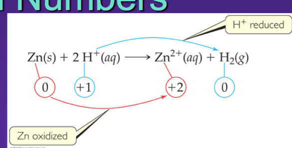
Electrochemistry

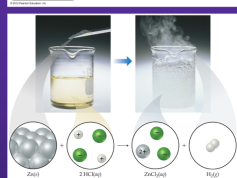
Electrochemical Reactions

In **electrochemical reactions,** electrons are transferred from one species to another.

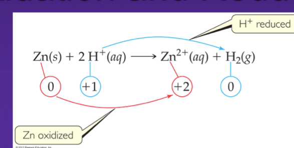
Oxidation Numbers

In order to keep track of what loses electrons and what gains them, we assign **oxidation numbers**.





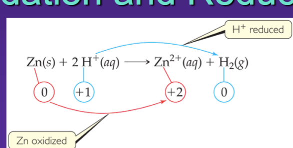
Oxidation and Reduction



A species is **oxidized** when it loses electrons.

- Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.

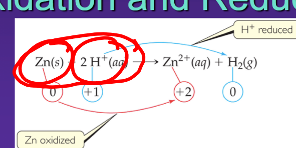
Oxidation and Reduction



A species is **reduced** when it gains electrons.

- Here, each of the H^+ gains an electron, and they combine to form H_2.

Oxidation and Reduction



What is reduced is the **oxidizing agent**.

- H^+ oxidizes Zn by taking electrons from it.

What is oxidized is the **reducing agent**.

- Zn reduces H^+ by giving it electrons.

Redox Reactions

oxidation-reduction (redox) reaction: involves a transfer of electrons from the reducing agent to the oxidizing agent.

oxidation: increase in oxidation state (loss of electrons)

reduction: decrease in oxidation state (gain of electrons)

Rules for Assigning Oxidation States

1. Oxidation state of an atom in an element = 0
2. Oxidation state of monatomic element = charge
3. Oxygen = −2 in covalent compounds (except in peroxides where it = −1)
4. H = +1 in covalent compounds, -1 when bonded to metals
5. Fluorine = −1 in compounds
6. Sum of oxidation states = 0 in compounds
7. Sum of oxidation states = charge of the ion

Cl^{-} (−1), CO_2, CH_4

CO_2: $1(x) + 2(-2) = 0$, $x = 4$

CH_4: $1(x) + 4(+1) = 0$, $x = -4$

$\overset{-4}{C}\overset{+1}{H_4} + 2\overset{0}{O_2} \rightarrow \overset{+4}{C}\overset{-2}{O_2} + 2\overset{+1}{H_2}\overset{-2}{O}$

NH_4^+ (−3): $1(x) + 4(+1) = 1$, $x = -3$

NO_3^- (+5): $1(x) + 3(-2) = -1$, $x = 5$

TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \rightarrow Li^+(aq) + e^-$
Potassium	$K(s) \rightarrow K^+(aq) + e^-$
Barium	$Ba(s) \rightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \rightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \rightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$
Copper	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \rightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \rightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \rightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \rightarrow Au^{3+}(aq) + 3e^-$

Ease of oxidation increases (upward)

$Zn_{(s)}$

$Cu_{(s)}$

$ZnSO_4\ (aq) \rightarrow Zn^{2+} + SO_4^{2-}$

Balancing Oxidation-Reduction Equations

Perhaps the easiest way to balance the equation of an oxidation-reduction reaction is via the **half-reaction method**.

Balancing Oxidation-Reduction Equations

This method involves treating (on paper only) the oxidation and reduction as two separate processes, balancing these half-reactions, and then combining them to attain the balanced equation for the overall reaction.

Balancing by Half-Reaction Method

1. **Write separate reduction, oxidation reactions.**
2. **For each half-reaction:**
   - **Balance elements (except H, O)**
   - **Balance O using H_2O**
   - **Balance H using H^+**
   - **Balance charge using electrons**

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Balancing by Half-Reaction Method (continued)

3. If necessary, multiply by integer to equalize electron count.
4. Add half-reactions.
5. Check that elements and charges are balanced.

Half-Reaction Method - Balancing in Base

1. Balance as in acid.
2. Add OH^- that equals H^+ ions (both sides!)
3. Form water by combining H^+, OH^-.
4. Check elements and charges for balance.

Problem

Complete and balance the following equations, and identify the oxidizing and reducing agents:

(c) Equation

$I_2(s) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-$

(acidic solution)

(e) Equation

$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$

(basic solution)

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

$5(2e^- + OCl^- + 2H^+ \rightarrow Cl^- + H_2O)$

$10e^- + 5OCl^- + 10H^+ \rightarrow 5Cl^- + 5H_2O$

$I_2 + H_2O + 5OCl^- \rightarrow 2IO_3^- + 2H^+ + 5Cl^-$

Electrochemistry

The study of the interchange of chemical and electrical energy.

Half-Reactions

The overall reaction is split into two half-reactions, one involving oxidation and one reduction.

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

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

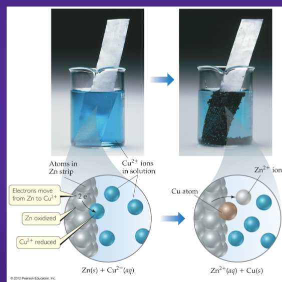
Oxidation: $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

Voltaic Cell

A device in which chemical energy is changed to electrical energy.

Voltaic Cells

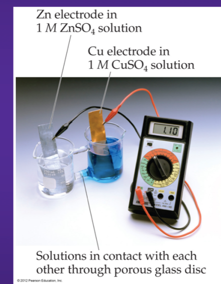
In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.



Voltaic Cells

We can use that energy to do work if we make the electrons flow through an external device.

We call such a setup a **voltaic cell.**

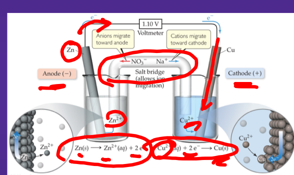


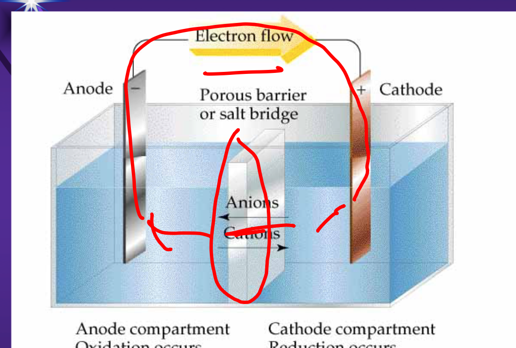
Voltaic Cells

A typical cell looks like this.

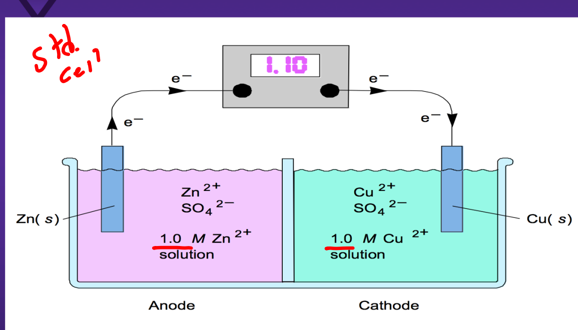
The oxidation occurs at the **anode**.

The reduction occurs at the **cathode**.





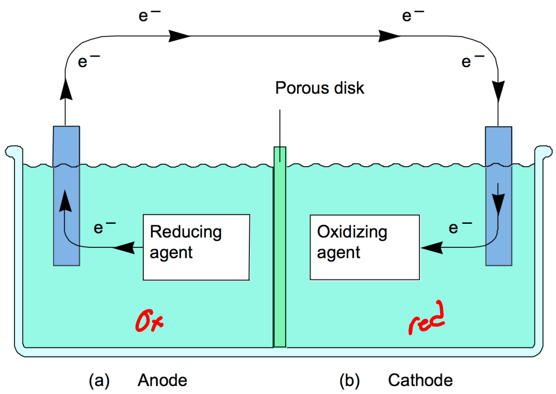
Voltaic Cell



Anode and Cathode

OXIDATION occurs at the ANODE.

REDUCTION occurs at the CATHODE.



Cell Potential

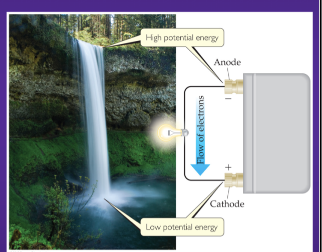
E°_{cell}

Cell Potential or Electromotive Force (emf): The "pull" or driving force on the electrons.

Electromotive Force (emf)

Water only spontaneously flows one way in a waterfall.

Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.



Electromotive Force (emf)

The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.

It is also called the **cell potential** and is designated E_{cell}.

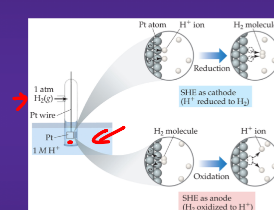
Cell Potential

Cell potential is measured in volts (V).

$$1\ V = 1\ \frac{J}{C}$$

Standard Hydrogen Electrode

Their values are referenced to a standard hydrogen electrode (SHE).

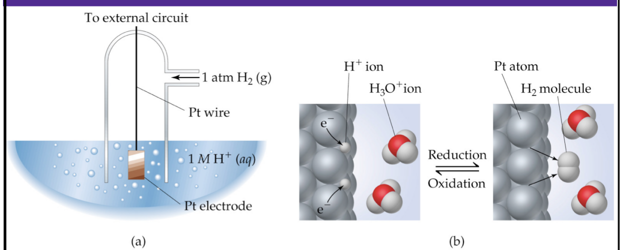


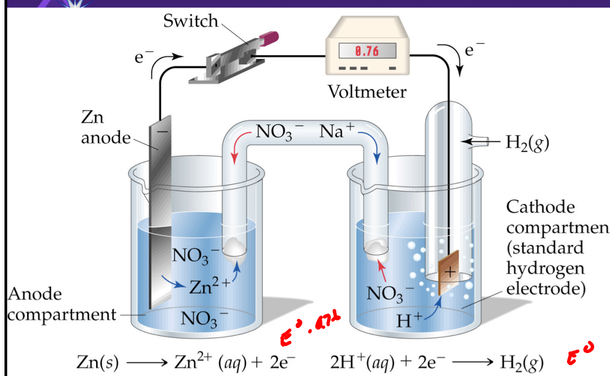
By definition, the reduction potential for hydrogen is 0 V:

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

$E^\circ = 0.00V$

SHE





Standard Reduction Potentials

The $E°$ values corresponding to reduction half-reactions with all solutes at 1M and all gases at 1 atm.

$Cu^{2+} + 2e^- \rightarrow Cu$ $E° = 0.34$ V vs. SHE

$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$

$E° = 0.20$ V vs. SHE

Table 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	ξ ° (V)	Half-reaction	ξ ° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.34
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	–0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	–0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	–0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	–0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	–0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow ½I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	–0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$VO_2 + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	–2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	–2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg^+$	0.80	$Na^+ + e^- \rightarrow Na$	–2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	–2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	–2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	–2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	–3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

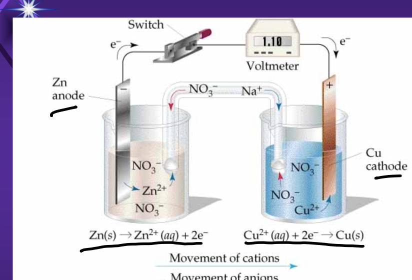
Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E°_{cell} = E°_{red}\text{(cathode)} - E°_{red}\text{(anode)}$$

$= 0.34 - (-0.76) = 1.10$ V

Because cell potential is based on the potential energy per unit of charge, it is an intensive property.



~~$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$ −0.76 V~~

red $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ 0.34 V

ox $Zn_{(s)} \rightarrow Zn^{2+} + 2e$ 0.76 V

1.10 V

Table 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	ξ° (V)	Half-reaction	ξ° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.34
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	–0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
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$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	–0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	–0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	–0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	–0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	–0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
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$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	–3.05
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Cell Potentials

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$$
$$= +0.34\text{ V} - (-0.76\text{ V})$$
$$= +1.10\text{ V}$$

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$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	–0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	–0.23
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$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	–1.66
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$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	–2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	–2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	–3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Problem

A 1 M solution of $Cu(NO_3)_2$ is placed in a beaker with a strip of Cu metal. A 1 M solution of $SnSO_4$ is placed in a second beaker with a strip of Sn metal. The two beakers are connected by a salt bridge, and the two metal electrodes are linked by wires to a voltmeter.

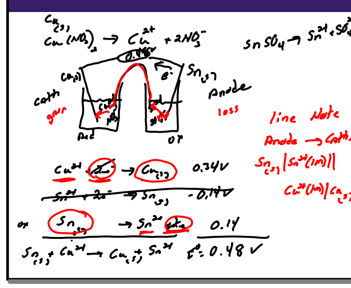
(a) Write the equation for the overall cell reaction.

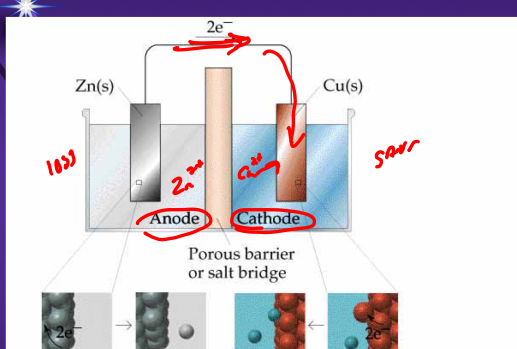
(b) What is the emf generated by the cell under standard conditions?

(c) Which electrode serves as the anode, and which as the cathode?

(d) Which electrode gains mass and which loses mass as the cell reaction proceeds?

(e) Using line notation, describe the cell.





emf and Work

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

Free Energy and Cell Potential

$$\Delta G = -nFE$$

n = number of moles of electrons

F = Faraday = 96,485 coulombs per mole of electrons

Free Energy

Under standard conditions,

$$\Delta G^\circ = -nFE^\circ$$

$\Delta G = -nFE$

Nernst Equation

Remember that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

This means

$$-nFE = -nFE^\circ + RT \ln Q$$

Nernst Equation

Dividing both sides by $-nF$, we get the **Nernst equation**:

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

or, using base-10 logarithms,

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

Nernst Equation

At room temperature (298 K),

$$\frac{2.303RT}{F} = 0.0592 \text{ V}$$

Thus, the equation becomes

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

The Nernst Equation

We can calculate the potential of a cell in which some or all of the components are not in their standard states.

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

at Equil $E = 0$ $Q = K$

Calculation of Equilibrium Constants for Redox Reactions

At equilibrium, $E_{cell} = 0$ and $Q = K$.

$$\log(K) = \frac{nE^\circ}{0.0592} \text{ at } 25^\circ\text{C}$$

Problem

For a galvanic cell, at 25 degrees celcius, based on the following half reactions:

$Au^{3+} + 3e^- \rightarrow Au(s)$ $E^\circ = 1.50$ V

$Tl^+(aq) + e^- \rightarrow Tl(s)$ $E^\circ = -0.34$ V

1. Determine the overall cell reaction and E° for the cell.
2. Calculate ΔG^0 and K for the cell reaction.
3. What is the potential of the cell if the concentration of $[Au^{3+}(aq)] = 1.0\times10^{-2}$M, $[Tl+(aq)] = 1.0\times10^{-4}$M?
4. Use line notation to represent the cell in #3.

$Tl_{(s)} | Tl^+(1.0\times10^{-4}M) || Au^{3+}(1.0\times10^{-2}M) | Au_{(s)}$

1.) $Au^{3+} + 3e^- \rightarrow Au_{(s)}$ 1.50 V

$3Tl_{(s)} \rightarrow 3Tl^+ + 3e^-$ 0.34

$3Tl_{(s)} + Au^{3+} \rightarrow Au_{(s)} + 3Tl^+$ $E^\circ = 1.84$ V

$Q = \frac{[Tl^+]^3}{[Au^{3+}]}$

2.) $\Delta G^\circ = -nFE^\circ$

$= -(3)(96,485 \frac{C}{mol})(1.84 \frac{J}{C}) = -5.3\times10^5$ J

$\log K = \frac{nE^\circ}{0.0592} = \frac{(3)(1.84)}{0.0592} = 93.24$

$K = 10^{93.24} = 1.75\times10^{93}$

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

$E = 1.84\text{ V} - \frac{0.0592}{3}\log(1.0\times10^{-10}) = 2.04$ V

$Q = \frac{[Tl^+]^3}{[Au^{3+}]} = \frac{(1.0\times10^{-4})^3}{(1.0\times10^{-2})} = 1.0\times10^{-10}$

Problem

For a galvanic cell, at 25 degrees celcius, based on the following half reactions:

$Cr^{3+} + 3e^- \rightarrow Cr(s)$ $E^\circ = -0.73$ V

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ $E^\circ = +1.09$ V

1. Determine the overall cell reaction and E° for the cell. $E^\circ = 1.82$ V
2. Calculate ΔG^0 and K for the cell reaction. $\Delta G^\circ = -1.05\times10^6$ J
3. What is the potential of the cell if the concentration of $[Br_2(aq)] = 0.50$M, $[Br^-(aq)] = 0.10$M, and $[Cr^{3+}] = 0.20$M? $E =$
4. Use line notation to represent the cell in #3.

2.) $\log K = \frac{nE^\circ}{0.0592} =$ $\log K = 184.46$, $K = 10^{184.46}$

3.) $E = 1.82 - \frac{0.0592}{6}\log(3.2\times10^{-7}) = 1.88$ V

$Q = \frac{[Cr^{3+}]^2[Br^-]^6}{[Br_2]^3} = 3.2\times10^{-7}$

$Cr_{(s)} | Cr^{3+}(0.20M) || Br_2(0.50M), Br^-(0.1M) | Pt_{(s)}$

Problem – Electrochemical Sensors

A voltaic cell is constructed that is based on the following reaction:

$$Sn^{2+}(aq) + Pb(s) \longrightarrow Sn(s) + Pb^{2+}(aq)$$

(a) If the concentration of Sn^{2+} in the cathode compartment is 1.00 *M* and the cell generates an emf of +0.22 V, what is the concentration of Pb^{2+} in the anode compartment?

$Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$ 0.13 V

$Sn^{2+} + 2e^- \rightarrow Sn_{(s)}$ −0.14 V

$E^\circ = -0.01$ V

$E = E^\circ - \frac{0.0592}{n}\log\frac{[Pb^{2+}]}{[Sn^{2+}]}$

$[Pb^{2+}] = 1.7\times10^{-8}$ M

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

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

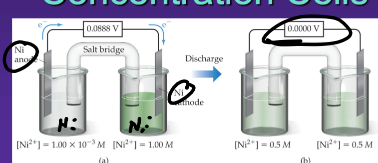
$Q = 10^{\left[\frac{-(E-E^\circ)n}{0.0592}\right]} = 1.7\times10^{-8}$

$\frac{[Pb^{2+}]}{[Sn^{2+}]} = 1.7\times10^{-8}$

Concentration Cell

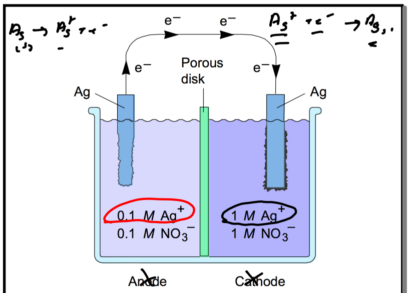
. . . a cell in which both compartments have the same components but at different concentrations.

Concentration Cells



Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.

- For such a cell, E°_{cell} would be 0, but Q would not.
- Therefore, as long as the concentrations are different, E will not be 0.



Cathode

$Ag^+_{(1.0)} + e^- \rightarrow Ag_{(s)}$ $\quad E^\circ = 0.80V$

Anode

$Ag_{(s)} \rightarrow Ag^+_{(0.1)} + e^-$ $\quad E^\circ = -0.80V$

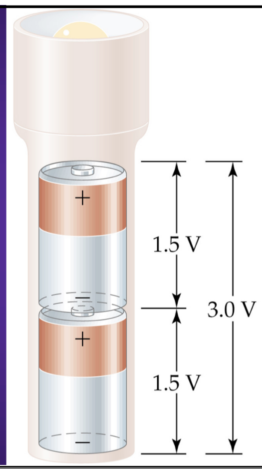
$E^\circ_{cell} = 0.0$

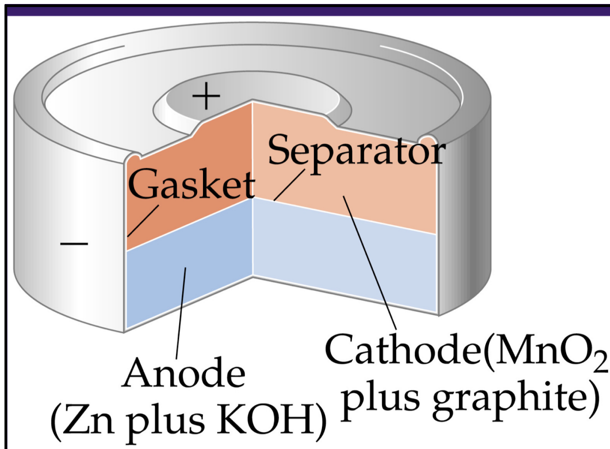
$$E = E^\circ - \frac{0.0592}{n} \log \frac{[0.1]}{[1.0]}$$

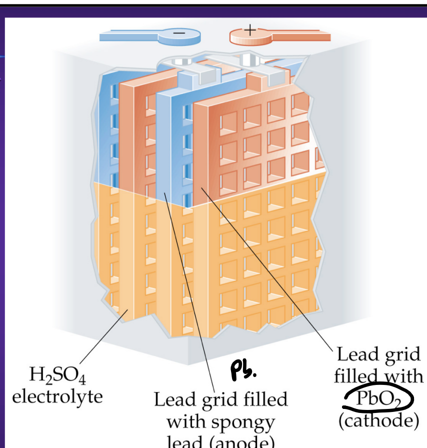
$$E = 0 - \frac{0.0592}{1} \log \frac{(0.1)}{(1.0)} = 0.059\,V$$

Batteries

A battery is a galvanic cell or, more commonly, a group of galvanic cells connected in series.







Problem

During a period of discharge of a lead-acid battery, 402 g of Pb from the anode is converted into $PbSO_4(aq)$. What mass of $PbO_2(s)$ is reduced at the cathode during this same period?

$PbSO_{4(aq)} \rightarrow Pb^{2+} + SO_4^{2-}$

What happens when this battery is recharged?

Anode

$Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$

Cathode

$2e^- + PbO_{2(s)} + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

$Pb_{(s)} + PbO_2 + 4H^+ \rightarrow 2Pb^{2+} + 2H_2O$

$$402\,g\,Pb \times \frac{1\,mol\,Pb}{207.2\,g\,Pb} \times \frac{1\,mol\,PbO_2}{1\,mol\,Pb} \times \frac{239.2\,g\,PbO_2}{1\,mol\,PbO_2} = 464\,g\,PbO_2$$

Fuel Cells

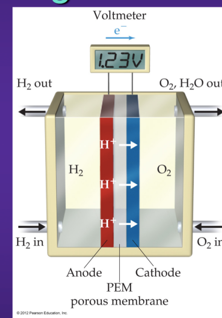
. . . galvanic cells for which the reactants are continuously supplied.

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

anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

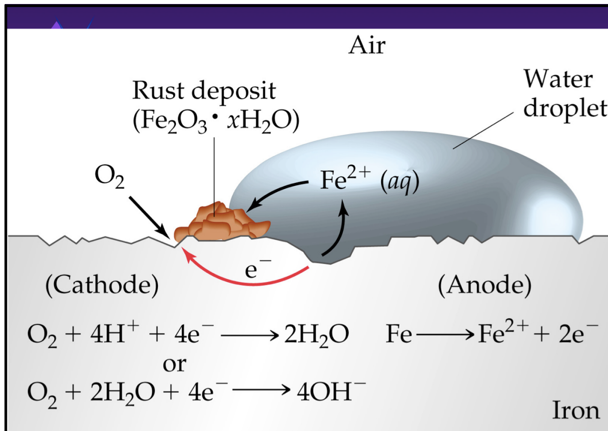
cathode: $4e^- + O_2 + 2H_2O \rightarrow 4OH^-$

Hydrogen Fuel Cells



Corrosion

Some metals, such as copper, gold, silver and platinum, are relatively difficult to oxidize. These are often called noble metals.



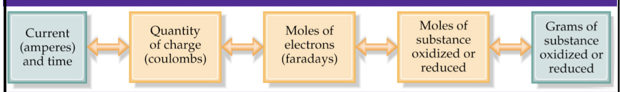
Electrolysis

. . . forcing a current through a cell to produce a chemical change for which the cell potential is negative.

Stoichiometry of Electrolysis

- How much chemical change occurs with the flow of a given current for a specified time?

current and time → quantity of charge → moles of electrons → moles of analyte → grams of analyte



END

Problem 20.59

A voltaic cell utilizes the following reaction and operates at 298 K:

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

(a) What is the emf of this cell under standard conditions?

(b) What is the emf of this cell when $[Ni^{2+}] = 3.00\ M$ and $[Zn^{2+}] = 0.100\ M$?

(c) What is the emf of the cell when $[Ni^{2+}] = 0.200\ M$ and $[Zn^{2+}] = 0.900\ M$?

Energy and Electrochemistry Review

Spontaneity, Entropy, and Free Energy

1. For the reaction at 298 K,

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)}$$

ΔS^o = -176.6 J/K mole and
ΔH^o = -58.03 kJ/mole

a. What is the value of ΔG^o at 298 K?

b. Assume that ΔH^o and ΔS^o do not depend on temperature. At what temperature is $\Delta G^o = 0$?

c. Is ΔG^o negative above or below this temperature, why?

2. Hydrogen sulfide can be removed from natural gas by the reaction,

$$2H_2S_{(g)} + SO_{2(g)} \leftrightarrow 3S_{(s)} + 2H_2O_{(g)}$$

a. Calculate ΔG^o and K for this reaction at 298K.

b. Would this reaction be favored at high or low temperatures, why?

Electrochemistry

3. For the galvanic cell, at 25 degrees Celsius, based on the following half reactions:

$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $E^o = -1.66$ V

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ $E^o = -0.23$ V

a. Determine the overall cell reaction and E^o for the cell.

b. Calculate ΔG^0 and K for the cell reaction.

c. Draw as complete a picture of the cell as you can **(Label everything)**.

Challenge Problem

4. Combine the equations

$$\Delta G^o = -nFE^0 \quad \text{and} \quad \Delta G^o = \Delta H^o - T\Delta S^o$$

to derive an expression for E^o as a function of temperature. Describe how one can graphically determine ΔH^o and ΔS^o from the measurements of E^o at different temperatures.