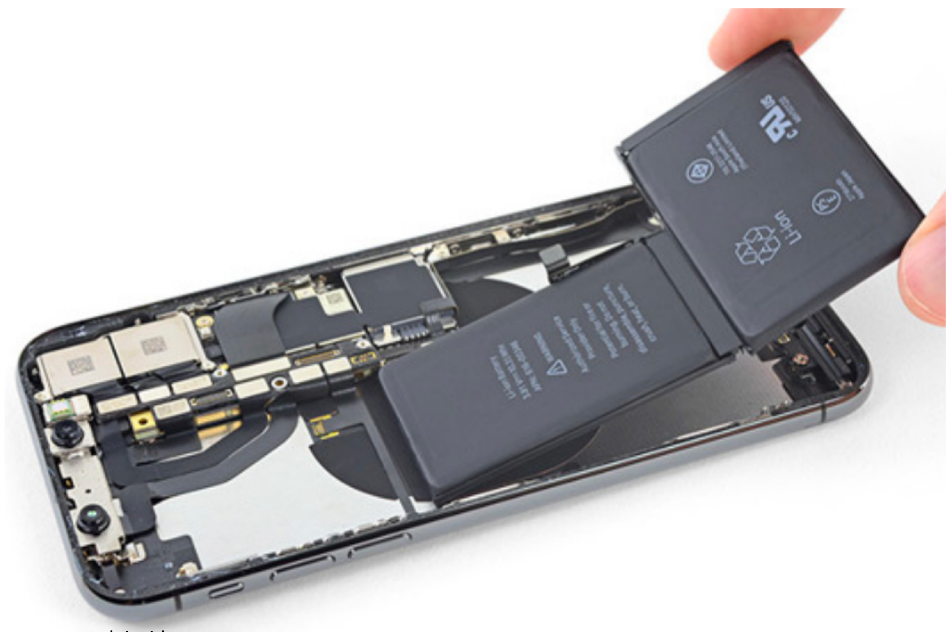
Chapter 19

Redox Reactions & Electrochemistry



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Electrochemistry

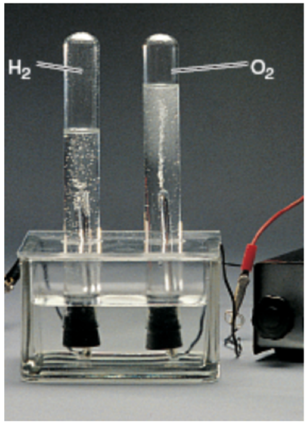
Branch of chemistry that deals with the relationships between electricity & chemical reactions

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.

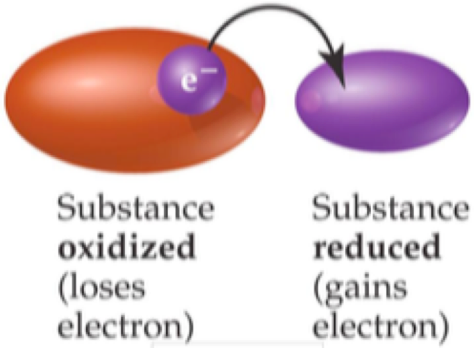
Can be used to monitor reactions by controlling electron transfer

- 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

OIL RIG

Oxidation
Is
Loss

Reduction
Is
Gain

Oxidation Number Rules

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 positive)

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 8B	9 8B	10 8B	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

$$\overset{0}{4\,Na} + \overset{0}{O_2} \rightarrow 2\,\overset{+1}{Na_2}\overset{-2}{O}$$

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^{+} – <u>reducing agent</u>

Reduction:

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

Oxidizing & Reducing Agents

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

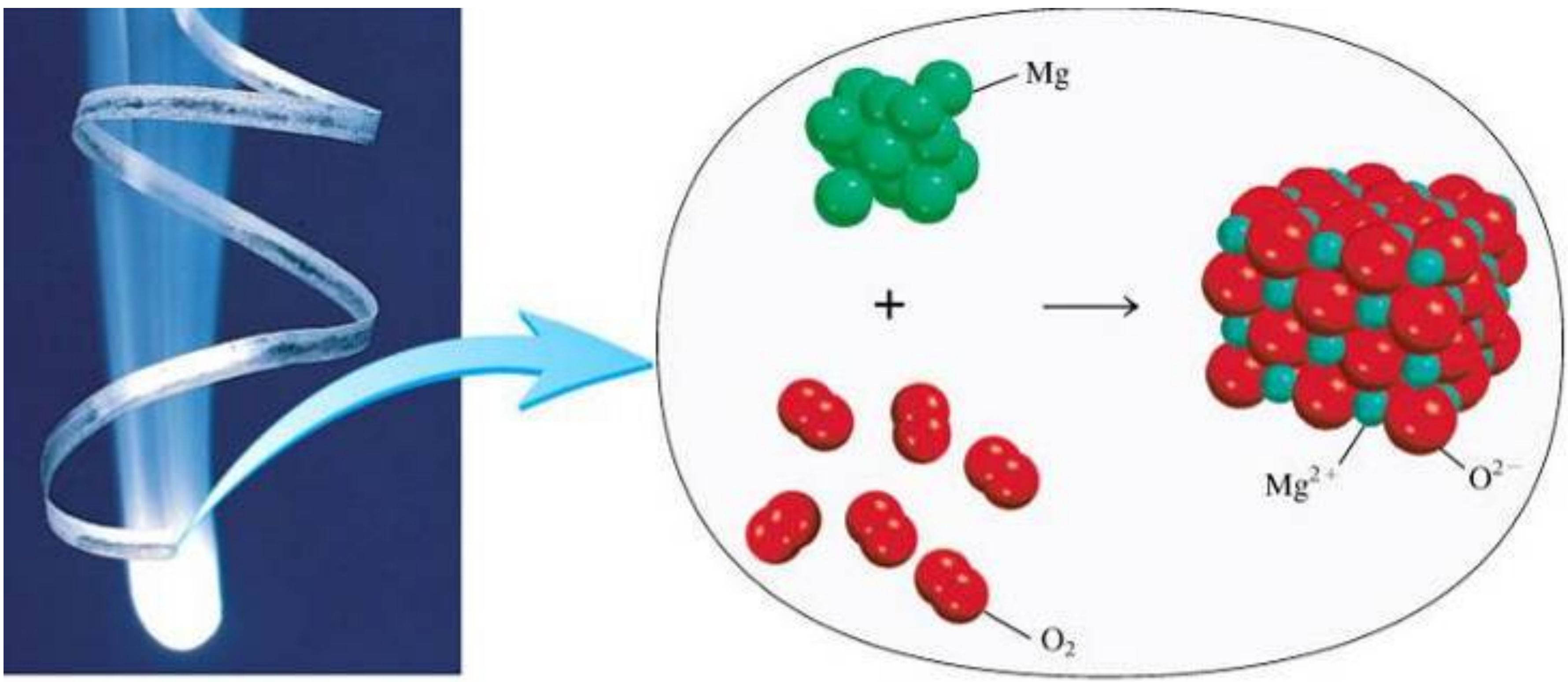
$$Cd(s) + NiO_2(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Redox Reaction: Half-reactions

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

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

Sum of half-reactions: $Mg\,(s) + 1/2O_2(g) \rightarrow MgO(s)$



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.

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

3. Balance each half-reaction.

   a. Balance elements other than H & O first

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

   b. Balance O by adding H_2O.

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

   c. Balance H by adding H^+.

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

Balancing Redox Reactions (Acidic)

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

4. Add in the electrons

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

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

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

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.

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

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

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.

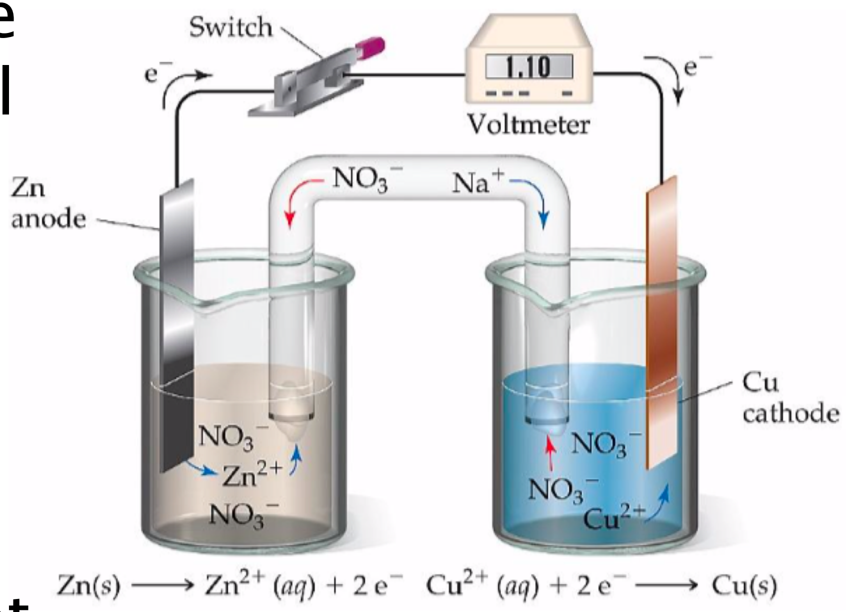
$$NO_2^-(aq) + Al(s) \rightarrow NH_3(aq) + Al(OH)_4^-(aq)$$

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

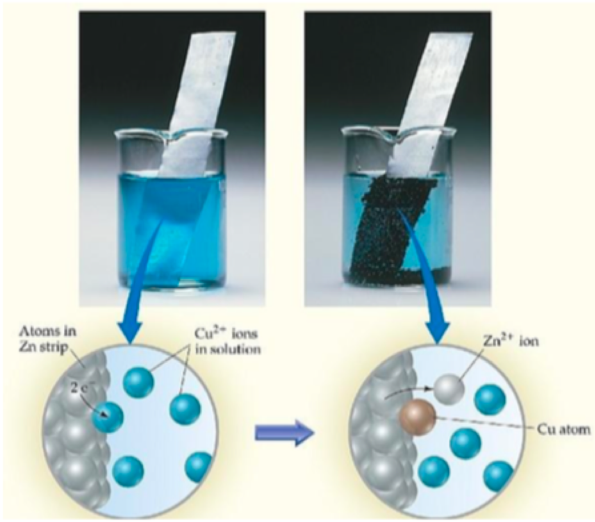
Metal Wires:

- 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



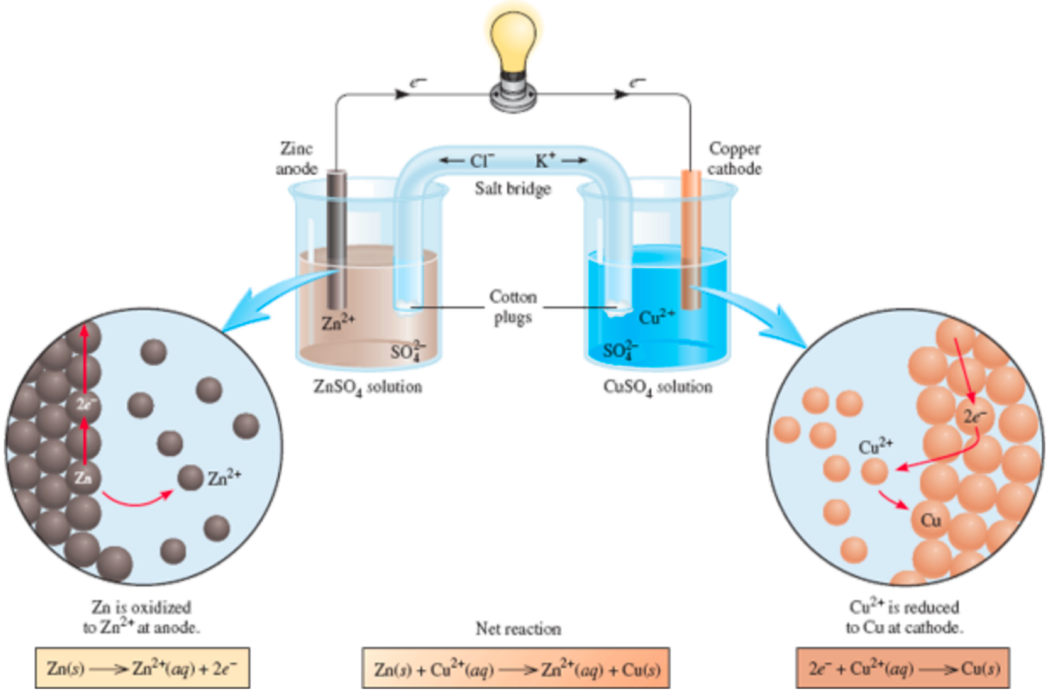
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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.

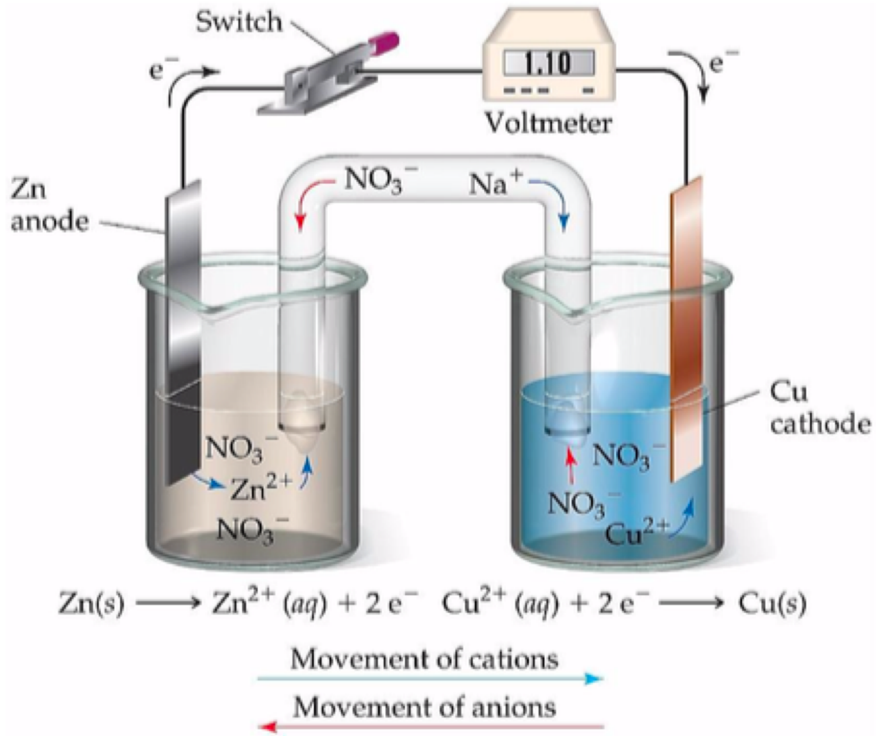
A galvanic cell uses the flow of electrons from a spontaneous reaction to do work.

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

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

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

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

Cell Diagram:

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

Solid Zinc is anode electrode

Solid Copper is cathode electrode

Salt bridge

$$\overbrace{Zn(s)\,|\,Zn^{2+}(aq)}^{\text{Anode half-cell}}\;\|\;\overbrace{Cu^{2+}(aq)\,|\,Cu(s)}^{\text{Cathode half-cell}}$$

Anode

Cathode

Phase boundary

Electrons flow this way $\longrightarrow$

Phase boundary

Solution

Solution

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.

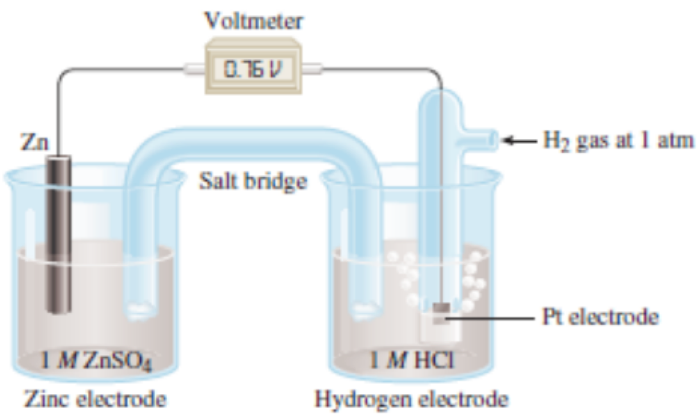
- E° is for the reaction as written (reduction).
- The more positive E° the greater the tendency for the substance to be reduced.
- The half-cell reactions are reversible.
- The sign of E° changes when the reaction is reversed.
- The greater the difference between the E° of two electrodes, the greater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

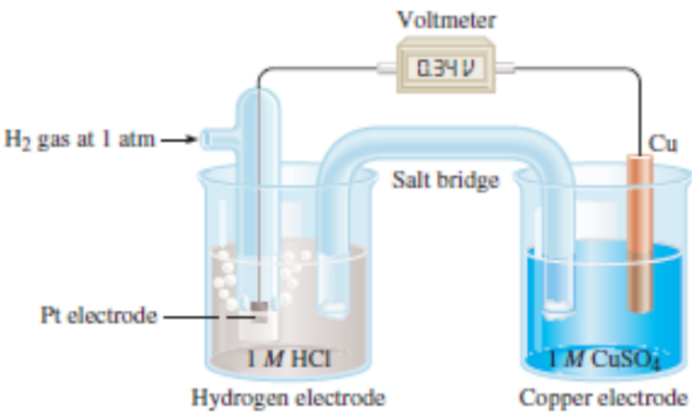
Standard Reduction Potential (E°)

Standard Cell Potential: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

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

$0.76V = 0 - E_{anode}$

$E^\circ_{Zn^{2+}/Zn} = -0.76$

SHE acting as anode

$0.34V = E^\circ_{cathode} - 0$

$E^\circ_{Cu^{2+}/Cu} = +0.34$

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

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

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = 0.34V - (-0.76V) = +1.10V$$

For all spontaneous reactions at standard conditions $E^\circ_{cell} > 0$

$E^\circ_{cell} < 0$ = 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 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: $Cu(s)|Cu^{2+}(aq)||Cl_2(g)|Cl^{-}(aq)|C(s)$