- **Electrical work (w)**
  $$w = (\text{charge transferred}) \times (\text{voltage})$$
  – $n \to$ # mol e$^-$ transferred
  – $F \to$ charge of 1 mol e$^-$

  (charge transferred) = nF
  (voltage) = E_{cell}

⇒ $w = -nFE_{cell}$ ($w < 0$ since the system does work)
  – ΔG is the maximum work the system can do, so
  $$\Delta G = w_{max}$$
⇒ If the process is carried out reversibly ($w = w_{max}$)

$$\boxed{\Delta G_r = -nFE_{cell} \quad \text{and} \quad \Delta G_r{}^o = -nFE^o{}_{cell}}$$

→ $F = \textbf{96485 C/mol} \to$ **Faraday constant**

– ΔG_r, $\Delta G_r{}^o$, E_{cell}, and $E^o{}_{cell}$ are all dependent on T (superscripts, T, are omitted for simplicity)
  – ΔG_r, $\Delta G_r{}^o$ are **extensive** properties
  – E_{cell}, $E^o{}_{cell}$, E, and E^o are **intensive** properties
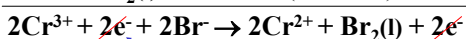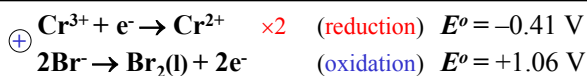⇒ If a redox equation is multiplied by a number, ΔG is also multiplied, but E is not

Example: Using E^o values from appendix D, calculate $\Delta G_r{}^o$ at 298 K for the reaction:
$$2Cr^{3+} + 2Br^- \to 2Cr^{2+} + Br_2(l)$$
→ Find the redox couples in Appendix D (298 K):
$Cr^{3+} + e^- \to Cr^{2+}$ $E^o = -0.41$ V
$Br_2(l) + 2e^- \to 2Br^-$ $E^o = +1.06$ V
→ Invert the 2nd half-reaction to match the overall eq.
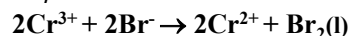
⊕ $Cr^{3+} + e^- \to Cr^{2+}$ ×2   (reduction) $E^o = -0.41$ V
   $2Br^- \to Br_2(l) + 2e^-$ (oxidation) $E^o = +1.06$ V
————————————————————————
$2Cr^{3+} + 2\not{e^-} + 2Br^- \to 2Cr^{2+} + Br_2(l) + 2\not{e^-}$
→ Calculate $E^o{}_{cell}$
$E^o{}_{cell} = E^o{}_{cath} - E^o{}_{anod} = -0.41 - (+1.06) = -\textbf{1.47 V}$
→ Calculate $\Delta G_r{}^o$ ($n = 2 \to$ # mol e$^-$ in overall eq.)
$\Delta G_r{}^o = -nFE^o{}_{cell} = -(2 \text{ mol}) \times (96485 \text{ C/mol}) \times (-1.47 \text{ V})$
$\Delta G_r{}^o = 2.84 \times 10^5$ C·V $= 2.84 \times 10^5$ J $= \boxed{+\textbf{284 kJ}}$
⇒ $\Delta G_r{}^o > 0$ and $E^o{}_{cell} < 0 \to$ the reaction is **non-spontaneous** at standard conditions
⇒ The reverse reaction is **spontaneous** at standard conditions

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Relationship Between $E^o{}_{cell}$ and K

- From $\Delta G_r{}^o = -nFE^o{}_{cell}$ and $\Delta G_r{}^o = -RT \ln K$
  $\to -nFE^o{}_{cell} = -RT \ln K$

$$\boxed{\Rightarrow \quad E^o{}_{cell} = \frac{RT}{nF} \ln K} \qquad K = e^{\frac{nFE^o{}_{cell}}{RT}}$$

→ At 298 K, $RT/F = 0.0257$ V

$$\boxed{\Rightarrow \quad E^o{}_{cell} = \frac{0.0257}{n} \ln K} \qquad K = e^{\frac{nE^o{}_{cell}}{0.0257}}$$

→ $\ln K = 2.303 \times \log K$ and $0.0257 \times 2.303 = 0.0592$

$$\boxed{\Rightarrow \quad E^o{}_{cell} = \frac{0.0592}{n} \log K} \qquad K = 10^{\frac{nE^o{}_{cell}}{0.0592}}$$

Example: Using E^o values from appendix D, calculate K at 298 K for the reaction:

$$2Cr^{2+} + Br_2(l) \rightarrow 2Cr^{3+} + 2Br^-$$
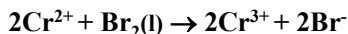
→ This is the reverse of the reaction in the previous example ($E^o_{cell} = -1.47$ V from previous example)

→ $E_{reverse} = -E_{forward}$

⇒ $E^o_{cell} = -(-1.47 \text{ V}) = +1.47$ V and $n = 2$

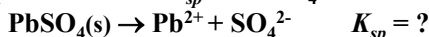$$\Rightarrow K = e^{\frac{nE^o_{cell}}{0.0257}} = e^{\frac{2 \times 1.47}{0.0257}} = 4.8 \times 10^{49}$$

→ $E^o_{cell} > 0$ → the reaction is **spontaneous** at standard conditions

→ $K \gg 1$ → the products are favored at equilibrium

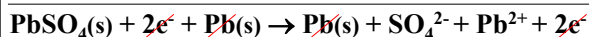
Interrelationship between ΔG_r^o, E^o_{cell}, and K

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
<0	>1	>0	Spontaneous
0	1	0	At equilibrium
>0	<1	<0	Nonspontaneous

$$\Delta G^0 = -nFE^0_{cell}$$
$$\Delta G^0 = -RT \ln K$$
$$E^0_{cell} = \frac{RT}{nF} \ln K$$
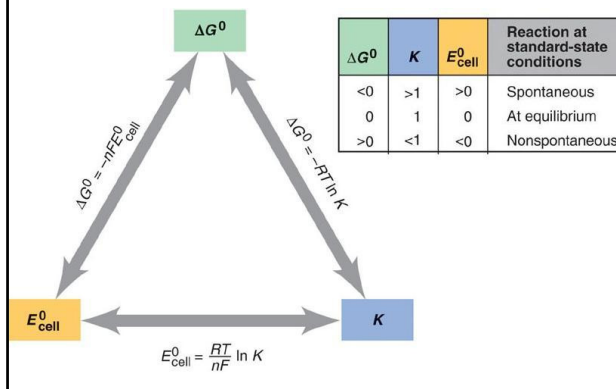
Example: Calculate K_{sp} of $PbSO_4$ at 298 K.
$$PbSO_4(s) \rightarrow Pb^{2+} + SO_4^{2-} \qquad K_{sp} = ?$$

→ Not a redox reaction, but it can be represented as a sum of two redox half-reactions

$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$ (reduction) $E^o = -0.36$ V
$Pb(s) \rightarrow Pb^{2+} + 2e^-$ (oxidation) $E^o = -0.13$ V

$\overline{PbSO_4(s) + 2e^- + Pb(s) \rightarrow Pb(s) + SO_4^{2-} + Pb^{2+} + 2e^-}$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.36 - (-0.13) = -0.23$ V

$$\Rightarrow K_{sp} = e^{\frac{nE^o_{cell}}{0.0257}} = e^{\frac{2 \times (-0.23)}{0.0257}} = 1.7 \times 10^{-8}$$

⇒ $E^o_{cell} < 0$ → the dissolution of $PbSO_4$ is non-spontaneous at 298 K ($K_{sp} \ll 1$)

The Effect of Concentration on E_{cell}

• The **Nernst equation** – gives the variation of the cell potential with composition

$$\Delta G_r = \Delta G_r^o + RT \ln Q$$
$$\Delta G_r = -nFE_{cell} \quad \text{and} \quad \Delta G_r^o = -nFE^o_{cell}$$
$$\Rightarrow -nFE_{cell} = -nFE^o_{cell} + RT \ln Q$$

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q}$$

→ **At 298 K**

$$\boxed{E_{cell} = E^o_{cell} - \frac{0.0257}{n} \ln Q} \quad \boxed{E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log Q}$$

• The Nernst equation applies also to half-reactions (E and E^o are used instead of E_{cell} and E^o_{cell})

Example: Calculate the electrode potential of the Cu^{2+}/Cu redox couple at 298 K, if the concentration of Cu^{2+} is 0.025 M.

$$Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad E^o = +0.34 \text{ V}$$
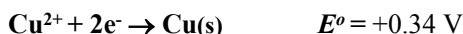
→ Use the Nernst eq. to get E

→ $Q = 1/[Cu^{2+}] = 1/0.025$ and $n = 2$

$$E = E^o - \frac{0.0257}{n} \ln Q = +0.34 - \frac{0.0257}{2} \ln\left(\frac{1}{0.025}\right)$$

$$E = +0.34 - 0.047 = \boxed{0.29 \text{ V}}$$

E_{cell} in Relation to Q and K

➢ From $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$:

⇒ If $Q < 1$ (more reactants), $\ln Q < 0$, and $E_{cell} > E^o_{cell}$

⇒ If $Q > 1$ (more products), $\ln Q > 0$, and $E_{cell} < E^o_{cell}$

⇒ If $Q = 1$ (standard state), $\ln Q = 0$, and $E_{cell} = E^o_{cell}$

➢ Combining $E_{cell} = E^o_{cell} - (RT/nF) \ln Q$ with $E^o_{cell} = (RT/nF) \ln K$ leads to:

→ $E_{cell} = (RT/nF) \ln K - (RT/nF) \ln Q$
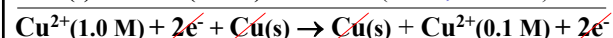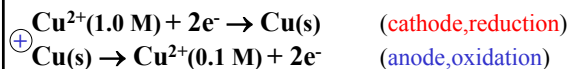
⇒ If $Q < K$, $E_{cell} > 0$ → forward reaction is spontaneous

⇒ If $Q > K$, $E_{cell} < 0$ → reverse reaction is spontaneous

⇒ If $Q = K$, $E_{cell} = 0$ → reaction is at equilibrium

Concentration Cells

- **Concentration cell** – contains the same redox couple in both the anode and cathode half-cells
  - The anode and cathode are the same
    $\Rightarrow E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0$
  - The concentrations of the components are different in the two half-cells $\Rightarrow E_{cell} = 0 - (RT/nF) \ln Q \neq 0$
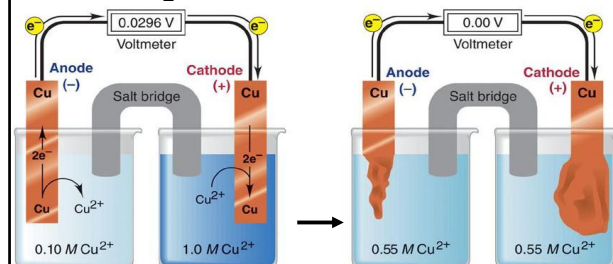
Example: Cu^{2+}/Cu concentration cell ($E^o_{Cu} = 0.34$ V)

⊕ $Cu^{2+}(1.0 \text{ M}) + 2e^- \rightarrow Cu(s)$ (cathode, reduction)

⊖ $Cu(s) \rightarrow Cu^{2+}(0.1 \text{ M}) + 2e^-$ (anode, oxidation)

$Cu^{2+}(1.0 \text{ M}) + 2\cancel{e^-} + \cancel{Cu(s)} \rightarrow \cancel{Cu(s)} + Cu^{2+}(0.1 \text{ M}) + 2\cancel{e^-}$

$E^o_{cell} = E^o_{Cu} - E^o_{Cu} = +0.34 - (+0.34) = \textbf{0 V}$

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n}\log Q = 0 - \frac{0.0592}{2}\log\left(\frac{0.1}{1.0}\right)$$

$$E = 0 - \frac{0.0592}{2}(-1) = 0 + 0.0296 = \textbf{0.0296 V}$$

$\rightarrow$ The cell continues to work until $[Cu^{2+}]$ is equalized in the two half-cells and E_{cell} decreases to zero

---

- **Ion-selective** electrodes – have potentials that are directly related to the concentration of specific ions such as H^+ (pH), K^+, F^-, Cl^-, Br^-, …

  Example: Calculate the *pH* of a solution in which the potential of the $H^+ \mid H_2(g, 1\text{atm}) \mid Pt$ electrode is $E = -0.15$ V.

  $2H^+ + 2e^- \rightarrow H_2(g, 1\text{atm})$ $E^o = 0.00$ V
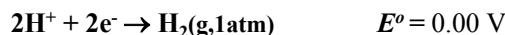
  $$Q = \frac{P_{H_2}}{[H^+]^2} = \frac{1 \text{ atm}}{[H^+]^2} \qquad n = 2$$

  $$E = E^o - \frac{0.0592}{n}\log Q = 0 - \frac{0.0592}{2}\log\left(\frac{1}{[H^+]^2}\right)$$

$$E = -\frac{0.0592}{2}\log\left(\frac{1}{[H^+]^2}\right) = -\frac{0.0592}{2}\log[H^+]^{-2}$$

$$E = -\frac{(-2)\times 0.0592}{2}\log[H^+] = -0.0592\,pH$$

$$\Rightarrow pH = \frac{E}{-0.0592} = \frac{-0.15}{-0.0592} = \textbf{2.5}$$
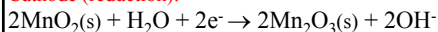
- The potential of an ion-selective electrode is measured by combining it in a cell with a **reference electrode** having a well known and constant electrode potential such as the **calomel** ($Hg/Hg_2Cl_2/Cl^-$) or the $Ag/AgCl/Cl^-$ electrodes
- Optionally, the ion-selective electrode can be operated in a concentration cell with the same electrode immersed in a solution with known concentration as a reference

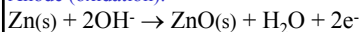---

21.5 Galvanic Cells as Batteries

- **Primary cells** – can't be recharged
  - The battery dies when the reactants are exhausted

Example: The alkaline battery – a dry cell

Cathode (reduction):
$2MnO_2(s) + H_2O + 2e^- \rightarrow 2Mn_2O_3(s) + 2OH^-$

Anode (oxidation):
$Zn(s) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

Overall:
$2MnO_2(s) + Zn(s) \rightarrow 2Mn_2O_3(s) + ZnO(s)$
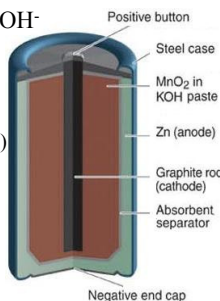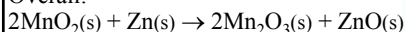
Since all reactants and products are solids (dry cell) $\rightarrow Q = 1$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln 1 = E^o_{cell} \approx \textbf{1.5 V}$$

- **Secondary cells** – can be recharged
  - The cell is periodically converted to an electrolytic cell in order to convert some of the products back to reactants

Example: The lead-acid battery

Cathode (reduction): $E^o = +1.685$ V
$PbO_2(s) + 3H^+ + HSO_4^- + 2e^- \rightarrow PbSO_4(s) + 2H_2O$
Anode (oxidation): $E^o = -0.356$ V
$Pb(s) + HSO_4^- \rightarrow PbSO_4(s) + H^+ + 2e^-$
Overall (cell) reaction:
$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O$

$$E^o_{cell} = 1.685 - (-0.356) = 2.041 \approx \textbf{2 V}$$

$$E_{cell} = E^o_{cell} - \frac{0.0257}{2}\ln\left(\frac{1}{[H_2SO_4]^2}\right)$$

$\rightarrow$ As H_2SO_4 is consumed, E_{cell} drops
$\Rightarrow$ The cell needs to be recharged

- **Fuel cells** – use combustion reactions
  - The cell must be continuously provided with fuel and oxygen (**flow cells**)

Example: The hydrogen fuel cell

$E^o_{cell} = E^o_{cath} - E^o_{anod}$
$E^o_{cell} = 1.23 - (0.00) \approx \mathbf{1.2\ V}$

$$Q = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$$

$$E_{cell} = E^o_{cell} - \frac{0.0257}{2} \ln Q$$

Anode (oxidation): $H_2(g) \longrightarrow 2H^+ + 2e^-$
Cathode (reduction): $\frac{1}{2}O_2(g) + 2H^+ + 2e^- \longrightarrow H_2O(g)$
Overall (cell) reaction: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

$\Rightarrow \uparrow P_{H_2}$ and $\uparrow P_{O_2}$ leads to $\uparrow E_{cell}$

21.6 Corrosion
- Unwanted oxidation of metals in the environment
  - If the metal (M) is in contact with water

Cathode, reduction:
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^o = $ -0.83 V
$\qquad$ (at $pH = 7$) $\rightarrow$ $E = $ -0.42 V

Anode, oxidation:
$M(s) \rightarrow M^{n+} + ne^-$ $\qquad\qquad$ $E^o < $ -0.42 V

$\Rightarrow$ Any metal with $E^o < $ -0.42 V can be oxidized by H_2O

Cathode, reduction:
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$ $E^o = $ +1.23 V
$\qquad$ (at $pH = 7$) $\rightarrow$ $E = $ +0.82 V

Anode, oxidation:
$M(s) \rightarrow M^{n+} + ne^-$ $\qquad\qquad$ $E^o < $ +0.82 V

$\Rightarrow$ Any metal with $E^o < $ +0.82 V can be oxidized by H_2O in the presence of O_2

- At $pH < 7$ (acid rain, etc.), the reduction potentials of H_2O and O_2 are even higher
  $\Rightarrow$ Easier oxidation of the metal

Example: Rusting of iron (Fe $\rightarrow$ $E^o = $ -0.44 V)

Cathode, reduction:
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$ $E = $ +0.82 V ($pH = 7$)

Anode, oxidation:
$Fe(s) \rightarrow Fe^{2+} + 2e^-$ $\qquad$ (×2) $E^o = $ -0.44 V

Overall:
$2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O(l)$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = $ +0.82 – (-0.44) = **+1.26 V**

$\Rightarrow E^o_{cell} > 0 \rightarrow$ spontaneous reaction

$\rightarrow$ **Further oxidation**: $\qquad\qquad$ Rust
$2Fe^{2+} + \frac{1}{2}O_2(g) + (n+2)H_2O(l) \rightarrow \overbrace{Fe_2O_3 \cdot nH_2O(s)} + 4H^+$

---

③ The Fe^{2+} migrates through the drop and reacts with O_2 and H_2O to form rust

Water droplet

$\frac{3}{2}O_2$

nH_2O $2H_2O$

$2Fe^{2+}$

② Electrons at the Fe (inactive) cathode reduce O_2 to H_2O

Rust $Fe_2O_3 \cdot nH_2O$

$4H^+$ O_2

$2Fe$ (anodic region)

$4e^-$ (cathodic region)

IRON BAR

① Oxidation of Fe forms a pit and yields electrons, which travel through the metal

$\rightarrow$ **Overall rusting process:**
$2Fe(s) + O_2(g) + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O(l)$
$2Fe^{2+} + \frac{1}{2}O_2(g) + (n+2)H_2O(l) \rightarrow Fe_2O_3 \cdot nH_2O(s) + 4H^+$

$\mathbf{2Fe(s) + 3/2 O_2(g) + nH_2O(l) \rightarrow Fe_2O_3 \cdot nH_2O(s)}$

$\rightarrow$ Corrosion is enhanced by acidic conditions ($\uparrow[H^+]$) and by salty solutions (improved conductivity)

- **Corrosion protection**
  - **Anodic protection** – preoxidation of the metal by formation of a thin layer of protective metal oxide
  - **Cathodic protection** – connecting the metal to a more strongly reducing metal with lower E^o value called **sacrificial anode**

Example: Protecting **Fe** construction elements by connecting them to blocks of **Mg** or **Al** (sacrificial anodes)

$E^o_{Mg} = $ **-2.36 V**
$E^o_{Fe} = $ **-0.44 V**

Example: Galvanization of **Fe** by coating it with **Zn**

$E_{Zn}^o = $ **-0.76 V**

Mg rod anode, oxidation

cathode, reduction
Iron pipe

21.7 Electrolytic Cells and Electrolysis
- **Electrolytic cells** – use external electrical source to drive a non-spontaneous reaction

0.48 V
Voltmeter

Anode (–) Sn   Salt bridge   Cathode (+) Cu

$2e^-$ $2e^-$

Sn Sn^{2+} Cu^{2+} Cu

1 M Sn^{2+} 1 M Cu^{2+}

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

Voltaic cell

External source greater than 0.48 V

Cathode (–) Sn   Salt bridge   Anode (+) Cu

$2e^-$ $2e^-$

Sn Sn^{2+} Cu^{2+} Cu

1 M Sn^{2+} 1 M Cu^{2+}

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

Electrolytic cell

> **Electrolytic cells** act in reverse (non-spontaneous) direction compared to galvanic cells
> > $E^o_{cell} < 0$ and $\Delta G > 0$ (non-spontaneous reaction)
> > The **anode is positive** and the **cathode is negative**
> There are some **similarities** between **electrolytic** and **galvanic** cells
> > **Oxidation** is always on the **anode** and **reduction** is always on the **cathode**
> > Electrons always flow from anode toward cathode

Cell Type	ΔG	E_{cell}	Electrode		
			Name	Process	Sign
Voltaic	<0	>0	Anode	Oxidation	−
			Cathode	Reduction	+
Electrolytic	>0	<0	Anode	Oxidation	+
			Cathode	Reduction	−

- **Electrolysis** – the passage of electrical current through an electrolyte by applying external voltage (the process in electrolytic cells)
  - Electrolysis causes a non-spontaneous reaction (often a splitting of a substance to its elements)
  - The applied voltage must be greater than the cell potential of the reverse spontaneous reaction
  - The electrolyte can be a molten salt or an aqueous electrolyte solution
  - Salt bridges are often not necessary
  - During electrolysis the cations are attracted to the cathode (negative) and the anions are attracted to the anode (positive)
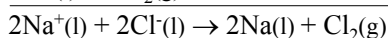
Predicting the Products of Electrolysis

 – The cations (+) are attracted to the cathode (-) and the anions (-) are attracted to the anode (+)

- **Electrolysis of molten salts –** used for industrial isolation of the most active elements (Na, Li, Mg, Al, …; F_2, Cl_2, Br_2, …)
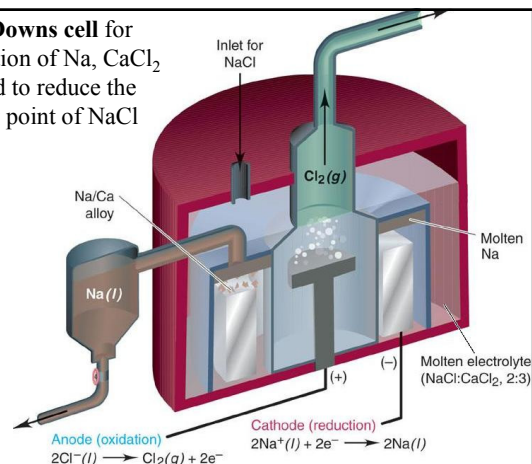 - The cation is reduced at the cathode
  - The anion is oxidized at the anode

Example: Isolation of Na and Cl_2 by electrolysis of molten NaCl

$Na^+(l) + e^- \rightarrow Na(l)$ (×2)   cathode, reduction
$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ anode, oxidation
$\overline{2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)}$

In the **Downs cell** for production of Na, $CaCl_2$ is added to reduce the melting point of NaCl

Anode (oxidation)
$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

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

- **Electrolysis of mixed molten salts**
  - The cation with higher E^o value (the **stronger oxidizing agent**) is reduced at the cathode
  - The anion with lower E^o value (the **stronger reducing agent**) is oxidized at the anode

Note: E^o values in appendix D are for aqueous ions and can be used only as approximate guidance. Instead, EN values can be used to estimate the stronger oxidizing and reducing agents.

Example: Predict the products of the electrolysis of a molten mixture of NaCl and AlF_3

→ Possible cathode half-reactions (reduction)
 1) Reduction of Na^+ and **2)** Reduction of Al^{3+}

→Al^{3+} is the stronger oxidizing agent because Al is more EN than Na, so Al^{3+} gains electrons easier
⇒ Cathode half-reaction: $\mathbf{Al^{3+}(l) + 3e^- \rightarrow Al(l)}$

→ Possible anode half-reactions (oxidation)
 1) Oxidation of F^- and **2)** Oxidation of Cl^-
 →Cl^- is the stronger reducing agent because Cl is less EN than F, so Cl^- looses electrons easier
⇒ Anode half-reaction: $\mathbf{2Cl^-(l) \rightarrow Cl_2(g) + 2e^-}$

$Al^{3+}(l) + 3e^- \rightarrow Al(l)$ (×2)   cathode, reduction
$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ (×3)   anode, oxidation
$\overline{\mathbf{2Al^{3+}(l) + \cancel{6e^-} + 6Cl^-(l) \rightarrow 2Al(l) + 2Cl_2(g) + \cancel{6e^-}}}$
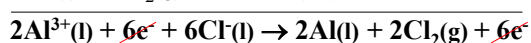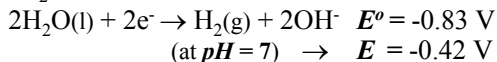
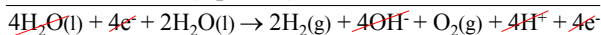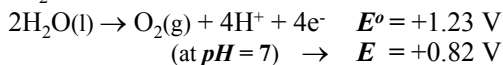⇒ The products are **Al(l)** and $\mathbf{Cl_2(g)}$

- **Electrolysis of water**
  - Pure water is hard to electrolyze (low conductivity), so a small amount of a non-reactive salt ($NaNO_3$) is added (can be neglected)

$\rightarrow$ H_2O is reduced at the cathode:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^o = -0.83$ V

(at $pH = 7$) $\rightarrow$ $E = -0.42$ V

$\rightarrow$ H_2O is oxidized at the anode:

$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^o = +1.23$ V

(at $pH = 7$) $\rightarrow$ $E = +0.82$ V

$\overline{4H_2O(l) + 4e^- + 2H_2O(l) \rightarrow 2H_2(g) + 4OH^- + O_2(g) + 4H^+ + 4e^-}$

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

$E_{cell} = E_{cath} - E_{anod} = -0.42 - (+0.82) = -1.24$ V

$\rightarrow$ $E_{cell} < 0 \Rightarrow$ non-spontaneous reaction

$\Rightarrow$ To drive the reaction, the external voltage must be greater than 1.24 V

- **Overvoltage** – the extra voltage (in the case of water over 1.24) needed to drive the reaction
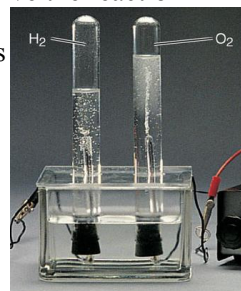 - For H_2O on most inert electrodes, the overvoltage is **0.4** to **0.6 V per electrode**

$\rightarrow$ Cathode, reduction:

$E = -0.42 - 0.6 \approx -1.0$ V

$\rightarrow$ Anode, oxidation:

$E = +0.82 + 0.6 \approx +1.4$ V

$\rightarrow$ Total:

$E_{cell} = -1.0 - (+1.4) \approx -2.4$ V

- **Electrolysis of aqueous solutions**

$\rightarrow$ Possible cathode half-reactions (reduction)

1. Reduction of H_2O
2. Reduction of **cations** in the solution

$\rightarrow$ Possible anode half-reactions (oxidation)

1. Oxidation of H_2O
2. Oxidation of **active metal electrodes**
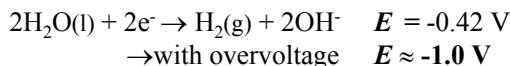3. Oxidation of **anions** in the solution

$\rightarrow$ The half-reaction with the **higher E^o value** (having the stronger oxidizing agent) **occurs on** the **cathode**

$\rightarrow$ The half-reaction with the **lower E^o value** (having the stronger reducing agent) **occurs on** the **anode**

Example: Predict the products of the electrolysis of a mixture of 1M NaCl(aq) and 1M KNO_3(aq) with inert electrodes at $pH = 7$.

$\rightarrow$ Possible cathode half-reactions (reduction)
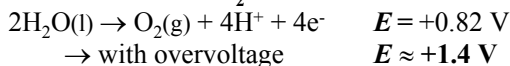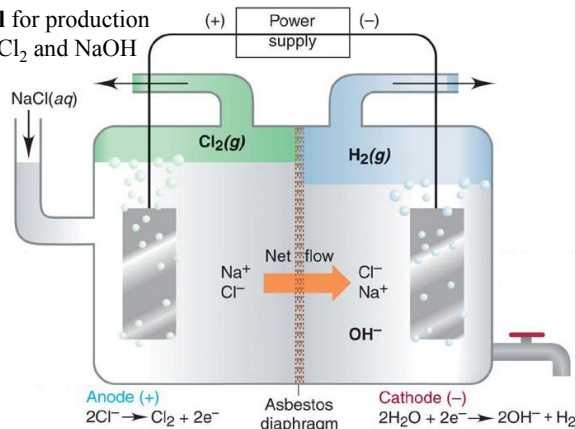
1. Reduction of H_2O

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E = -0.42$ V

$\rightarrow$ with overvoltage $E \approx -1.0$ V

2. Reduction of **cations** in the solution

$Na^+ + e^- \rightarrow Na(s)$ $E^o = -2.71$ V

$K^+ + e^- \rightarrow K(s)$ $E^o = -2.93$ V

$\rightarrow$ Half-reaction **(1)** has the highest (most positive) E value $\Rightarrow$ H_2O **is reduced** to H_2 on the **cathode**

$\rightarrow$ Possible anode half-reactions (oxidation)

1. Oxidation of H_2O

$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ $E = +0.82$ V

$\rightarrow$ with overvoltage $E \approx +1.4$ V

2. Oxidation of **active metal electrodes – none**

3. Oxidation of **anions** in the solution

$2Cl^- \rightarrow Cl_2(g) + 2e^-$ $E^o = +1.36$ V

Note: NO_3^- can't be further oxidized (not a product in any half-reaction in appendix D)

$\rightarrow$ Half-reaction **(3)** has the lowest E^o value $\Rightarrow$ **Cl$^-$ is oxidized** to Cl_2 on the **anode**

$\rightarrow$ Overall: $2H_2O(l) + 2Cl^- \rightarrow H_2(g) + 2OH^- + Cl_2(g)$

Note: Without the overvoltage, H_2O would be oxidized to O_2 at the anode

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The **Chlor-alkali cell** for production of Cl_2 and NaOH

- ➢ Electrolysis of aqueous solutions is often used for production or purification of less active elements
  - ➢ Cations of **less active metals** (Cu, Ag, Au, Pt, …) **are reduced** on the cathode
  - ➢ Anions of **less active nonmetals** (I_2, Br_2, …) **are oxidized** on the anode (including Cl_2 due to the overvoltage of water)
  - ➢ Cations of **more active metals** (Na, K, Mg, Ca, …) **are not reduced** (H_2O is reduced to H_2 instead) → can't be produced by electrolysis of aqueous soln.
  - ➢ Anions of **more active nonmetals** (F^-) and **oxoanions of elements in their highest oxidation state** (NO_3^-, CO_3^{2-}, SO_4^{2-}, …) **are not oxidized**

The Stoichiometry of Electrolysis
- • **Faraday's law** – the amount of substance produced on each electrode is directly proportional to the amount of charge transferred through the cell

  $I \rightarrow$ el. current $t \rightarrow$ time of electrolysis
  $Q \rightarrow$ charge transferred $n \rightarrow$ # mol e^- transferred

  $I = Q/t \quad \rightarrow \quad Q = I \times t$

  $Q = nF \quad \rightarrow \quad n = Q/F$

  $$\Rightarrow \quad n = \frac{I \times t}{F}$$

  → n is related to the amount of substance through the stoichiometry of the half-reaction

  → Allows the determination of the amount of substance produced by measuring I and t

---

Example: During electrorefining of Cu, how much time is needed to produce **250 g** Cu on the cathode if the current is kept at **11 A**?

$I = 11$ A $= 11$ C/s $t \rightarrow ?$

Half-reaction: $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

$$n = 250 \text{ g} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Cu}} = 7.9 \text{ mol}$$

$$n = \frac{I \times t}{F} \quad \Rightarrow \quad t = \frac{n \times F}{I}$$

$$t = \frac{7.9 \text{ mol} \times 96485 \text{ C/mol}}{11 \text{ C/s}} = 6.9 \times 10^4 \text{ s} = 19 \text{ hr}$$

Elctrorefining of Cu

$Cu^{2+} + 2e^- \rightarrow Cu$
Cathode (−)

$Cu \rightarrow Cu^{2+} + 2e^-$
Anode (+)

Pure copper   Anode mud   Acidified $CuSO_4(aq)$ Impure copper