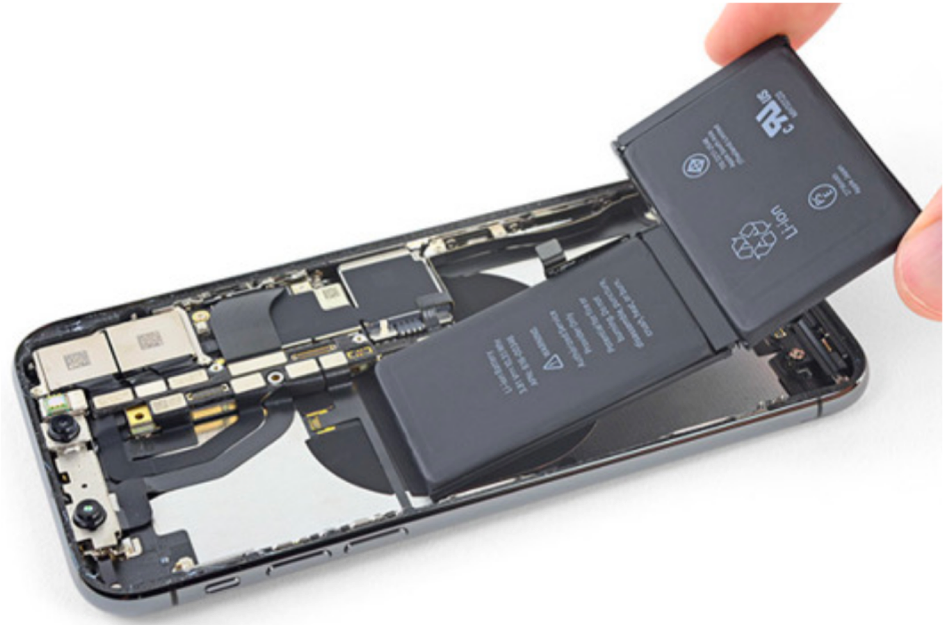
Chapter 19

Electrochemistry



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Electrochemistry

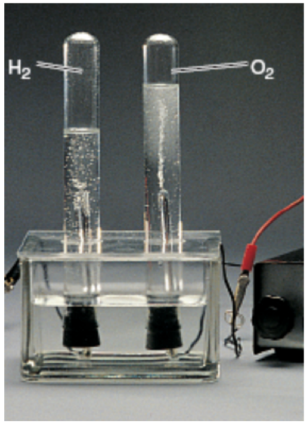
Branch of chemistry that deals with the relationships between electricity & chemical reactions

Electrochemical processes are oxidation–reduction reactions in which:

- The energy released by a spontaneous reaction is converted into electricity, or
- Electrical energy is used to cause a non-spontaneous reaction to occur.

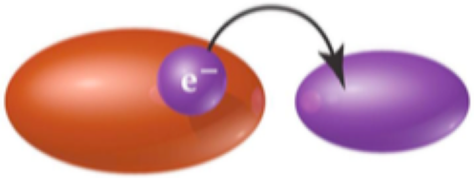
Can be used to monitor reactions by controlling electron transfer

- Reaction progress (kinetics)
- Composition at equilibrium
- Energy changes (thermodynamics)



Oxidation–Reduction (Redox) Reactions

Chemical reactions in which one or more electrons are transferred from one reactant to another. There is a change in oxidation number for both substances.



Oxidation Number: Theoretical charge on an atom/ion

Oxidation: Occurs when an atom/ion **loses** **electrons**

– involves an INCREASE in oxidation number

Reduction: Occurs when an atom/ion **gains** **electrons**

– involves a DECREASE in oxidation number

Must have oxidation & reduction – can't have just one

LEO the lion says GER

LEO

Lose
Electrons
Oxidation

GER

Gain
Electrons
Reduction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OIL RIG

Oxidation
Is
Loss

Reduction
Is
Gain

Oxidation Number Rules – CHM101

The rule earlier in the list always takes precedence

1.) Overall Ox # for a compound is zero

2.) Ox # = 0 for an element (not in a compound)

Ox # = ionic charge for an ion

3.) Ox # = +1 for IA elements & H (note: if w/metal H is –1)

4.) Ox # = +2 for 2A elements

5.) Ox # = –2 for oxygen (usually)

6.) Ox # = –1 for 7A elements (If both elements are in 7A, the one higher in the list is –1; with O can be pos.)

7.) Ox # = –2 for 6A elements other than oxygen

8.) Ox # = –3 for 5A elements (very shaky!!!)

Determining Oxidation Number (State)

Determine the oxidation states of the elements in each of the following:

a.) P_2O_5

b.) NaH

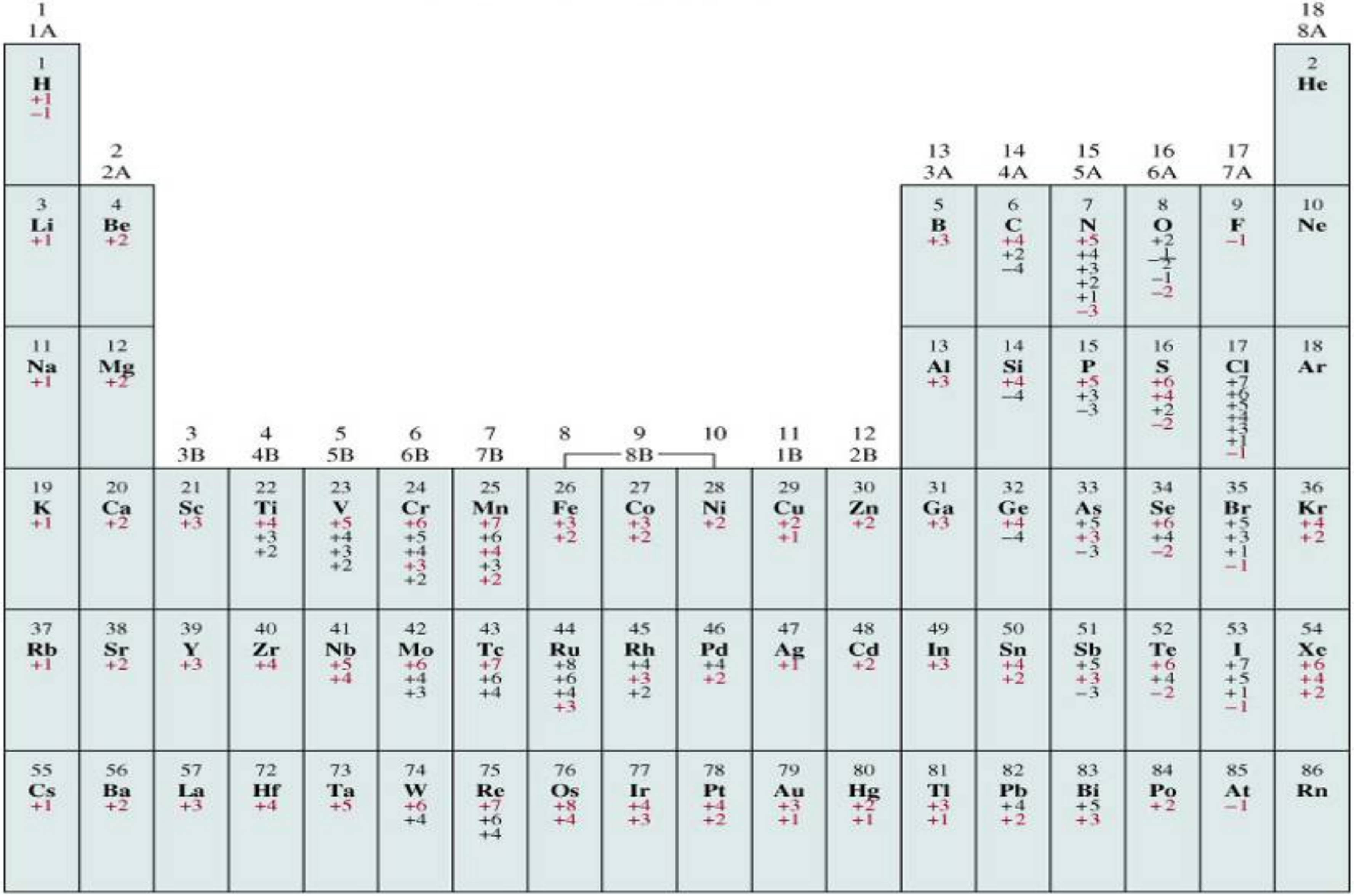
c.) $Cr_2O_7^{2-}$

d.) $SnBr_4$

e.) NO_2^-

f.) ClO_3^-

Elemental Oxidation Numbers



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** +1 −1																	2 **He**
3 **Li** +1	4 **Be** +2											5 **B** +3	6 **C** +4 +2 −4	7 **N** +5 +4 +3 +2 +1 −3	8 **O** +2 $-\frac{1}{2}$ −1 −2	9 **F** −1	10 **Ne**
11 **Na** +1	12 **Mg** +2											13 **Al** +3	14 **Si** +4 −4	15 **P** +5 +3 −3	16 **S** +6 +4 +2 −2	17 **Cl** +7 +6 +5 +4 +3 +1 −1	18 **Ar**
19 **K** +1	20 **Ca** +2	21 **Sc** +3	22 **Ti** +4 +3 +2	23 **V** +5 +4 +3 +2	24 **Cr** +6 +5 +4 +3 +2	25 **Mn** +7 +6 +4 +3 +2	26 **Fe** +3 +2	27 **Co** +3 +2	28 **Ni** +2	29 **Cu** +2 +1	30 **Zn** +2	31 **Ga** +3	32 **Ge** +4 −4	33 **As** +5 +3 −3	34 **Se** +6 +4 −2	35 **Br** +5 +3 +1 −1	36 **Kr** +4 +2
37 **Rb** +1	38 **Sr** +2	39 **Y** +3	40 **Zr** +4	41 **Nb** +5 +4	42 **Mo** +6 +4 +3	43 **Tc** +7 +6 +4	44 **Ru** +8 +6 +4 +3	45 **Rh** +4 +3 +2	46 **Pd** +4 +2	47 **Ag** +1	48 **Cd** +2	49 **In** +3	50 **Sn** +4 +2	51 **Sb** +5 +3 −3	52 **Te** +6 +4 −2	53 **I** +7 +5 +1 −1	54 **Xe** +6 +4 +2
55 **Cs** +1	56 **Ba** +2	57 **La** +3	72 **Hf** +4	73 **Ta** +5	74 **W** +6 +4	75 **Re** +7 +6 +4	76 **Os** +8 +4	77 **Ir** +4 +3	78 **Pt** +4 +2	79 **Au** +3 +1	80 **Hg** +2 +1	81 **Tl** +3 +1	82 **Pb** +4 +2	83 **Bi** +5 +3	84 **Po** +2	85 **At** −1	86 **Rn**

Oxidizing and Reducing Agents

Oxidizing agent: reactant that promotes oxidation

- Oxidation = loss of electrons
- Oxidizing agent takes e^- from other species → is reduced!
- Characteristic of nonmetals: ex: fluorine, oxygen.
- High electron affinity: easily gains electrons

Reducing agent: reactant that promotes reduction

- Reduction = gain in electrons
- Reducing agent loses e^- → is oxidized!
- Characteristic of an active metal, such as sodium.
- Low ionization energy: easily loses electrons

$$4\,\overset{0}{\mathrm{Na}} + \overset{0}{\mathrm{O}}_2 \rightarrow 2\,\overset{+1}{\mathrm{Na}}_2\overset{-2}{\mathrm{O}}$$

Na oxidized; is reducing agent

O reduced; is oxidizing agent

Oxidation and Reduction

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

Oxidation:

- Zinc loses two electrons (0 to +2)
- Becomes more positive = oxidized
- Zinc gives the electrons to H^+ – reducing agent

Reduction:

- Each H gains one electron (+1 to 0)
- Becomes more negative = reduced
- The hydrogen ions take the electrons from zinc – oxidizing agent

Oxidizing & Reducing Agents

Indicate which is the oxidizing agent and which is the reducing agent in the following reaction:

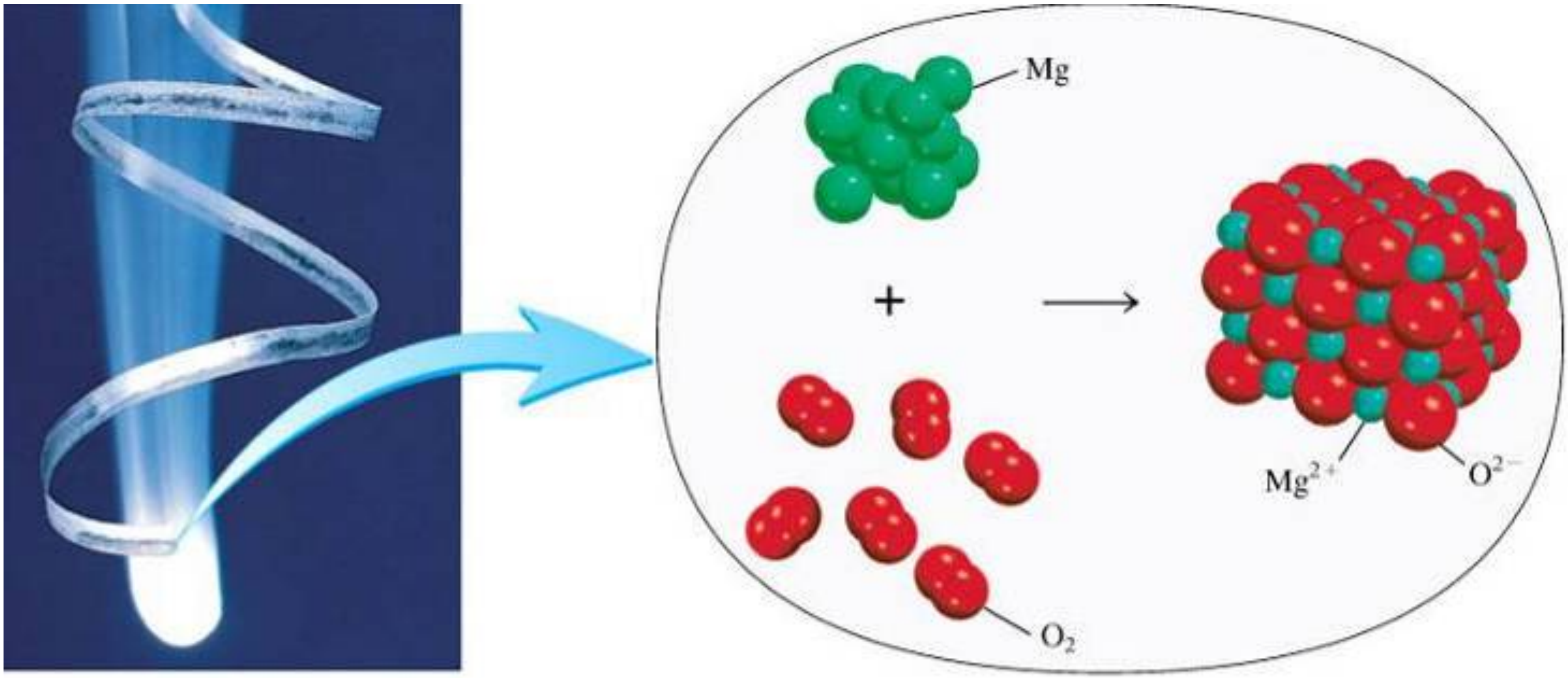
$$Cd(s) + NiO_2(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Redox Reaction: Half-reactions

Oxidation half-reaction: $Mg\ (s) \rightarrow Mg^{2+} + \mathbf{2e^-}$

Reduction half-reaction: $\frac{1}{2}O_2(g) + \mathbf{2e^-} \rightarrow O^{2-}$

Sum of half-reactions: $Mg\ (s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$



Balancing Redox Reactions (Acidic)

1. Assign oxidation numbers to determine what is oxidized/reduced.

$$Fe^{2+} + \overset{+6}{Cr}_2\overset{-2}{O}_7^{2-} \rightarrow Fe^{3+} + Cr^{3+}$$

2. Write the oxidation and reduction half reactions.

   $Fe^{2+} \rightarrow Fe^{3+}$ $Cr_2O_7^{2-} + \rightarrow Cr^{3+}$

3. Balance each half-reaction.
   a. Balance elements other than H & O first

      $Fe^{2+} \rightarrow Fe^{3+}$ $Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$

   b. Balance O by adding H_2O.

      $Fe^{2+} \rightarrow Fe^{3+}$ $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

   c. Balance H by adding H^+.

      $Fe^{2+} \rightarrow Fe^{3+}$ $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Balancing Redox Reactions (Acidic)

From step 3: $Fe^{2+} \rightarrow Fe^{3+}$ $\quad Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

4. Add in the electrons

$Fe^{2+} \rightarrow Fe^{3+} + 1e \quad Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

5. Multiply the half-reactions by integers to balance the charge.

$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^- \quad Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

6. Add the half-reactions, subtracting things that appear on both sides.

$6Fe^{2+} + Cr_2O_7^{2-} + \cancel{6e^-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + \cancel{6e^-}$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

7. Make sure the equation is balanced according to mass (same number of each atom on both sides).

6Fe, 2Cr, 7O, 14H on each side

8. Make sure the equation is balanced according to charge.

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

$(+12)+(-2)+(+14)=+24 \quad (+18)+(+6)+(0)=+24$

Balancing Redox Reactions in Acidic Solution

Complete and balance the following equation. The reaction occurs in acidic solution.

$$Mn^{2+}(aq) + BiO_3^-(s) \rightarrow Bi^{3+}(aq) + MnO_4^-(aq)$$

A: $2Mn^{2+}(aq) + 5BiO_3^-(s) + 14H^+(aq) \rightarrow 5Bi^{3+}(aq) + 2MnO_4^-(aq) + 7H_2O(l)$

Balancing Redox Reactions (Basic)

1. Follow the steps for balancing the equation in acidic solution.

   balanced eq. from slide 13:

   $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

2. Once the equation is balanced, add OH^- to each side to "neutralize" any H^+ in the equation.

   $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ + 14OH^- \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 14OH^-$

3. Combine OH^- and H^+ to make H_2O.

   $6Fe^{2+} + Cr_2O_7^{2-} + 14H_2O \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O + 14OH^-$

4. If there is water on both sides, cancel as much as possible.

   $6Fe^{2+} + Cr_2O_7^{2-} + 7H_2O \rightarrow 6Fe^{3+} + 2Cr^{3+} + 14OH^-$

5. Check to verify the equation is still balanced.

   atoms: 6Fe, 2Cr, 14O, 14H on each side

   charge: $12-2 = 10$ $18+6-14 = 10$

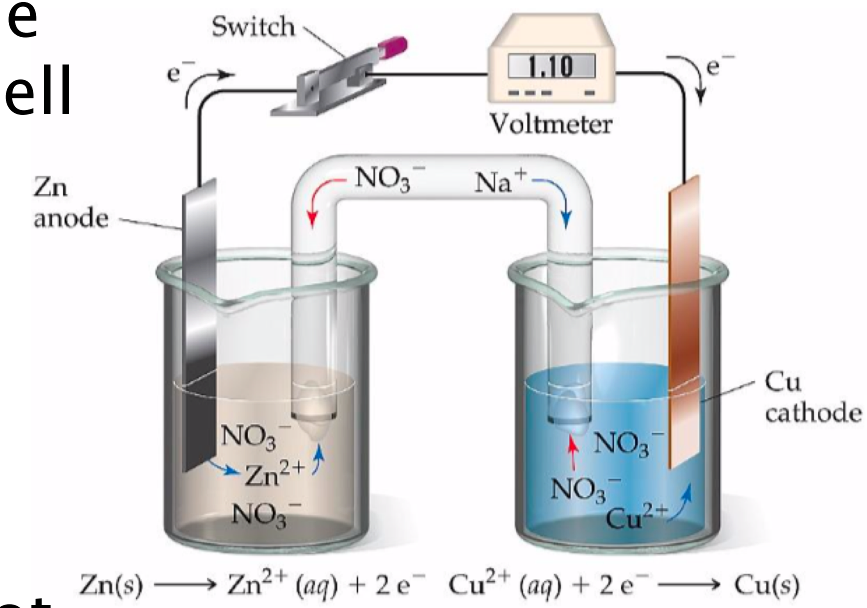
Balancing Redox Reactions in Basic Solution

Complete and balance the following equation. The reaction occurs in basic solution.

$$NO_2^-(aq) + Al(s) \rightarrow NH_3(aq) + Al(OH)_4^-(aq)$$

A: $NO_2^-(aq) + 2Al(s) + 5H_2O(l) + OH^-(aq) \rightarrow NH_3(aq) + 2Al(OH)_4^-(aq)$

Electrochemical Cells: Parts



Ionic Solutions:

- Provide ions to transfer charge
- Solution + Electrode = Half-cell

Electrodes:

- Anode: oxidation occurs
- Cathode: reduction occurs

Salt Bridge:

- Keeps 2 half-cells connected
- Ions flow but solution does not

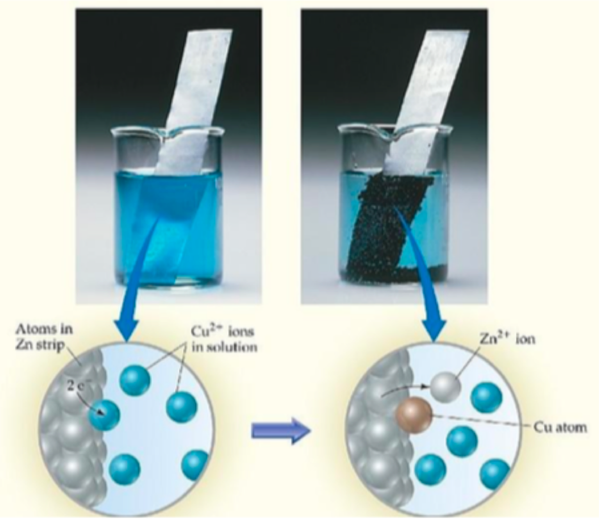
Metal Wires:

- Connect the electrodes to the terminals of the voltmeter
- Provide way to transport electrons between electrodes

Voltmeter

- Measures the electron flow in the system

Galvanic (aka Voltaic) Cell



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

In spontaneous redox reactions, electrons are transferred
– this releases energy

If the electrons are made to flow through an external device, the released energy can be used to do work.

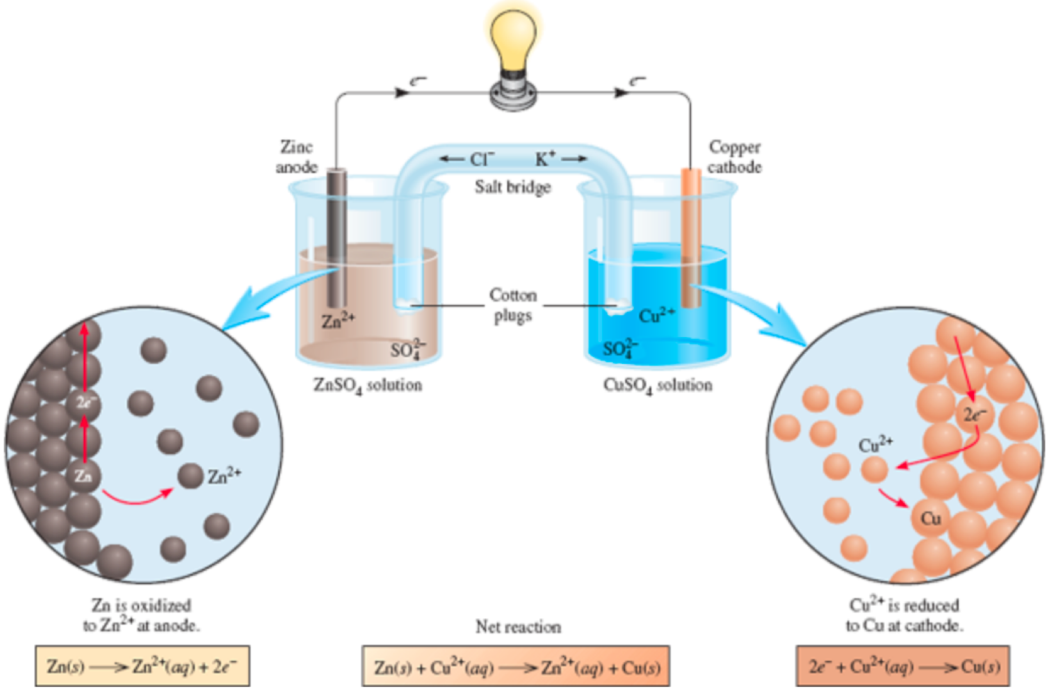
A galvanic cell uses the flow of electrons from a spontaneous reaction to do work.


Zn electrode in 1 M $ZnSO_4$ solution

Cu electrode in 1 M $CuSO_4$ solution

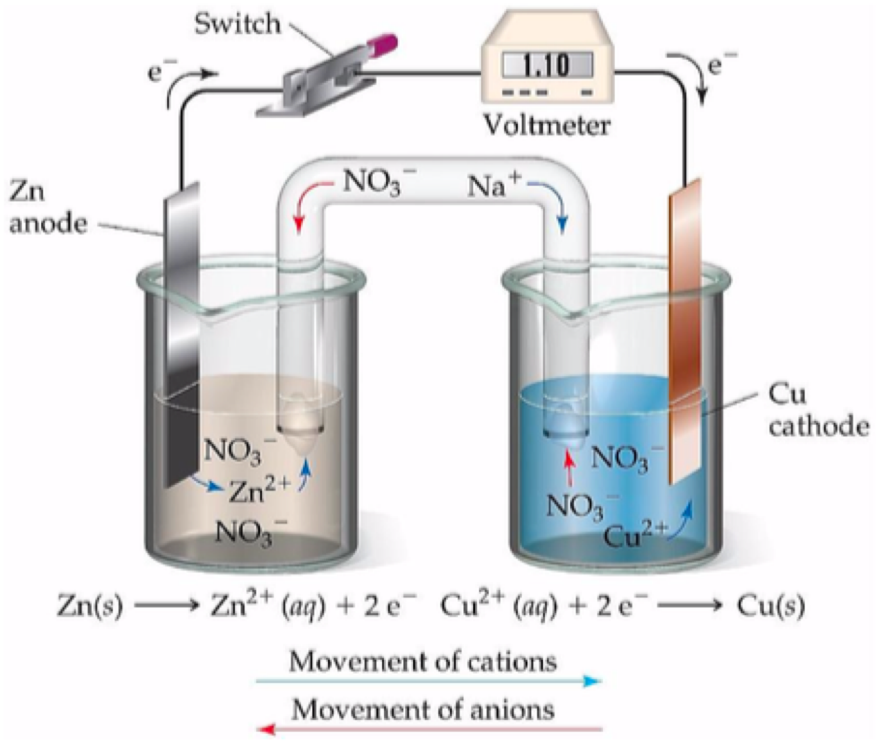
Solutions in contact with each other through porous glass disc

How Galvanic Cells Work



- Electrons leave the anode and flow through the wire to the cathode
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment
- As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode
- The electrons are taken by the cation, and the neutral metal is deposited on the cathode

How Galvanic Cells Work



- A salt bridge is used to prevent a charge imbalance from occurring and stopping the flow of electrons (keep the anode negative and the cathode positive)
  - Anions move toward the anode
  - Cations move toward the cathode

Shorthand Methods to Represent Galvanic Cells

Anode [O]: $Zn(s) \rightarrow Zn^{2+}(aq) + \cancel{2e^-}$

Cathode [R]: $Cu^{2+}(aq) + \cancel{2e^-} \rightarrow Cu(s)$

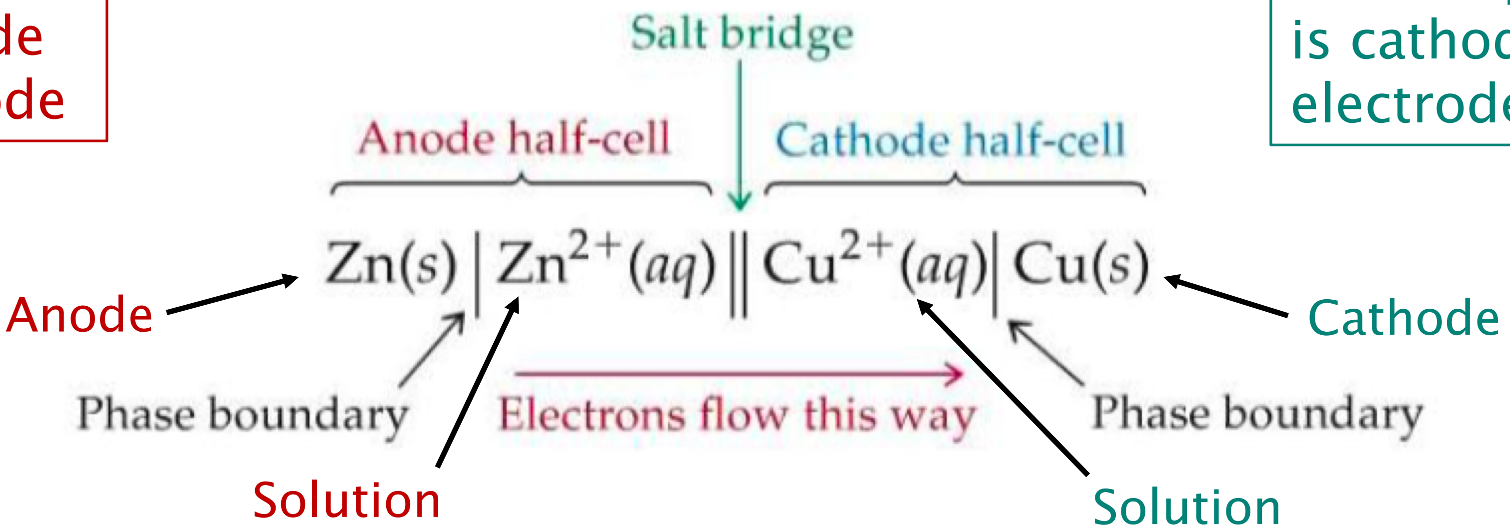
Net Reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Cell Diagram:

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

Solid Zinc is anode electrode

Solid Copper is cathode electrode



Galvanic Cells

A voltaic cell is constructed with one compartment consisting of an aluminum strip placed in a solution of $Al(NO_3)_3$, and the other has a nickel strip placed in a solution of $NiSO_4$. The overall cell reaction is:

$$2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$$

a.) What is being oxidized & what is being reduced?

b.) Write the half reactions that occur in the two electrode compartments.

c.) Indicate the signs of the electrodes.

d.) In which direction do the electrons flow?

e.) In which directions do the cations and anions migrate through the solution?

f.) Give the cell diagram for this voltaic cell.

Cell Potential (E_{cell}) [a.k.a cell voltage or electromotive force (emf)]

The potential difference between the anode and the cathode in a galvanic cell

- Measured in volts
- $E_{cell} > 0$ for a spontaneous reaction
- For 1M solutions or 1atm pressure for gases at 25°C, the standard cell potential is $E°_{cell}$.

Standard Reduction Potential (E°)

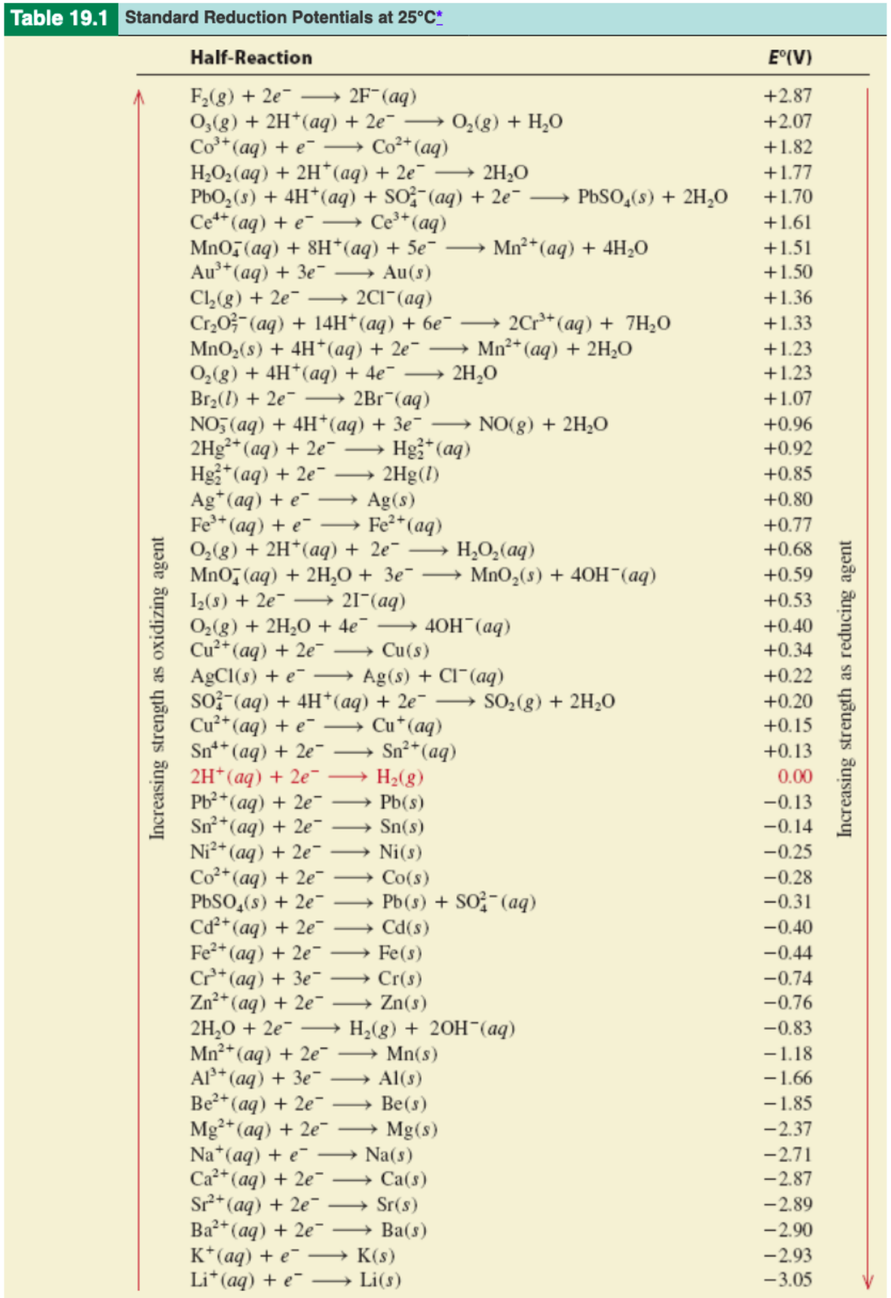


Table 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent

Increasing strength as reducing agent

The voltage associated with a reduction reaction at an electrode when all solutes are 1M & all gases are 1atm.

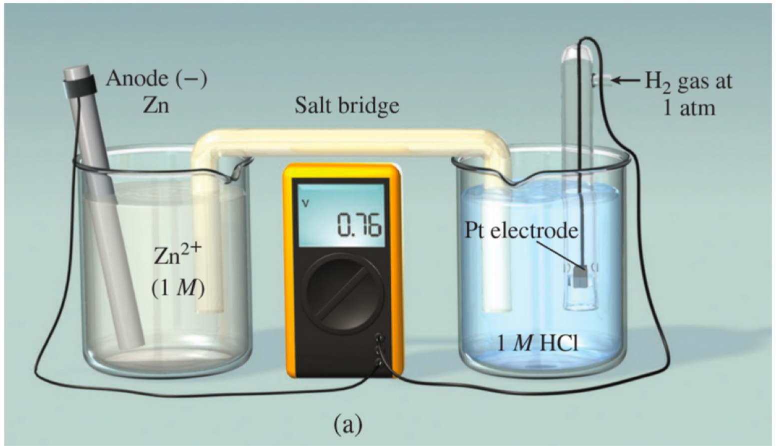
- E° is for the reaction as written in chart (reduction).
- The more positive E° the greater the tendency for the substance to be reduced.
- The half-cell reactions are reversible.
- The sign of E° changes when the reaction is reversed.
- The greater the difference between the E° of two electrodes, the greater the voltage of the cell.

Standard Reduction Potential (E°)

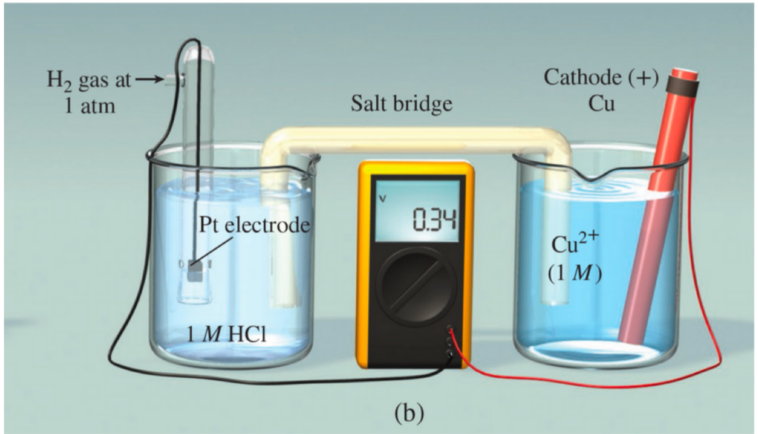
Standard Cell Potential: $E°_{cell} = E°_{cathode} - E°_{anode}$

E° for a given cathode or anode is determined using the Standard Hydrogen Electrode (SHE)

- E° for SHE is zero
- Reaction is $2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$
- Pt often used to provide a surface on which reduction takes place $(Zn(s)|Zn^{2+}(1M)||H^{+}(1M)|H_2(1atm)|Pt(s)$



SHE acting as cathode
$0.76V = 0 - E_{anode}$
$E°_{Zn^{2+}/Zn} = -0.76$



SHE acting as anode
$0.34V = E°_{cathode} - 0$
$E°_{Cu^{2+}/Cu} = +0.34$

Determining Cell Potentials ($E°_{cell}$)

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

Look up E° for each reaction in Table 19.1

Cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E° = +0.34V$

Anode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ $E° = -0.76V$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = 0.34V - (-0.76V) = +1.10V$$

For all spontaneous reactions at standard conditions $E°_{cell} > 0$

$E°_{cell} < 0$ = nonspontaneous (electrolytic cell)

Note that E° is an intensive property (changing stoichiometric coefficients doesn’t change E°)

Cell Potentials ($E°_{cell}$)

1.) Using data in Table 19.1, calculate the standard emf for a cell that employs the following overall cell reaction:

$$2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^-(aq)$$

A: 2.19V

2.) A voltaic cell is based on a Co/Co^{2+} half-cell and an Ag/AgCl half-cell.

(a) Write the half-cell reaction for each electrode.

(b) What is the standard cell potential (use Table 19.1)?

A: $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

0.50V

Cell Potentials ($E°_{cell}$)

3.) Will $Br_2(l)$ spontaneously oxidize $Fe^{2+}(aq)$?

4.) Will I^- spontaneously reduce $Cr^{3+}(aq)$ to the free metal?

Cell Diagrams

1.) Write the balanced equation for the given cell:

$$Pt(s)|Sn^{2+}(aq)|Sn^{4+}(aq)||Ag^{+}(aq)|Ag(s)$$

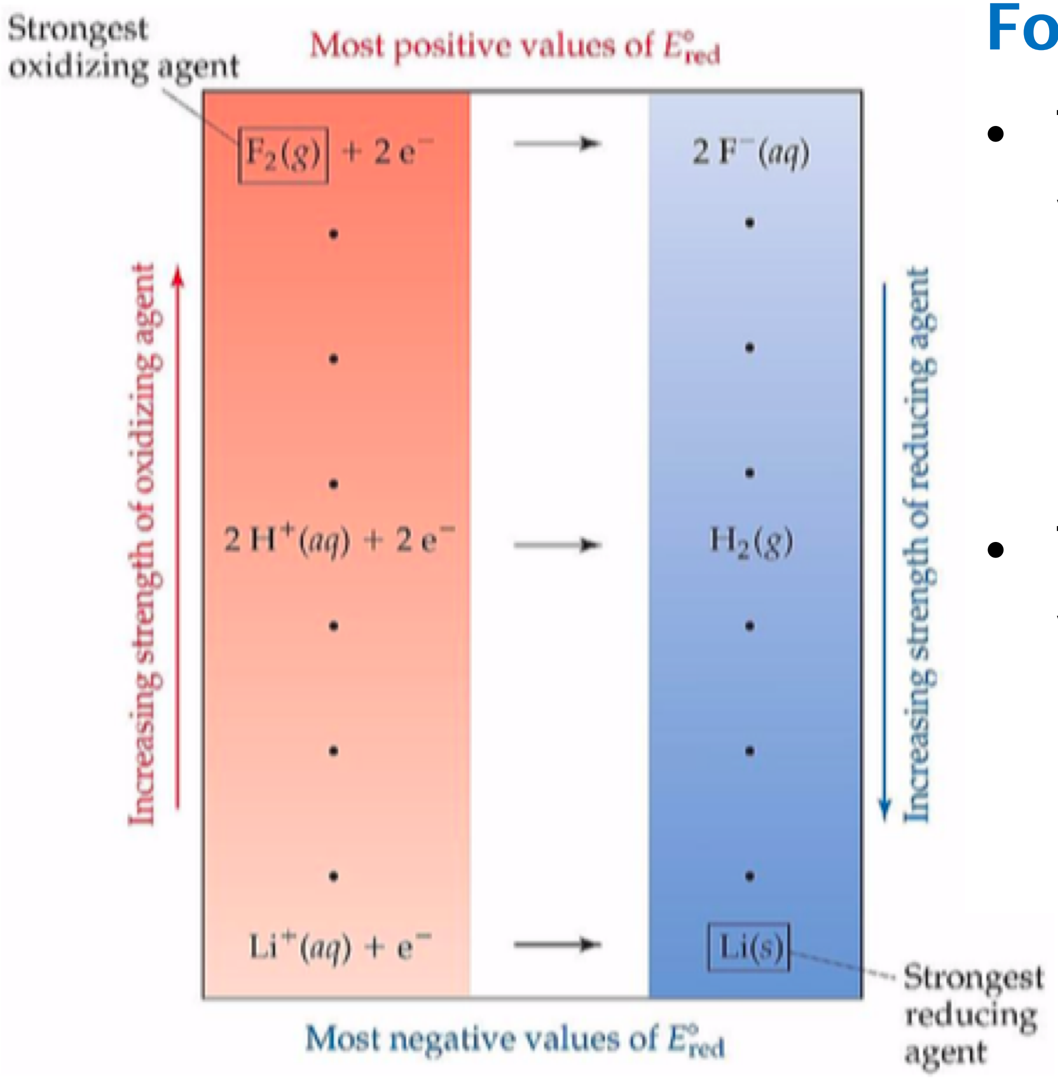
A: $Sn^{2+}(aq) + 2Ag^{+}(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$

2.) Give the shorthand notation for the following cell reaction with a graphite (carbon) cathode:

$$Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^{-}(aq)$$

A: $Cu(s)|Cu^{2+}(aq)||Cl_2(g)|Cl^{-}(aq)|C(s)$

Cell Potential & Redox



For a reduction half-rxn:

- The more positive the value of E°, the easier it is to reduce the reactant – the reactant is a stronger oxidizing agent
- The more negative the value of E°, the easier it is to oxidize the reactant – the reactant is a stronger reducing agent

Cell Potential & Redox

1.) Which of the following pairs of substances is the stronger reducing agent?

A: (a) Mg(s)
(b) Cr(s)

(a) Fe(s) or Mg(s)

(b) Cr(s) or Co(s)

Thermodynamics of Redox Reactions

We have already seen the connection between cell potential and spontaneity:

$$E° = E_{cathode} - E_{anode}$$

$$E° = E_{red} - E_{ox}$$

$E > 0$ = spontaneous **$E < 0$ = nonspontaneous**

There must also be a relationship between Gibbs Free Energy and cell potential. Since the movement of electrons allows work to be done by the cell, ΔG for a redox reaction can be found from the equation:

$$\Delta G = -nFE$$

n = number of moles of electrons transferred
F = Faraday's constant (amount of electrical charge on 1 mole of electrons; 1F = 96,485C/mol = 96,485J/V-mol)
E = cell potential

Since n & F are positive, if $E > 0$, then $\Delta G < 0$ – spontaneous!

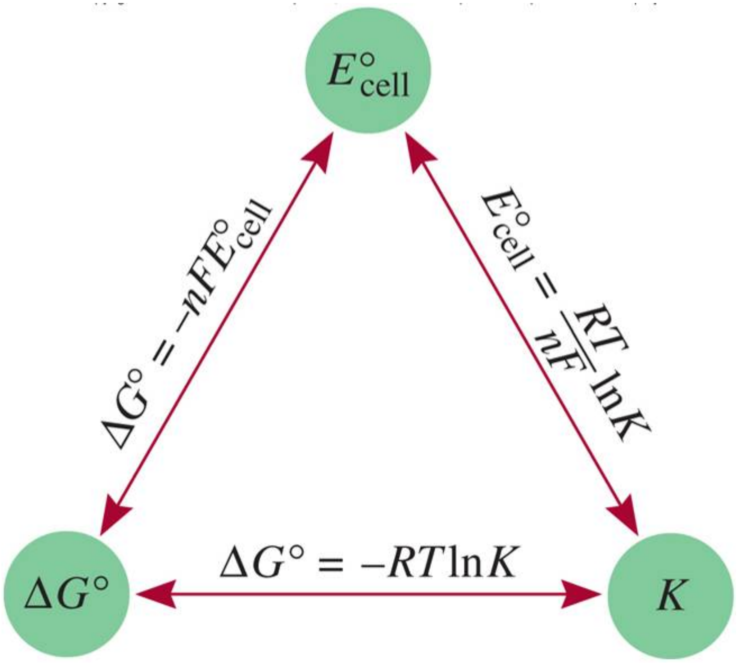
Thermodynamics of Redox Reactions

Since **$\Delta G^\circ = -RT\ln K$**, and under standard conditions **$\Delta G^\circ = -nFE^\circ$**, then

$$-RT\ln K = -nFE^\circ$$

$$E^\circ = (RT/nF)\ \ln K$$

For a Redox Reaction, Free Energy, Cell Potential, and the Equilibrium constant are all related!



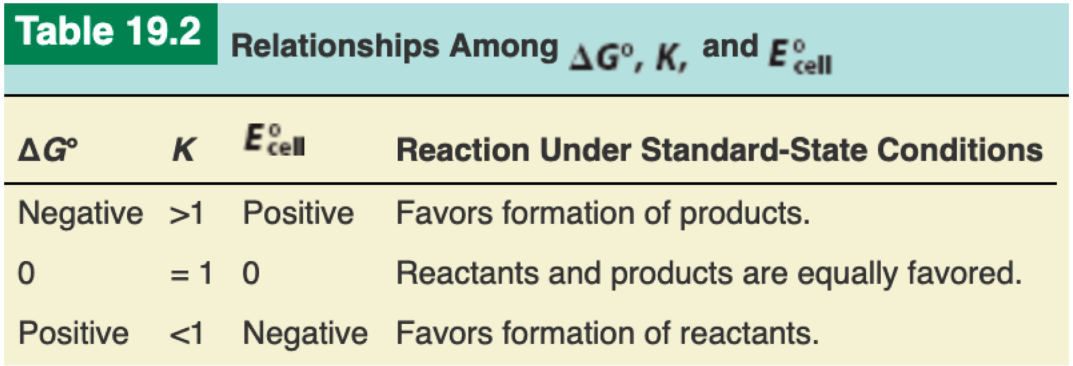


Table 19.2 Relationships Among ΔG°, K, and E°_{cell}

ΔG°	K	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	= 1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

Thermodynamics of Redox Reactions

1. What is the equilibrium constant at 25°C for the reaction:

$$\mathrm{Sn(s) + 2Cu^{2+}(aq) \longrightarrow Sn^{2+}(aq) + 2Cu^{+}(aq)}$$?

A: 6.4×10^{9}

Thermodynamics of Redox Reactions

2.) If the equilibrium constant for a two electron redox reaction at 298K is $1.5\text{x}10^{-4}$, calculate the corresponding $\Delta G°$ and $E°_{red}$.

A: $2.2\text{x}10^{4}$ J/mol;–0.11V

Cell Potentials at Nonstandard Conditions: The Nernst Equation

Free Energy at nonstandard conditions:

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

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

Therefore:

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

Dividing by $-nF$ gives the Nernst equation:

$$E = E^\circ_{cell} - (RT/nF)\ln Q$$

The Nernst can be used to evaluate the cell potential of systems that are not at 25°C and/or do not contain 1M solutions

The Nernst Equation

1. A voltaic cell utilizes the following reaction:

$2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^{-}(aq)$

(a) What is the E_{cell} under standard conditions?

(b) What is the E_{cell} when $[Al^{3+}] = 4.0\times10^{-3}M$ & $[I^{-}] = 0.010M$ (still at 298K)

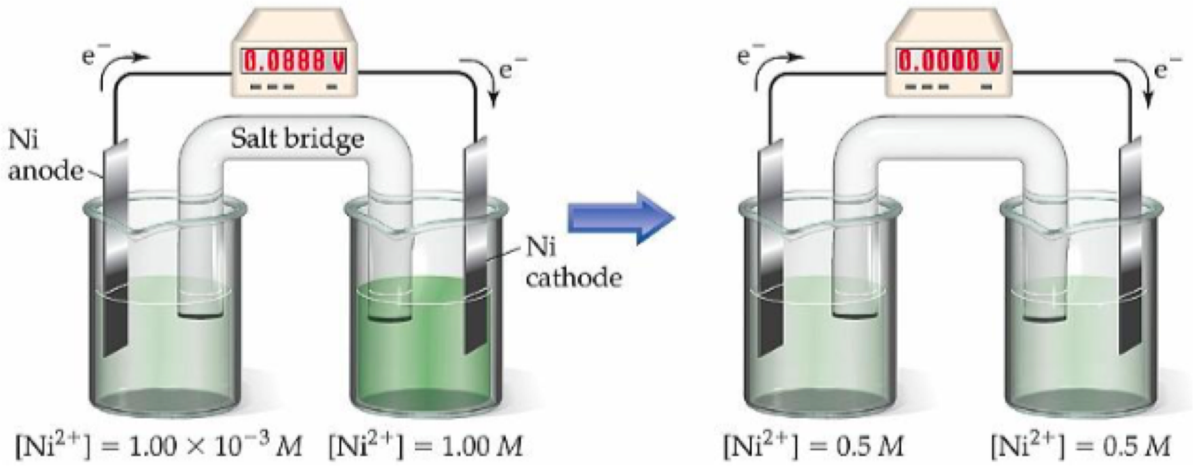
A:2.19V; 2.36V

Concentration Cells

Cells where the cell potential is generated entirely by a difference in concentration at the two electrodes (the ions present at the cathode and anode are the same)

Different Concentration:
Voltage
0.0888V

Same Concentration:
No voltage
(0.0000V)



$$Ni(s)\,|\,Ni^{2+}(0.001\ M)\,\|\,Ni^{2+}(1.00\ M)\,|\,Ni(s)$$

$$\text{Anode:}\quad \cancel{Ni(s)} \rightarrow Ni^{2+}(1.00 \times 10^{-3}\ M) + 2\,\cancel{e^-}$$

$$\text{Cathode:}\quad Ni^{2+}(1.00\ M) + 2\,\cancel{e^-} \rightarrow \cancel{Ni(s)}$$

$$Ni^{2+}(1.00\ M) \rightarrow Ni^{2+}\ (1.00 \times 10^{-3}\ M)$$

Concentration Cells

How are concentration cells possible?

For the voltage producing cell in the previous slide, the two concentrations of Ni^{2+} were 1.00M and 1.00×10^{-3}M.

Diffusion occurs naturally from high concentration to low concentration, so the process ("reaction") is:

$$Ni^{2+}(1.00M) \rightarrow Ni^{2+}(1.00 \times 10^{-3}M)$$

Using the Nernst equation:

$$E = E° - \frac{(8.314 J/molK)(298K)}{(2)(96{,}485 J/V\text{-}mol)} \ln \frac{[1.00 \times 10^{-3}]}{[1.00]}$$

$$E = 0V - [0.01284V \times (-6.908)] = 0.0887V$$

The voltage generated in this manner has physiological importance in systems such as the potassium ion system that controls nerve impulses.

Concentration Cells

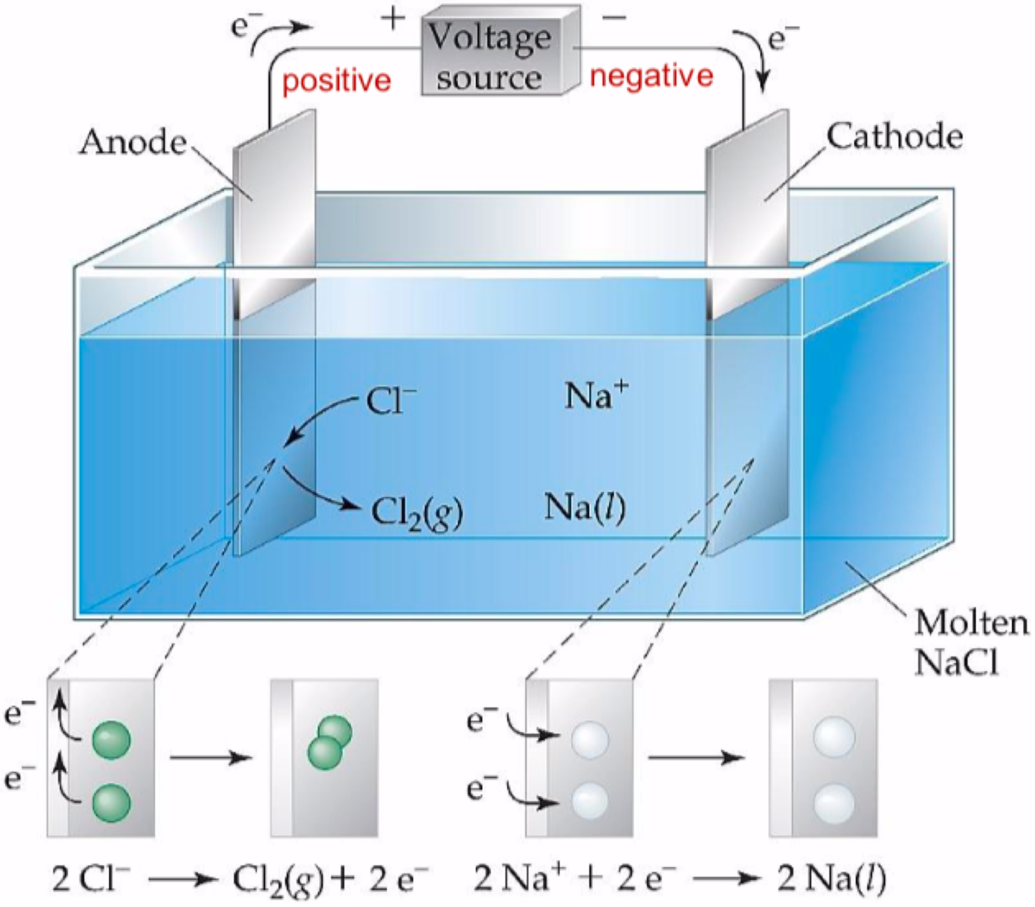
1. A concentration cell is constructed at 298K with two Zn(s)-Zn^{2+}(aq) half cells. One half-cell has a Zn^{2+} concentration of 1.35M, and the other has a Zn^{2+} concentration of 3.75×10^{-4}M. What is the cell potential?

Electrolysis

The process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur

Electrolysis takes place in electrolytic cells

- Electrons are forced to flow from the anode to the cathode



Electrolysis of Molten Salts

- Cation will be reduced, anion will be oxidized
  - Ex: $FeCl_3$ – Fe(s) formed at cathode, $Cl_2(g)$ at anode
- In mixtures of molten salts, the cation with the highest (most positive) reduction potential will be reduced.

Electrolysis of Aqueous Salts

- Redox reaction of water needs to be taken into account
- At the **cathode**, the reduction of H_2O will compete with reduction of the cation.
- Metal cation will only be reduced if it has a more positive reduction potential than water.
  - Ex: Electrolysis of $CaBr_2(aq)$:

$$2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{red} = -0.83V$$

$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad E^\circ_{red} = -2.87V$$

H_2 will be produced, not Ca(s)

Electrolysis of Aqueous Salts con't

- Redox reaction of water also needs to be taken into account at the anode
- At the **anode**, the oxidation of H_2O will compete with oxidation of the anion.
- The anion will only be oxidized if it has a more positive oxidation potential than water.
- Note that oxidation potential of an ion is the reduction potential with the opposite sign (not true for water).
  - Ex: Electrolysis of $CaBr_2(aq)$:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad E°_{ox} = -1.23V$

$2Br^- (aq) \rightarrow Br_2(l) + 2e^-$ $\quad E°_{ox} = -1.07V$

Br_2 will be produced instead of O_2

- Under acidic conditions, oxidation of H^+ must also be considered.

Electrolysis

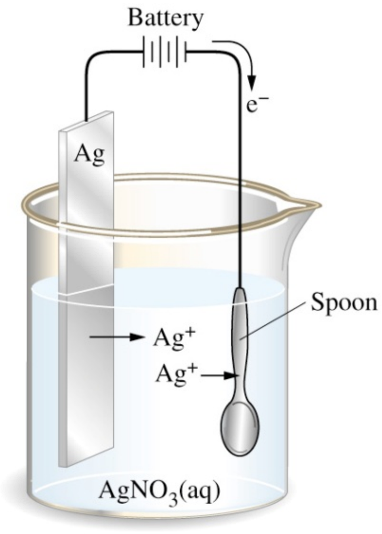
1.) A 1M aqueous solution of iron (II) chloride is electrolyzed. What are the products? $Fe(s)$, $O_2(g)$, $H^+(aq)$

2.) A 1M solution of potassium iodide is electrolyzed under acidic conditions. What are the products? $H_2(g)$, $I_2(s)$

Producing Products by Electrolysis

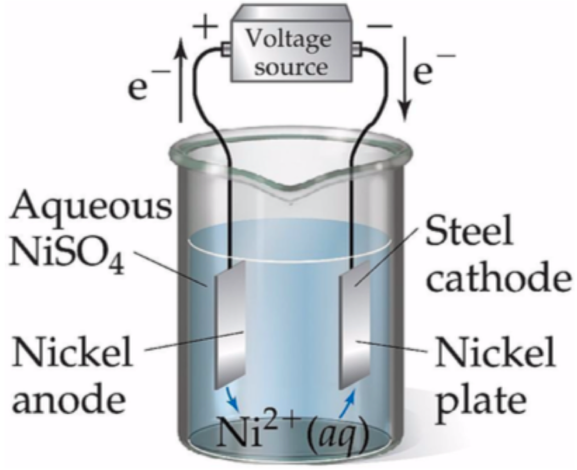
Electroplating:

- Coating one metal onto another
- Often silver or gold over iron or steel
- Cheaper/more durable product
- Method of protecting materials from corrosion
- **Ex: plating nickel**
  - Ni^{2+} preferentially reduced at cathode
  - Ni plates onto the inert electrode



Cathode (steel strip): $Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$ $E^\circ_{red} = -0.28\ V$

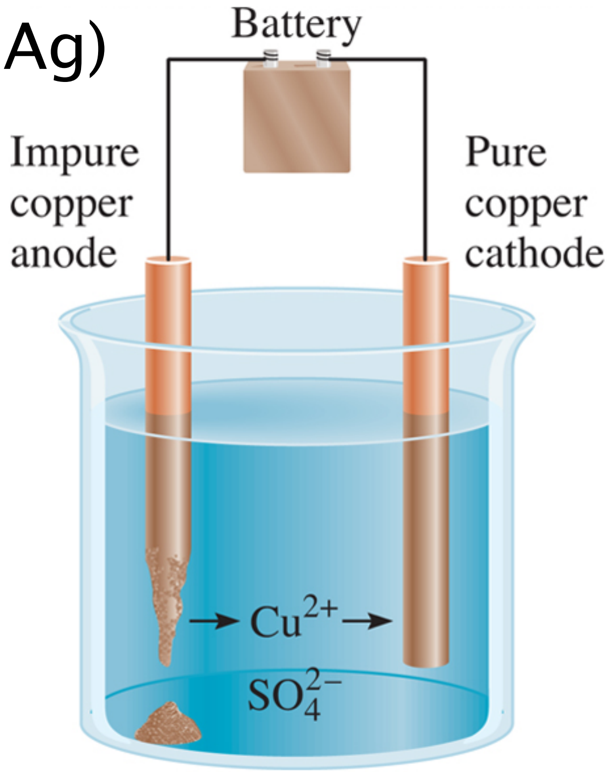
Anode (nickel strip): $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$ $E^\circ_{red} = -0.28\ V$



Producing Products by Electrolysis

Purification:

- Impure metal anode (ex: copper)
- More reactive impurities are oxidized
- Less reactive impurities fall to bottom
  - Isolate unreactive metals (Au, Ag)
- Build up pure metal on cathode
  - Copper up to 99.5% pure



Producing Products by Electrolysis

Amount of material produced through or consumed in electrolysis depends on amount of electrical charge that is used.

Coulomb: Amount of charge passing a point in a circuit in 1 second when the current is 1 ampere (A).

Coulomb = I•t

C = coulomb
I = current in amperes
t = time in seconds

nF = At

n = # moles electrons*
F = Faraday's constant
A = current in amperes
t = time in seconds

96,485C = charge on one mole of electrons = 1 Faraday

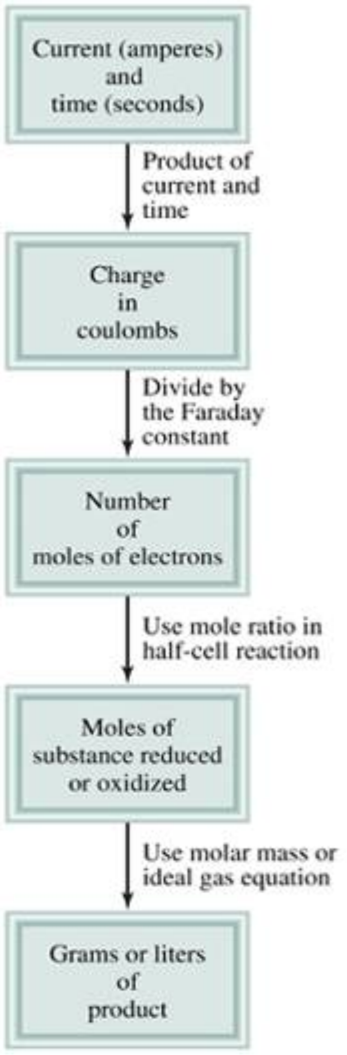
Faraday's constant = 96485 C/mol

* Connect refers to n as the number of Faradays

Producing Products by Electrolysis

1.) How many grams of Ca(s) will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

A: 0.51g



Producing Products by Electrolysis

2.) Water is electrolyzed in a cell at 25mA for 15 minutes. How many mL of oxygen gas are produced at 1.0 atm and 25°C?

A: 1.4mL

Producing Products by Electrolysis

3.) How many minutes are needed to plate out 25.00g Mg from molten $MgCl_2$ using 3.50 A of current?

A: 945 min

Electrical Work

Free Energy (ΔG) is a measure of the maximum amount of work that can be obtained from a system, $\Delta G = w_{max}$. Since $\Delta G = -nFE$,

$$w_{max} = -nFE$$

- The cell potential can be thought of as a measure of the driving force for a redox process.
- For a voltaic cell (spontaneous), E_{cell} is positive and w_{max} is negative (work is done by the system on the surroundings).
- For an electrolytic cell (nonspontaneous), the external electromotive force must be greater than E_{cell} to cause the redox reaction to occur.
  - w for an electrolytic cell is positive because work is being done by the surroundings on the system.

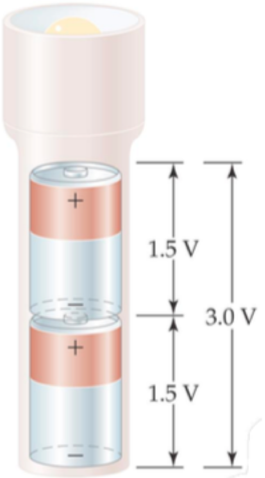
Electrical Work

1.) Consider the voltaic cell which is based on the cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Under standard conditions, what is the maximum electrical work, in Joules, that the cell can accomplish if 50.0g of copper is plated out?

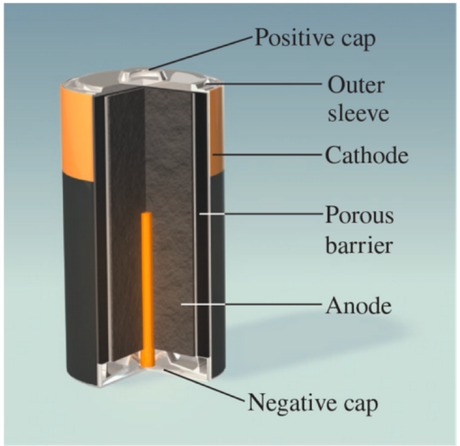
A: -1.67×10^5 J

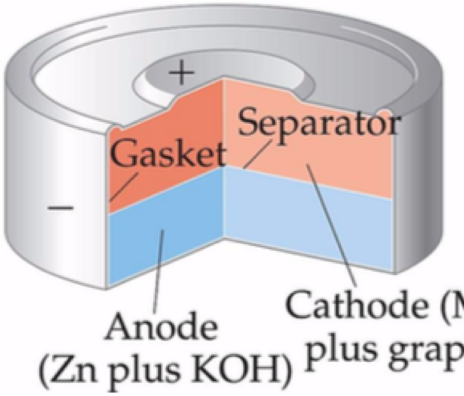
Batteries

A Battery is a self-contained electrochemical power source consisting of one or more voltaic cells.



The cells can be connected in a series to produce a voltage that is the sum of the cell potentials of each individual cell.





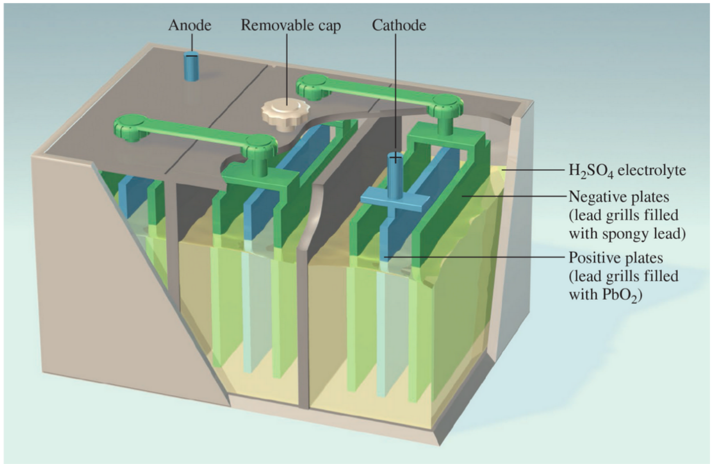
Alkaline Battery:

Most common non-rechargeable battery

- Irreversible reaction
- Reported voltage: +1.5V
- Anode: $Zn(s) + 2\ OH^{-}(aq) \rightarrow Zn(OH)_2 + 2e^{-}$
- Cathode: $2MnO_2(s) + 2H_2O(l) + 2e^{-} \rightarrow 2MnO(OH)(s) + 2OH^{-}(aq)$

Batteries

Lead Storage:



- Car & boat batteries
- Reversible reaction – reaction reverses when engine is running
- Reported voltage: +2.0V/cell Usually 6 cells = 12V
- Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
- Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Lithium Ion Battery:

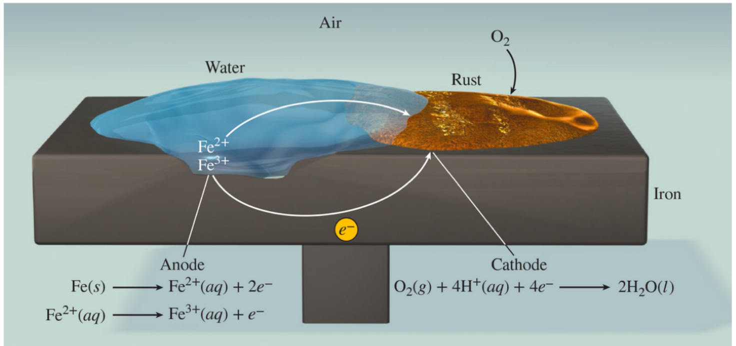
- Smartphones, cameras, laptops, etc. Rechargeable!
- Reported voltage: +3.4V
- Anode: $Li(s) \rightarrow Li^+ + e^-$
- Cathode: $Li^+ + CoO_2 + e^- \rightarrow LiCoO_2\,(s)$

Corrosion

A spontaneous redox reaction in which a metal is attacked by some substance in its environment converting it into an unwanted compound.

Deterioration of metal through an electrochemical process.

Products often referred to as rust, tarnish, or patina.



Ex: Rusting of iron

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E°_{red} = 1.23V$

Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ $E°_{red} = -0.44V$

$E°_{red}(Fe^{2+}) < E°_{red}(O_2)$

- Iron can be reduced by O_2
- Dissolved O_2 in water usually causes the oxidation of iron
- Fe^{2+} is further oxidized to the Fe^{3+} in rust (Fe_2O_3)

Corrosion Prevention

Cathodic protection – protection of a metal by making it the cathode

- Corrosion of iron can be prevented by coating iron with paint or other metals
  - Galvanized iron – coated with zinc
  - Zinc is easier to oxidize than iron
  - Zn^{2+} $E°_{red} = -0.763V$; Fe^{2+} $E°_{red} = -0.440V$
  - Zinc becomes the sacrificial anode
- Same reason “zincs” are added to the propeller shafts on boats