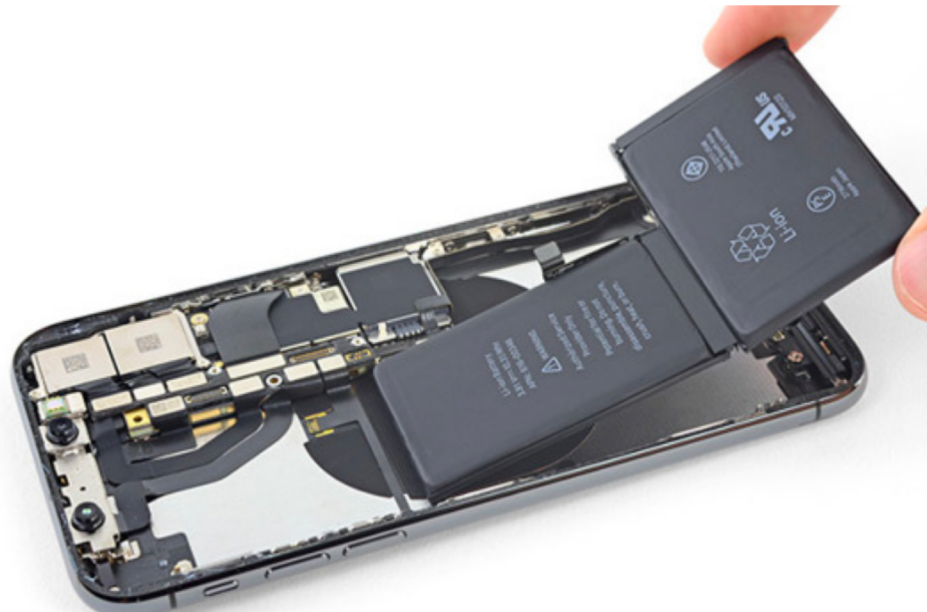


# Chapter 19

## Electrochemistry



appleinsider.com

# Electrochemistry

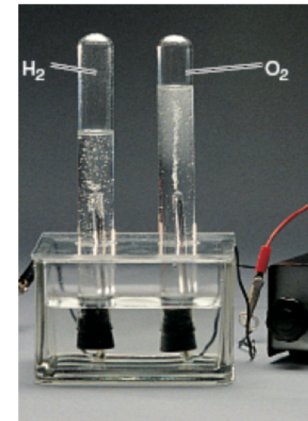
Branch of chemistry that deals with the relationships between electricity & chemical reactions

**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**

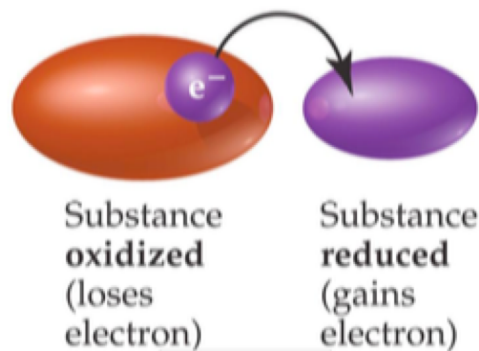
- Reaction progress (kinetics)
- Composition at equilibrium
- Energy changes (thermodynamics)



# 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**

**L**ose  
**E**lectrons  
**O**xidation

**GER**

**G**ain  
**E**lectrons  
**R**eduction

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## OIL RIG

**O**xidation  
**I**s  
**L**oss

**R**eduction  
**I**s  
**G**ain

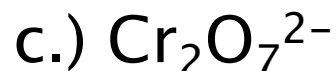
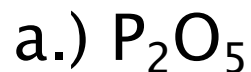
# Oxidation Number Rules

**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 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:



# Elemental Oxidation Numbers

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

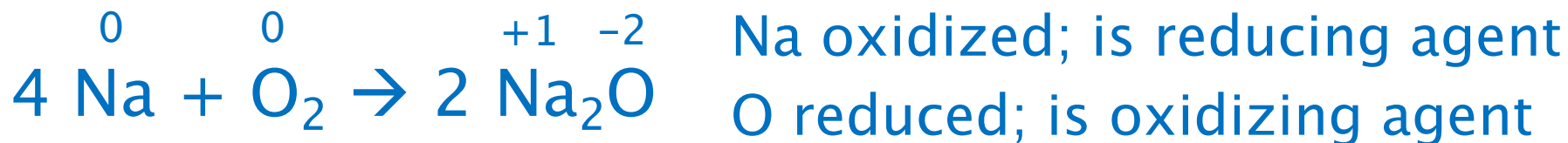
# Oxidizing and Reducing Agents

## Oxidizing agent: reactant that promotes oxidation

- Oxidation = loss of electrons
- Oxidizing agent takes  $e^-$  from other species  $\rightarrow$  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  $e^- \rightarrow$  is oxidized!
- Characteristic of an active metal, such as sodium.
- Low ionization energy: easily loses electrons





# Oxidation and Reduction



## Oxidation:

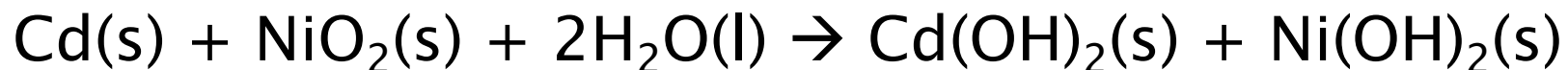
- Zinc loses two electrons (0 to +2)
- Becomes more positive = oxidized
- Zinc gives the electrons to  $\text{H}^+$  - reducing agent

## 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:



# Redox Reaction: Half-reactions

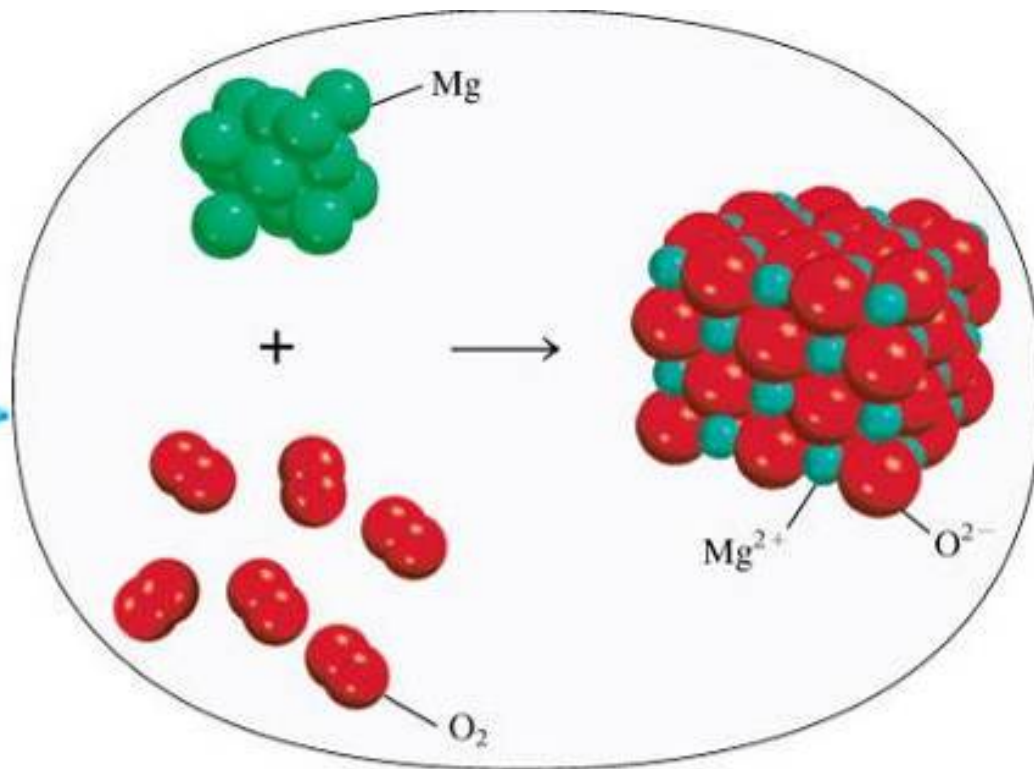
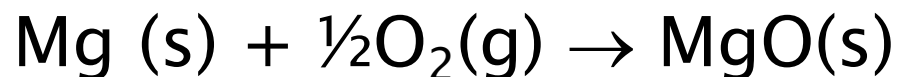
Oxidation half-reaction:



Reduction half-reaction:

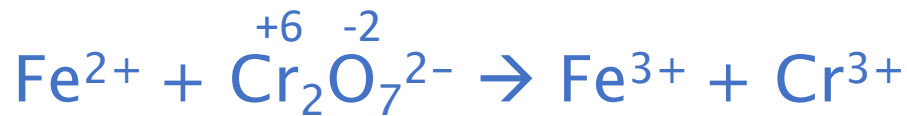


Sum of half-reactions:



# Balancing Redox Reactions (Acidic)

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



2. Write the oxidation and reduction half reactions.



3. Balance each half-reaction.

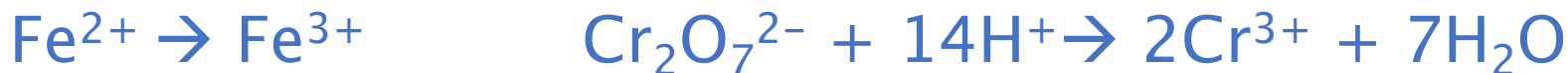
- a. Balance elements other than H & O first



- b. Balance O by adding H<sub>2</sub>O.



- c. Balance H by adding H<sup>+</sup>.



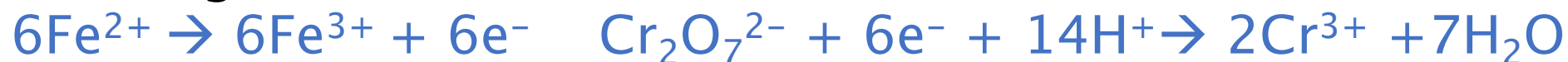
## Balancing Redox Reactions (Acidic)

From step 3:  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$        $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

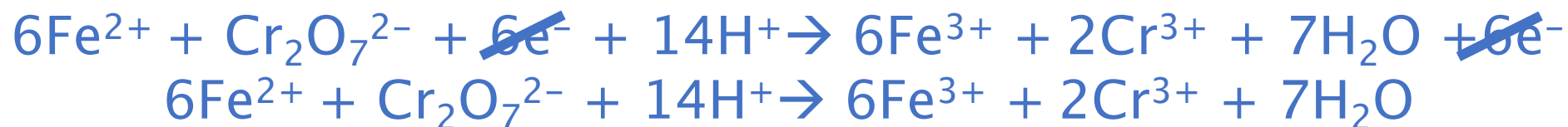
4. Add in the electrons



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



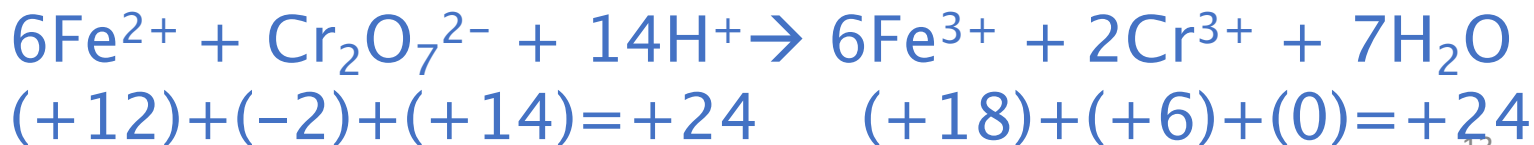
6. Add the half-reactions, subtracting things that appear on both sides.



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.



# Balancing Redox Reactions in Acidic Solution

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



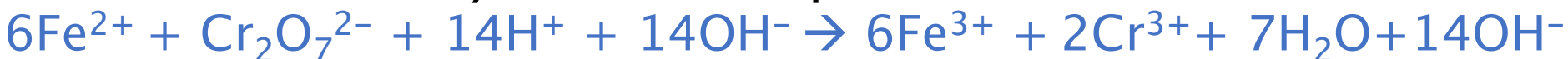
# Balancing Redox Reactions (Basic)

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

balanced eq. from slide 13:



2. Once the equation is balanced, add  $\text{OH}^-$  to each side to “neutralize” any  $\text{H}^+$  in the equation.



3. Combine  $\text{OH}^-$  and  $\text{H}^+$  to make  $\text{H}_2\text{O}$ .



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



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.





# Electrochemical Cells: Parts

## Ionic Solutions:

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

## Electrodes:

- Anode: oxidation occurs
- Cathode: reduction occurs

## Salt Bridge:

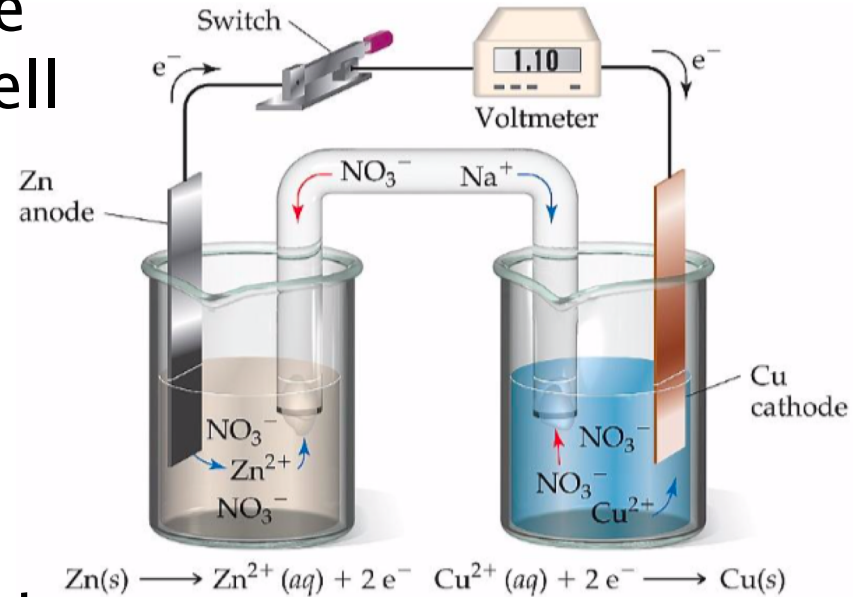
- Keeps 2 half-cells connected
- Ions flow but solution does not

## Metal Wires:

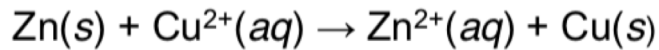
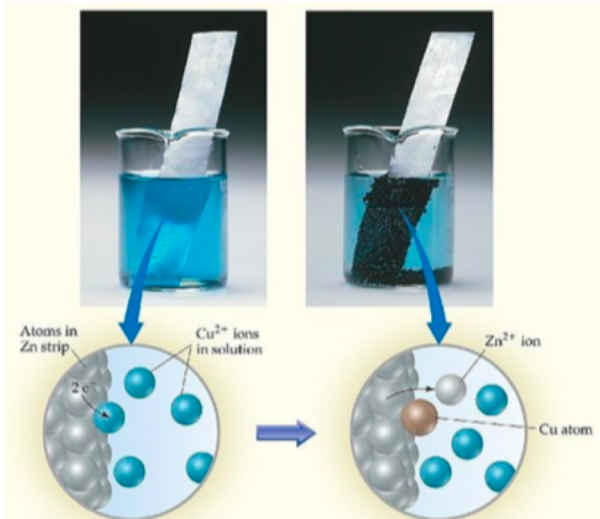
- Connect the electrodes to the terminals of the voltmeter
- Provide way to transport electrons between electrodes

## Voltmeter

- Measures the electron flow in the system



# Galvanic (aka Voltaic) Cell



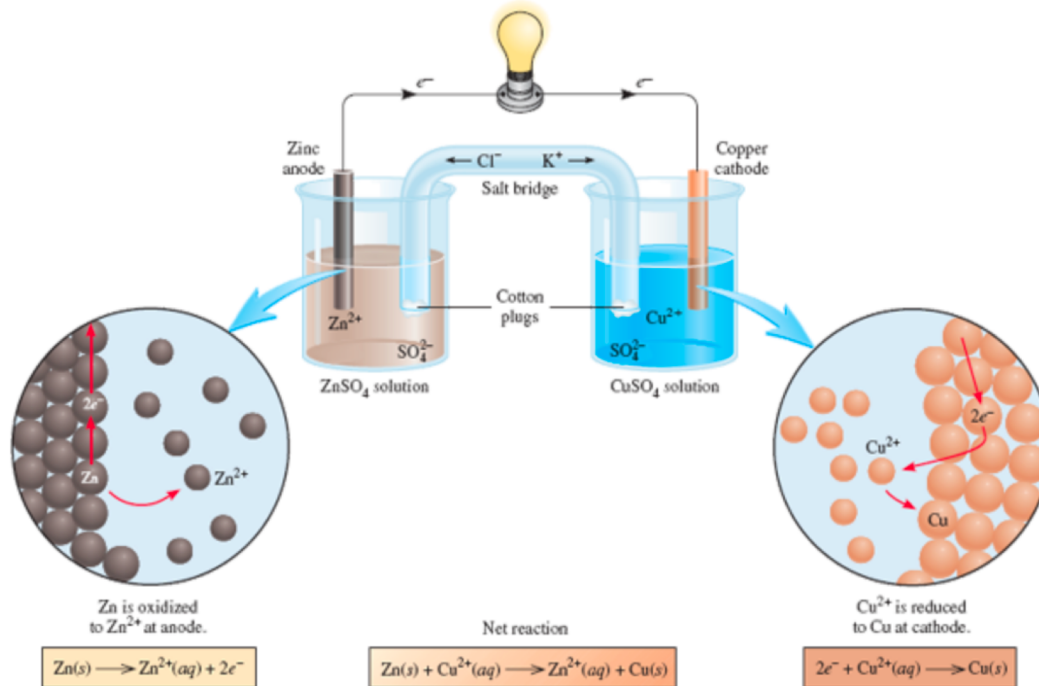
In spontaneous redox reactions, electrons are transferred – this releases energy

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



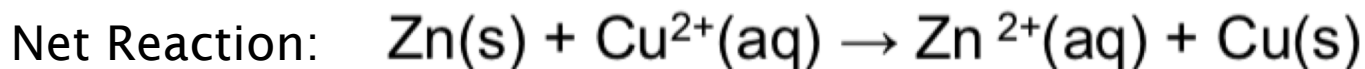
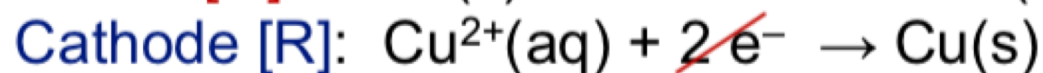
- Electrons leave the anode and flow through the wire to the cathode
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment
- As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode
- The electrons are taken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

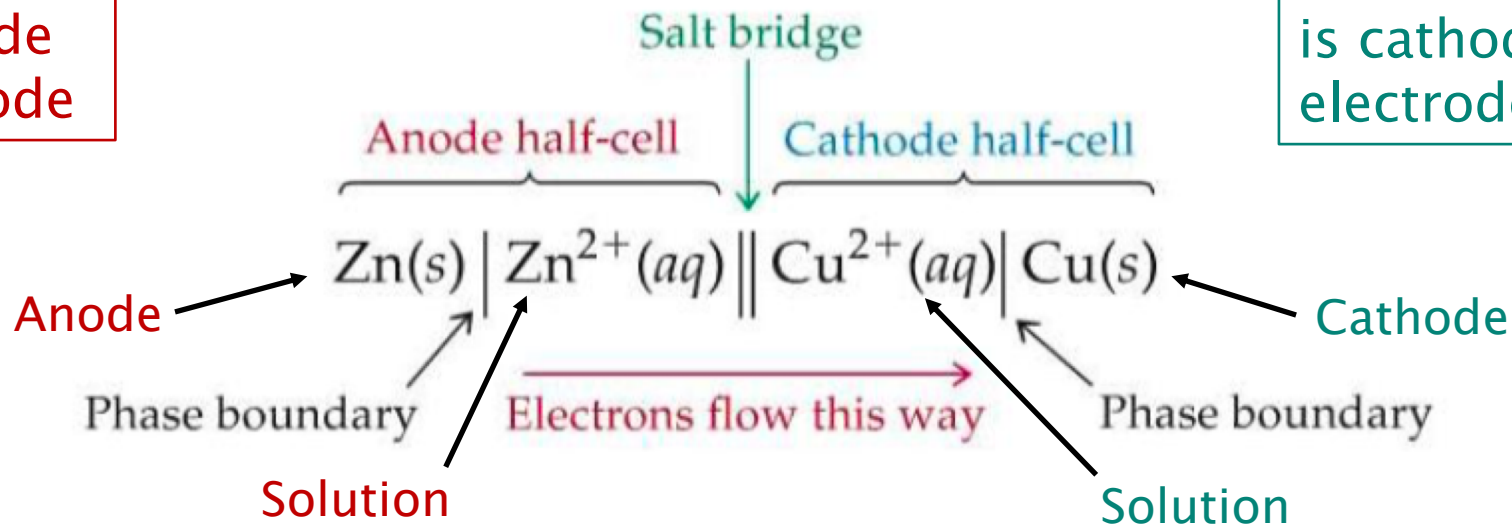


Cell Diagram:



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  $\text{Al}(\text{NO}_3)_3$ , and the other has a nickel strip placed in a solution of  $\text{NiSO}_4$ . The overall cell reaction is:



- 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 ( $E_{\text{cell}}$ ) [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
- $E_{\text{cell}} > 0$  for a spontaneous reaction
- For 1M solutions or 1atm pressure for gases at 25°C, the standard cell potential is  $E^{\circ}_{\text{cell}}$ .

# 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
$2Hg_2^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+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.

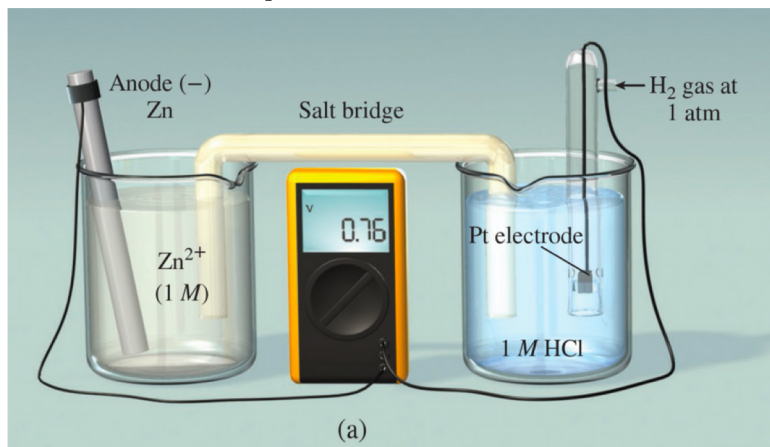


# Standard Reduction Potential ( $E^\circ$ )

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

$E^\circ$  for a given cathode or anode is determined using the Standard Hydrogen Electrode (SHE)

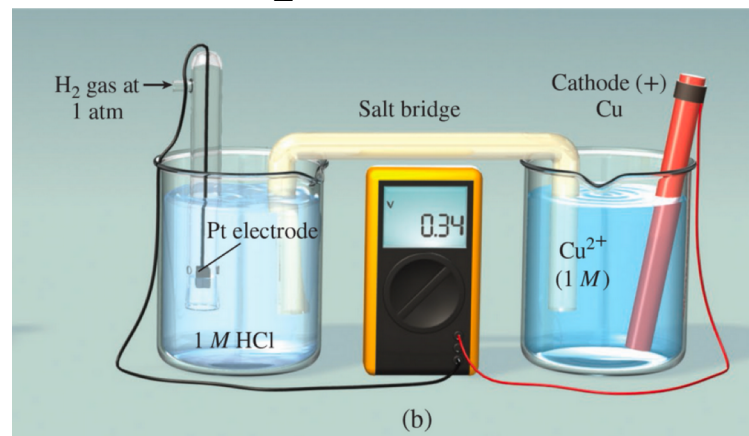
- $E^\circ$  for SHE is zero
- Reaction is  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
- Pt often used to provide a surface on which reduction takes place ( $\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{1M})||\text{H}^+(\text{1M})|\text{H}_2(\text{1atm})|\text{Pt}(\text{s})$ )



SHE acting as cathode

$$0.76\text{V} = 0 - E_{\text{anode}}$$

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



SHE acting as anode

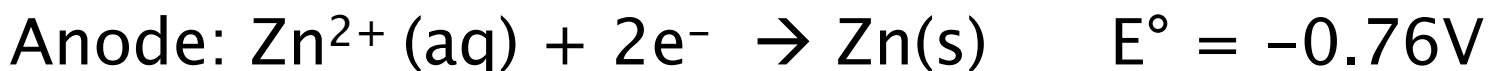
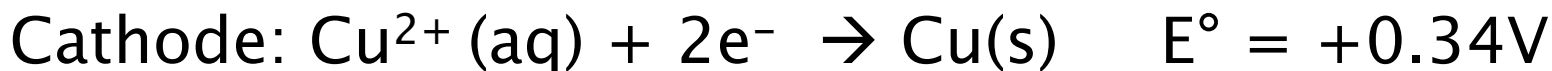
$$0.34\text{V} = E^\circ_{\text{cathode}} - 0$$

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

# Cell Potentials ( $E^\circ_{\text{cell}}$ )



Look up  $E^\circ$  for each reaction in Table 19.1



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

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

**For all spontaneous reactions at standard conditions**

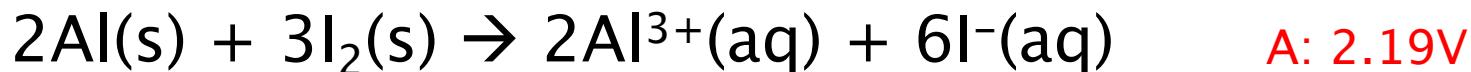
$$E^\circ_{\text{cell}} > 0$$

$E^\circ_{\text{cell}} < 0 = \text{nonspontaneous (electrolytic cell)}$

**Note that  $E^\circ$  is an intensive property (changing stoichiometric coefficients doesn't change  $E^\circ$ )**

# Cell Potentials ( $E^\circ_{\text{cell}}$ )

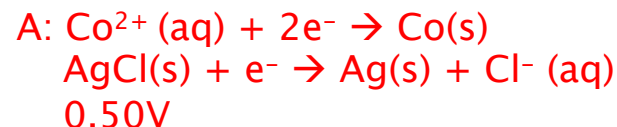
1.) Using data in Table 19.1, calculate the standard emf for a cell that employs the following overall cell reaction:



2.) A voltaic cell is based on a Co/Co<sup>2+</sup> 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)?



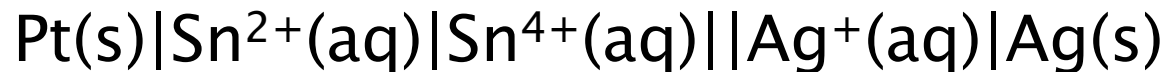
# Cell Potentials ( $E^\circ_{\text{cell}}$ )

3.) Will  $\text{Br}_2(\text{l})$  spontaneously oxidize  $\text{Fe}^{2+}(\text{aq})$ ?

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

# Cell Diagrams

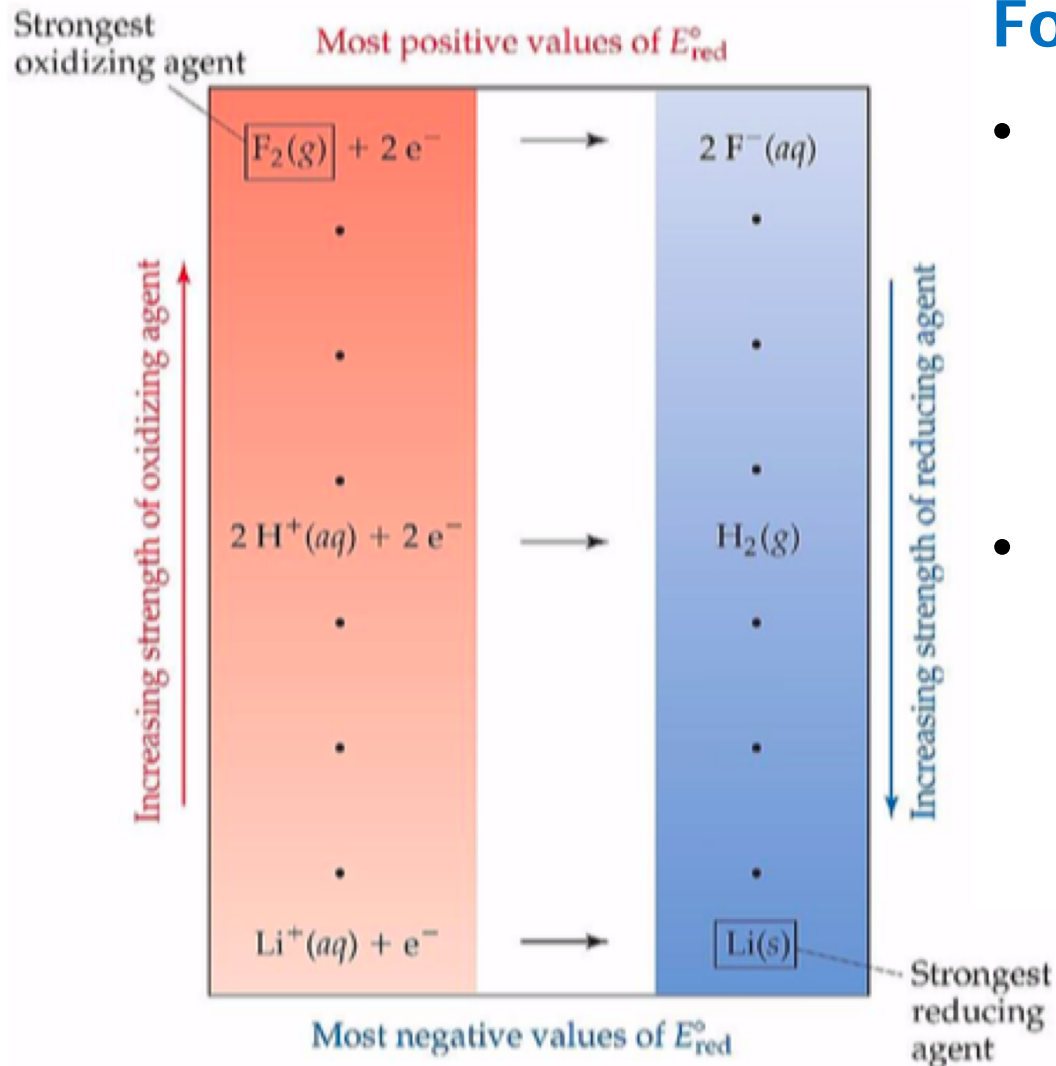
1.) Write the balanced equation for the given cell:



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



# Cell Potential & Redox



## For a reduction half-rxn:

- The more positive the value of  $E^{\circ}$ , the easier it is to reduce the reactant – the reactant is a stronger oxidizing agent
- The more negative the value of  $E^{\circ}$ , 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:

$$E^{\circ} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E^{\circ} = E_{\text{red}} - E_{\text{ox}}$$

$E > 0 = \text{spontaneous}$

$E < 0 = \text{nonspontaneous}$

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,  $\Delta G$  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;  $1F = 96,485\text{C/mol} = 96,485\text{J/V-mol}$ )

$E$  = cell potential

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



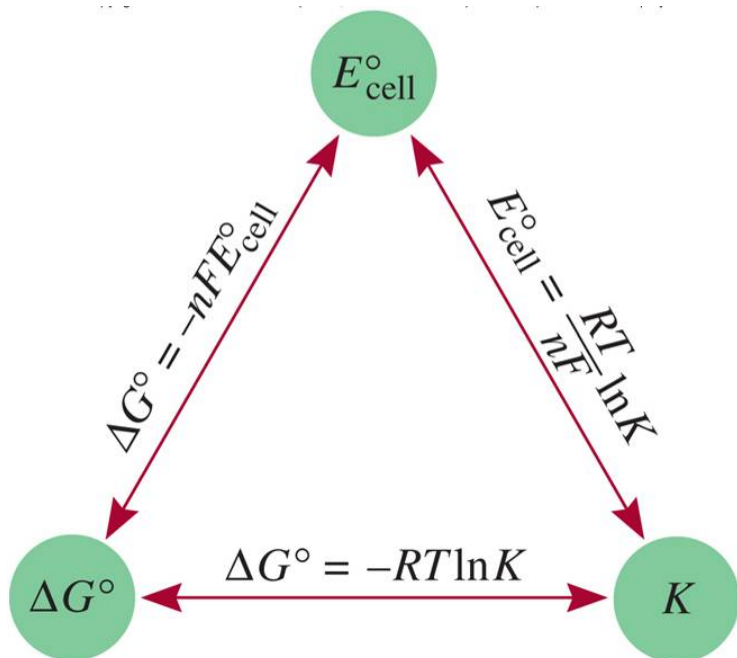
# Thermodynamics of Redox Reactions

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  $\Delta G^\circ$ ,  $K$ , and  $E^\circ_{\text{cell}}$

$\Delta G^\circ$	$K$	$E^\circ_{\text{cell}}$	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:  
$$\text{Sn(s)} + 2\text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{Cu}^{+}(\text{aq})?$$

A:  $6.4 \times 10^9$

# Thermodynamics of Redox Reactions

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

A:  $2.2 \times 10^4$  J/mol;  $-0.11$ V <sup>35</sup>

# 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:

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

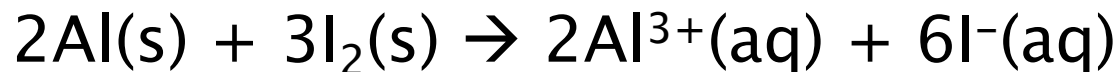
Dividing by  $-nF$  gives the Nernst equation:

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

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:



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

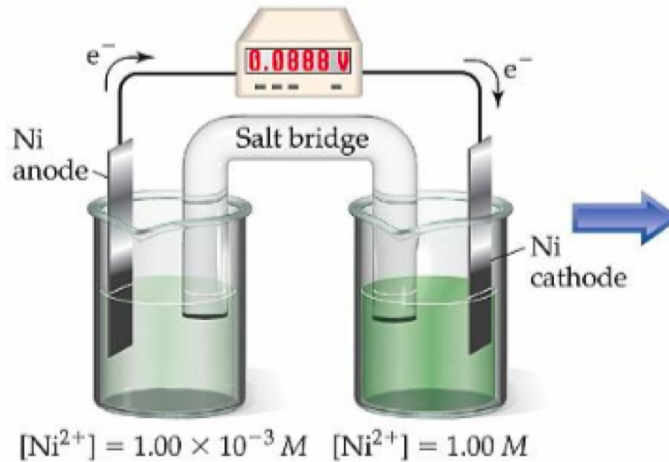
(b) What is the  $E_{\text{cell}}$  when  $[\text{Al}^{3+}] = 4.0 \times 10^{-3}\text{M}$  &  $[\text{I}^{-}] = 0.010\text{M}$   
(still at 298K)

A: 2.19V; 2.36V

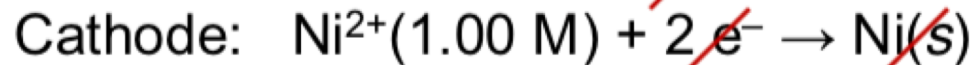
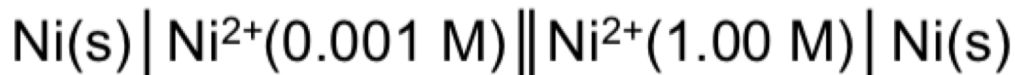
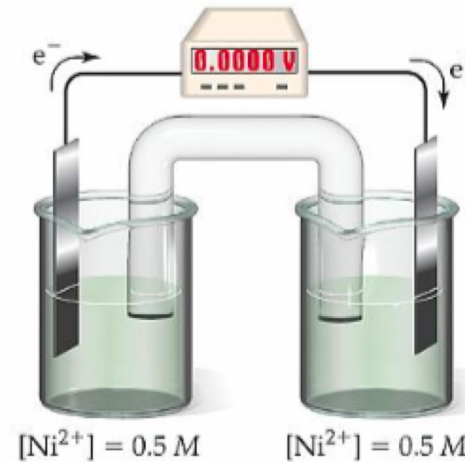
# Concentration Cells

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)



# Concentration Cells

How are concentration cells possible?

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

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



Using the Nernst equation:

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

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

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<sup>2+</sup>(aq) half cells. One half-cell has a Zn<sup>2+</sup> concentration of 1.35M, and the other has a Zn<sup>2+</sup> concentration of 3.75×10<sup>-4</sup>M. What is the cell potential?

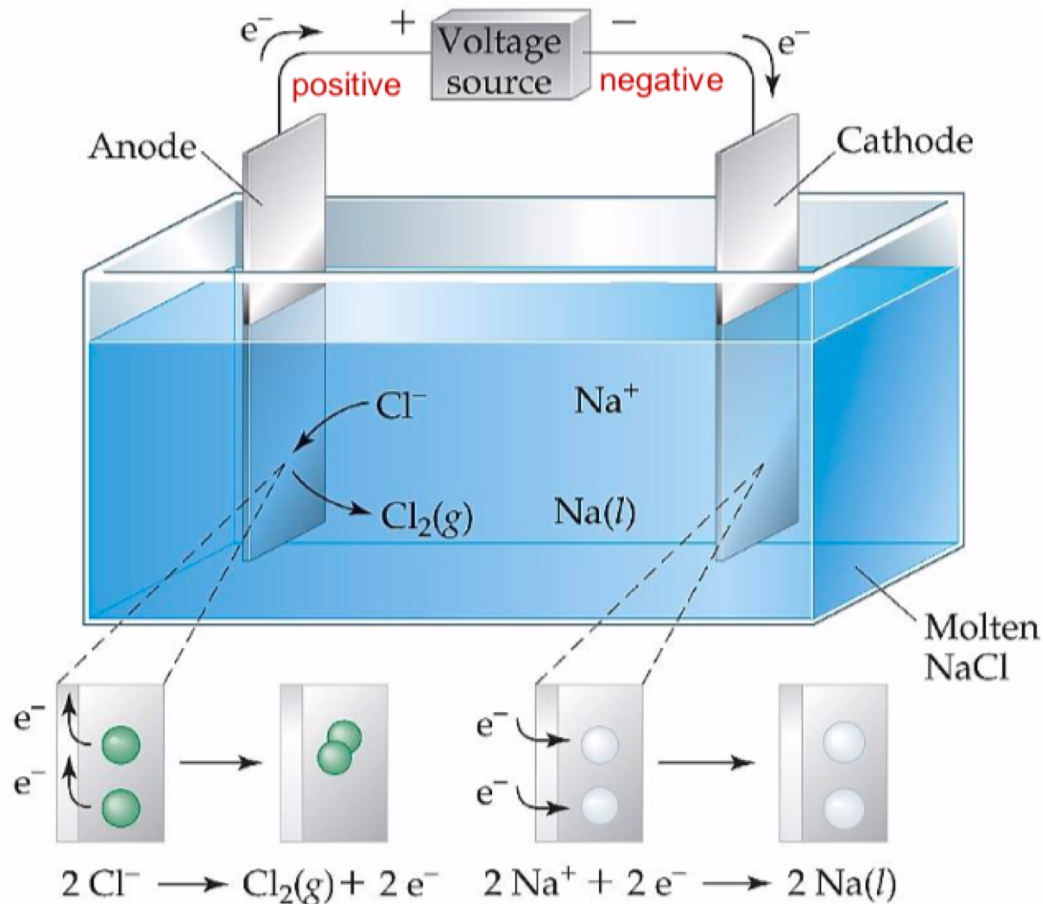


# Electrolysis

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:  $\text{FeCl}_3$  –  $\text{Fe(s)}$  formed at cathode,  $\text{Cl}_2(\text{g})$  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  $\text{H}_2\text{O}$  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  $\text{CaBr}_2(\text{aq})$ :

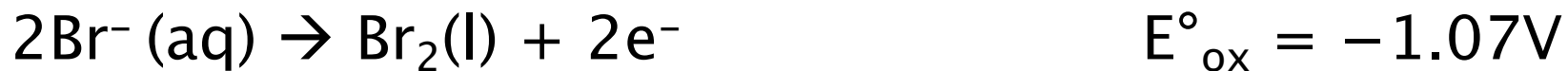
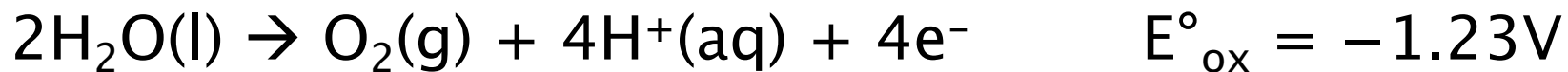


**$\text{H}_2$  will be produced, not  $\text{Ca(s)}$**

## 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<sub>2</sub>O 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<sub>2</sub>(aq):



**Br<sub>2</sub> will be produced instead of O<sub>2</sub>**

- Under acidic conditions, oxidation of H<sup>+</sup> must also be considered.

# Electrolysis

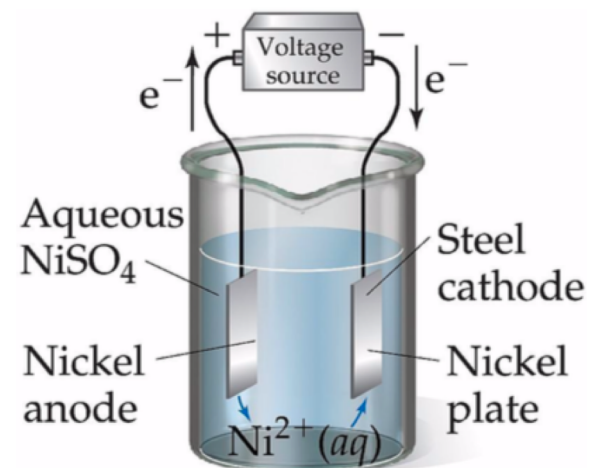
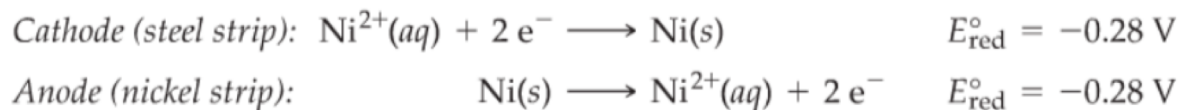
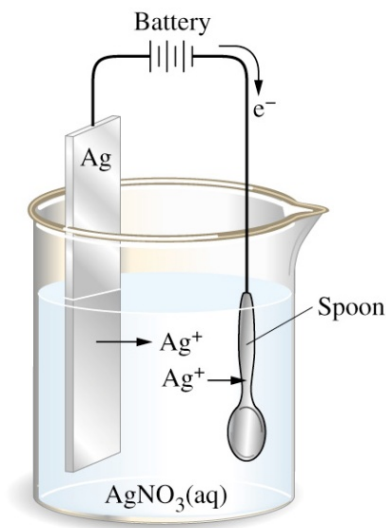
1.) A 1M aqueous solution of iron (II) chloride is electrolyzed. What are the products?  $\text{Fe(s)}$ ,  $\text{O}_2(\text{g})$ ,  $\text{H}^+(\text{aq})$

2.) A 1M solution of potassium iodide is electrolyzed under acidic conditions. What are the products?  $\text{H}_2(\text{g})$ ,  $\text{I}_2(\text{s})$

# Producing Products by Electrolysis

## Electroplating:

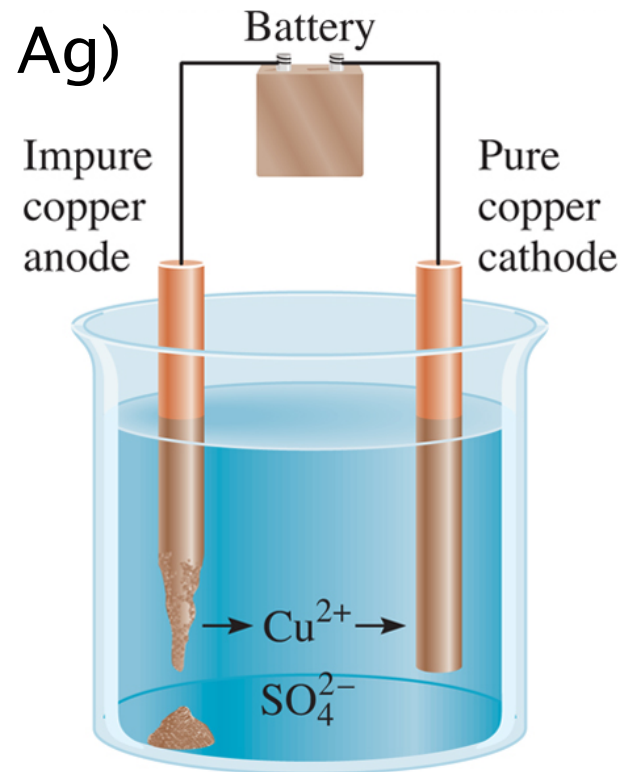
- Coating one metal onto another
- Often silver or gold over iron or steel
- Cheaper/more durable product
- Method of protecting materials from corrosion
- **Ex: plating nickel**
  - $\text{Ni}^{2+}$  preferentially reduced at cathode
  - Ni plates onto the inert electrode



# 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).

$$\text{Coulomb} = I \cdot t$$

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

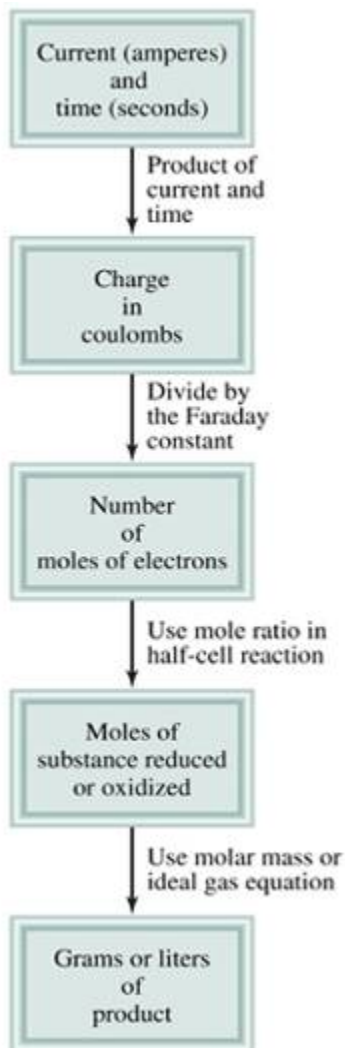
Faraday's constant = 96485 C/mol

\* 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  $\text{CaCl}_2$  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  $\text{MgCl}_2$  using 3.50 A of current? **A: 945 min**

# Electrical Work

Free Energy ( $\Delta G$ ) 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),  $E_{\text{cell}}$  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  $E_{\text{cell}}$  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

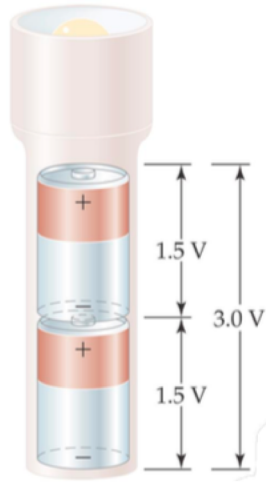
1.) Consider the voltaic cell which is based on the cell reaction:  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

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:  $-1.67 \times 10^5 \text{ J}$

# Batteries

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

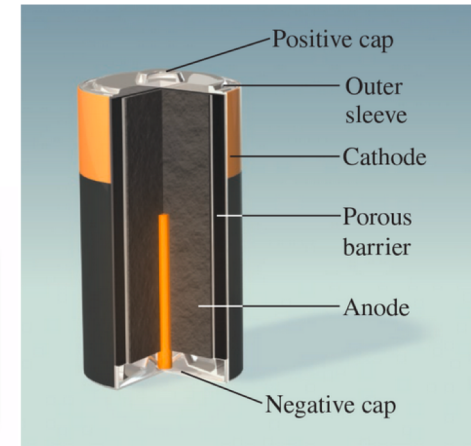
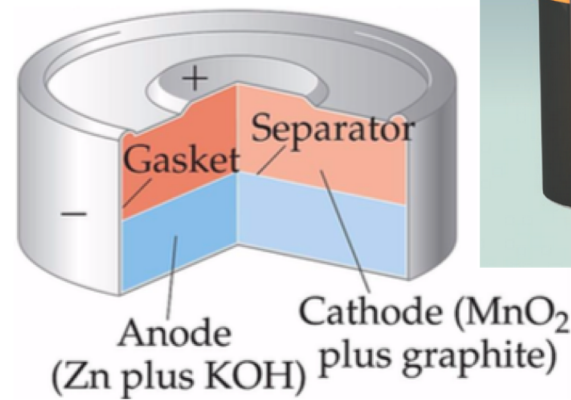


The cells can be connected in a series to produce a voltage that is the sum of the cell potentials of each individual cell.

## Alkaline Battery:

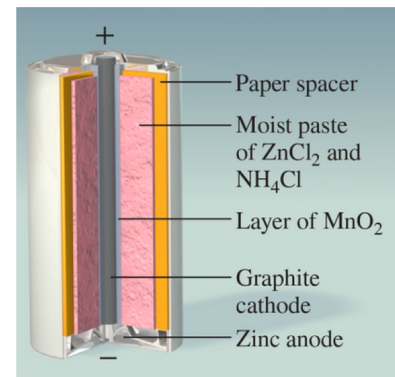
Most common non-rechargeable battery

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



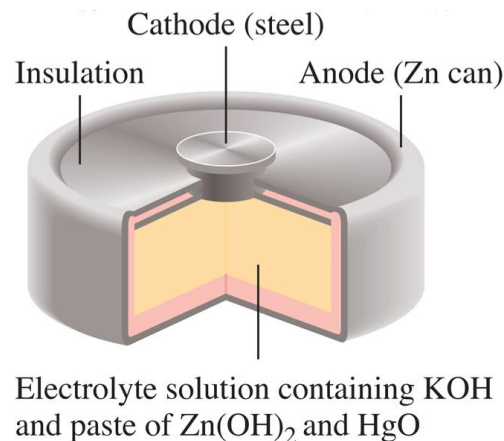
## Dry Cell Battery:

- Used in portable electronics
- Irreversible reaction
- Reported voltage: +1.5V
- Anode:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
- Cathode:  $2\text{MnO}_2 + 2\text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$



## Mercury (Button) Battery:

- Pacemakers, hearing aids, watches
- Irreversible reaction
- Reported voltage: +1.5V
- Anode:  $\text{Zn(s)} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$
- Cathode:  $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg} + 2\text{OH}^-$



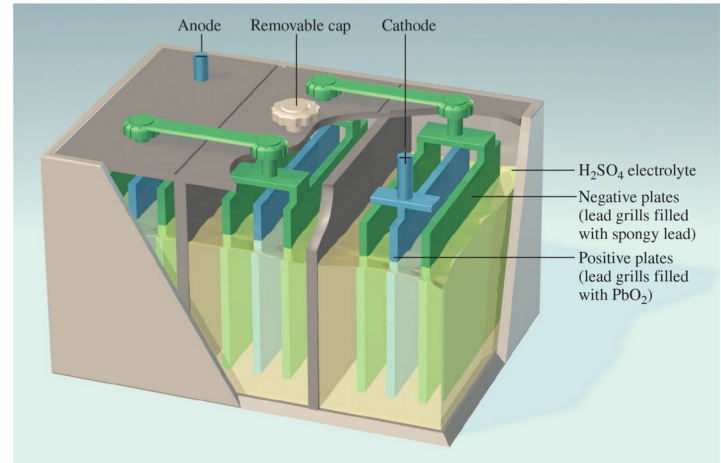
## Lithium Ion Battery:

- Smartphones, cameras, laptops, etc. Rechargeable!
- Reported voltage: +3.4V
- Anode:  $\text{Li(s)} \rightarrow \text{Li}^+ + \text{e}^-$
- Cathode:  $\text{Li}^+ + \text{CoO}_2 + \text{e}^- \rightarrow \text{LiCoO}_2 (\text{s})$

# Batteries

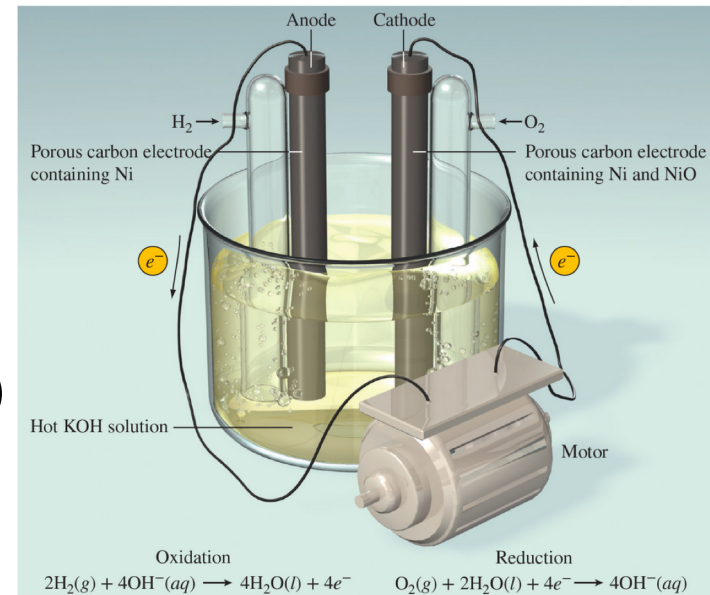
## Lead Storage:

- Car & boat batteries
- Reversible reaction – reaction reverses when engine is running
- Reported voltage: +2.0V/cell  
Usually 6 cells = 12V
- Anode:  $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^-$
- Cathode:  $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$



## Fuel Cells:

- Galvanic cells
- Irreversible reaction
  - Need to replenish reactants
  - Need to remove products
- Require electrocatalysts (ex: C-Ni)
- Reported voltage: +1.23V
- Anode:  $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4e^-$
- Cathode:  $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$



# Corrosion

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

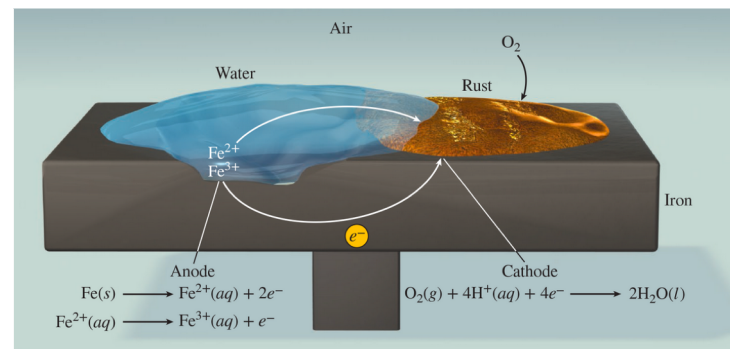
Deterioration of metal through an electrochemical process.

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

Ex: Rusting of iron

Cathode:  $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$   $E^\circ_{\text{red}} = 1.23\text{V}$

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



$E^\circ_{\text{red}}(\text{Fe}^{2+}) < E^\circ_{\text{red}}(\text{O}_2)$

- Iron can be reduced by O<sub>2</sub>
- Dissolved O<sub>2</sub> in water usually causes the oxidation of iron
- Fe<sup>2+</sup> is further oxidized to the Fe<sup>3+</sup> in rust (Fe<sub>2</sub>O<sub>3</sub>)





# 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
  - $\text{Zn}^{2+} \text{E}^{\circ}_{\text{red}} = -0.763\text{V}$ ;  $\text{Fe}^{2+} \text{E}^{\circ}_{\text{red}} = -0.440\text{V}$
  - Zinc becomes the sacrificial anode
- Same reason “zincs” are added to the propeller shafts on boats

Zinc

