Lecture 7.
Oxidation-reduction reactions

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Oxidation-Reduction Reactions

- **The term oxidation was originally used to describe reactions in which an element combines with oxygen.**
- **Example: The reaction between magnesium metal and oxygen to form magnesium oxide involves the oxidation of magnesium.**
- $2\ Mg(s) + O_{2(g)} \rightarrow 2\ MgO(s)$

- **The term reduction comes from the Latin stem meaning "to lead back." Anything that that leads back to magnesium metal therefore involves reduction.**
- **The reaction between magnesium oxide and carbon at 2000°C to form magnesium metal and carbon monoxide is an example of the reduction**
- **$MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$**

ORR

Oxidation-Reduction Reactions

("redox") reactions involve the transfer of electrons from one substance to another.

Oxidized substances lose electrons and reduced substances gain electrons.

Practice Problem 1:

Determine which element is oxidized and which is reduced when lithium reacts with nitrogen to form lithium nitride.

$$6\ Li(s) + N_2(g) \rightarrow 2\ Li_3N(s)$$

Oxidation and Reduction

An oxidation-reduction reaction

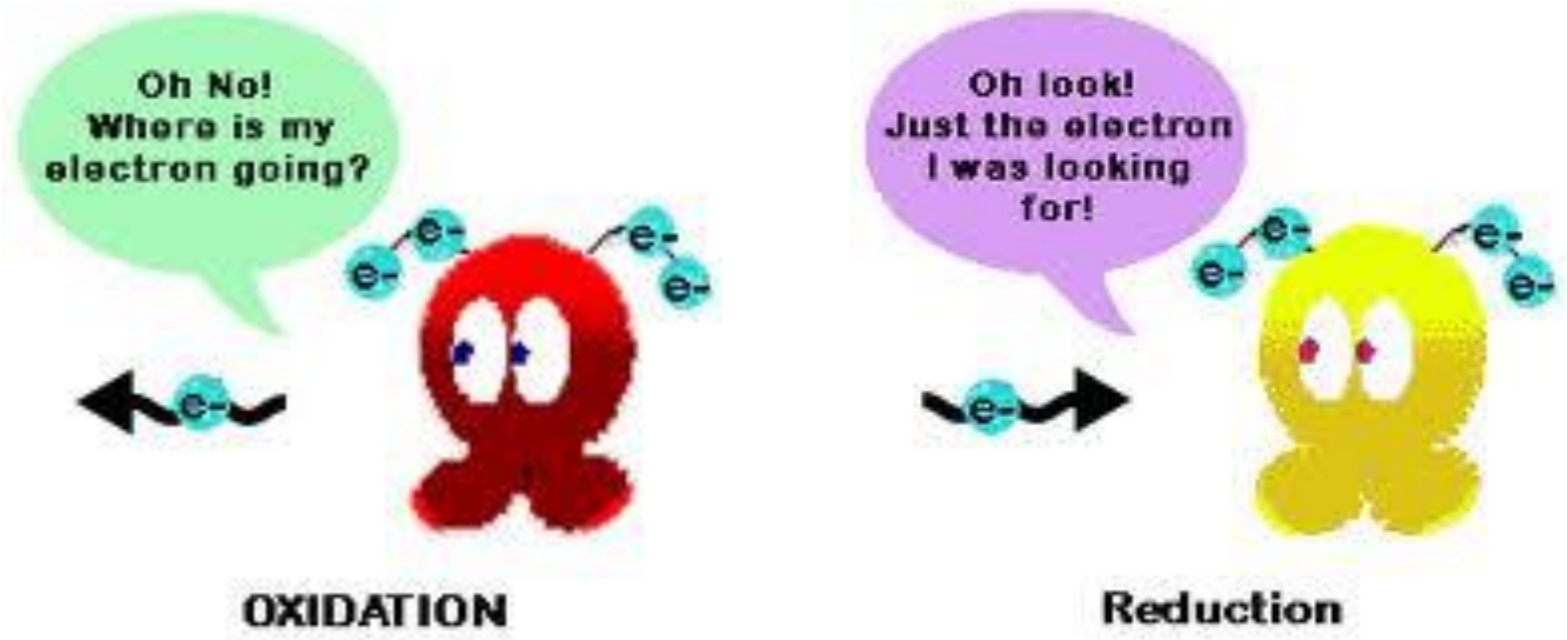
- provides us with energy from food.
- provides electrical energy in batteries.
- occurs when iron rusts.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

Remember this phrase: LEO the lion says GER.

- **LEO** = Loss of Electrons is Oxidation
- **GER** = Gain of Electrons is Reduction
- Another way is to simply remember that reduction is to reduce the oxidation number. Therefore, oxidation must increase the value.
- *Oxidizing Agent* - that substance which oxidizes somebody else. It is reduced in the process.
- *Reducing Agent* - that substance which reduces somebody else. It is oxidized in the process.

Electron Transfer Reactions

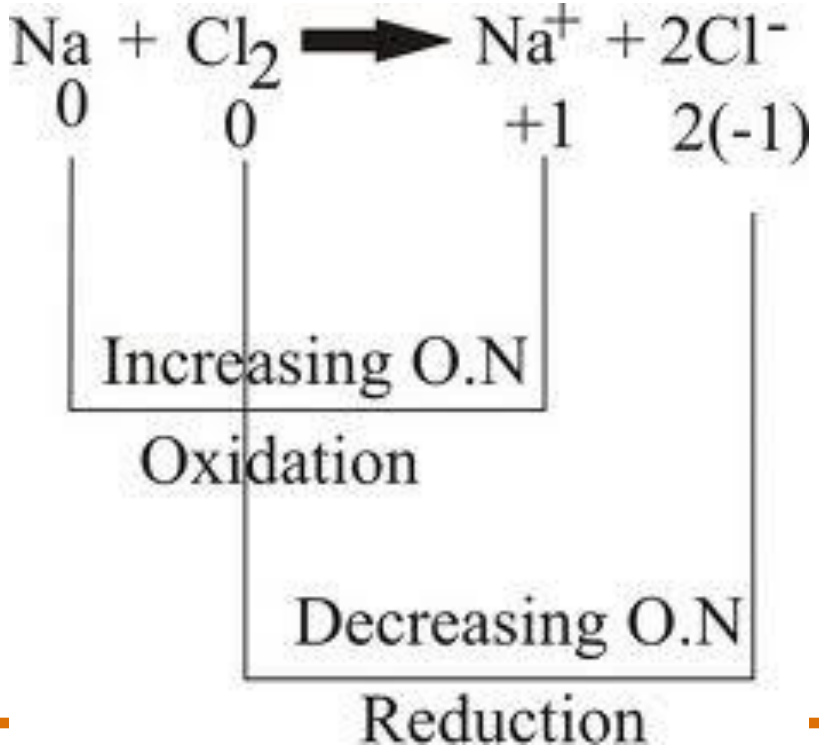


Oxidation: LOSS of one or more electrons.
Reduction: GAIN of one or more electrons

Redox Reactions:

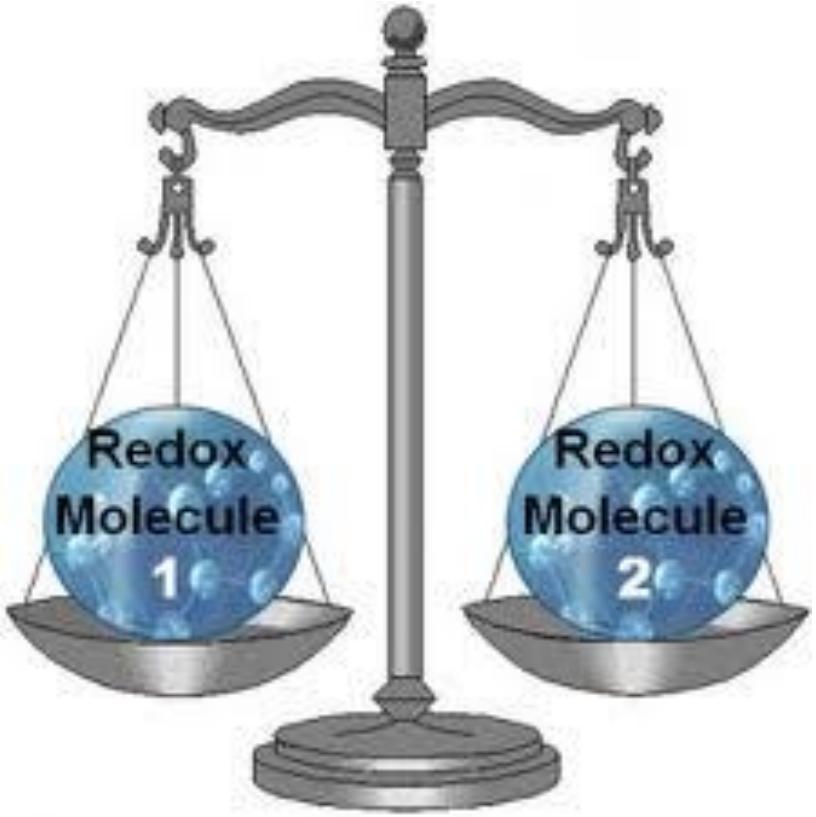
ALWAYS involve changes in charge

A competition for electrons between atoms!



Conservation of “Charge”

Total electrons lost = Total electrons gained



Rules for Assigning Oxidation Numbers

1. All free, uncombined elements have an oxidation number of zero. This includes diatomic elements such as O_2 or others like P_4 and S_8.
2. Hydrogen, in all its compounds except hydrides, has an oxidation number of +1 (positive one)
3. Oxygen, in all its compounds except peroxides, has an oxidation number of -2 (negative two).

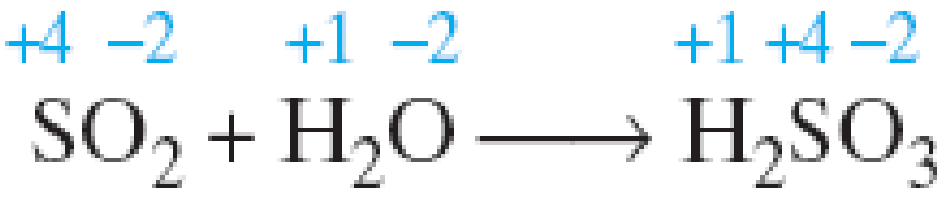
TABLE 19-1 *Rules for Assigning Oxidation Numbers*

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of Na(*s*) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is −1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is −2.
4. The oxidation number of fluorine in a compound is always −1.	The oxidation number of F in LiF is −1.
5. Oxygen has an oxidation number of −2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is −1.	The oxidation number of O in NO_2 is −2.
6. The oxidation state of hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is −1.	The oxidation number of H in LiH is −1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

Practice Problems

- What is the oxidation number of . . .
- 1) N in NO_3^-
- 2) C in CO_3^{2-}
- 3) Cr in CrO_4^{2-}
- 4) Cr in $Cr_2O_7^{2-}$
- 5) Fe in Fe_2O_3
- 6) Pb in $PbOH^+$
- 7) V in VO_2^+
- 8) V in VO^{2+}
- 9) Mn in MnO_4^-
- 10) Mn in MnO_4^{2-}

- If no atoms in reaction change oxidation state, it is NOT a redox reaction
- Ex. Sulfur dioxide gas dissolves in water to form acidic solution of sulfurous acid



Electron Loss and Gain

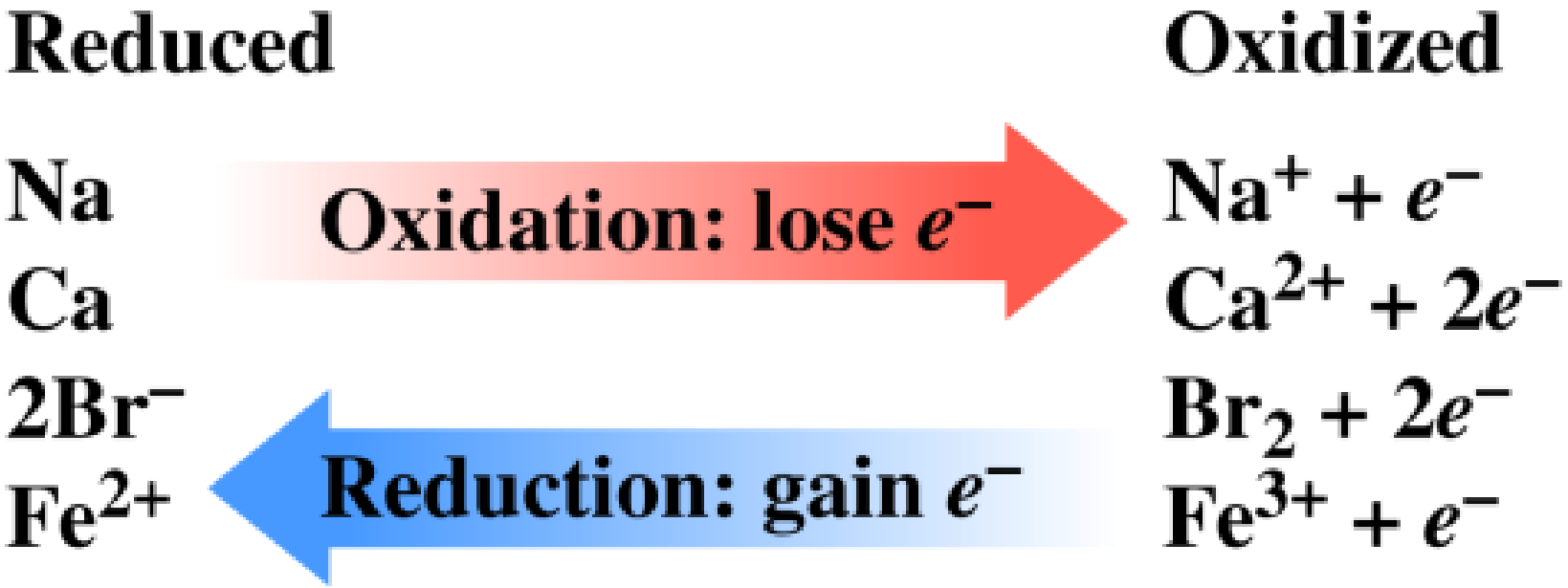
An oxidation-reduction reaction

- transfers electrons from one reactant to another.
- loses electrons in oxidation. (LEO) or (OIL)

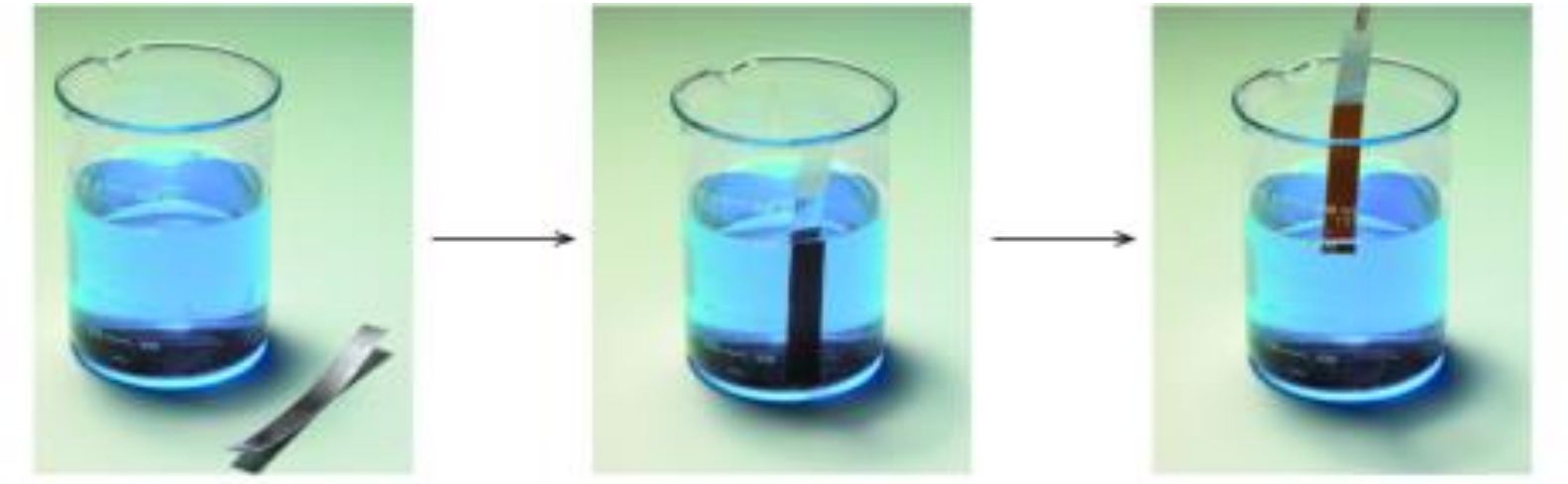
  $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (loss of electrons)
- gains electrons in reduction. (GER) or (RIG)

  $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (gain of electrons)

Oxidation and Reduction



Zn and Cu^{2+}



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ oxidation

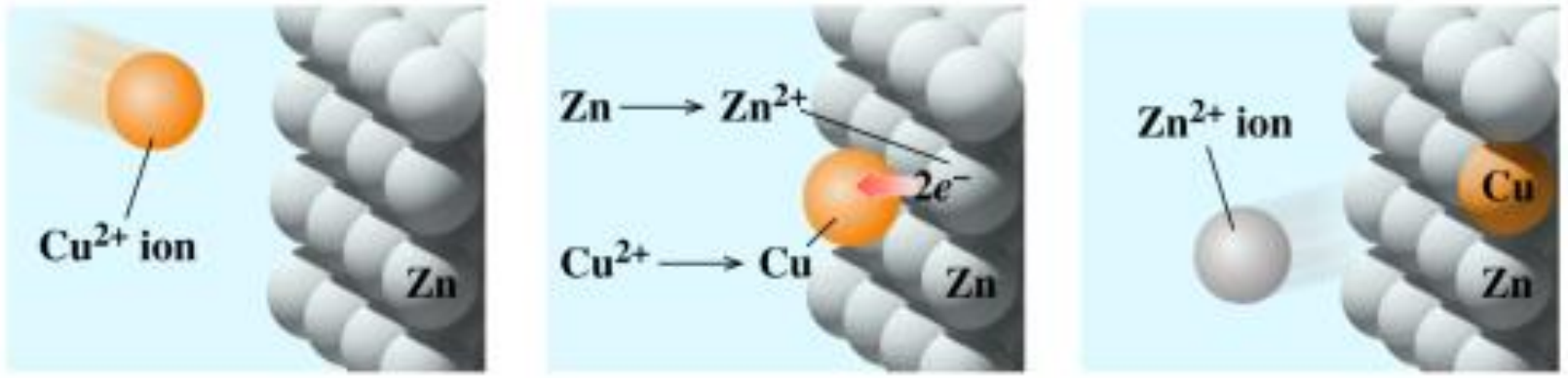
Silvery metal

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ reduction

Blue orange

Electron Transfer from Zn to Cu^{2+}

Oxidation: electron loss



Reduction: electron gain

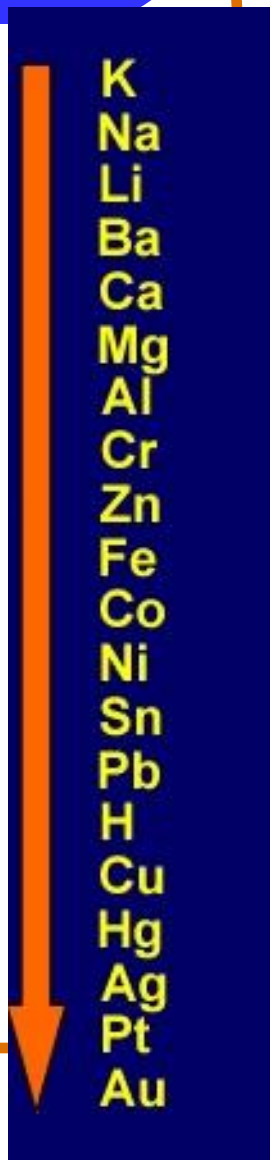
Oxidation-Reduction

(a): Placing Al in $CuCl_2$ dissolved in H_2O forms Cu^{2+} ions

(b): Cu^{2+} in solution is reduced to Cu metal

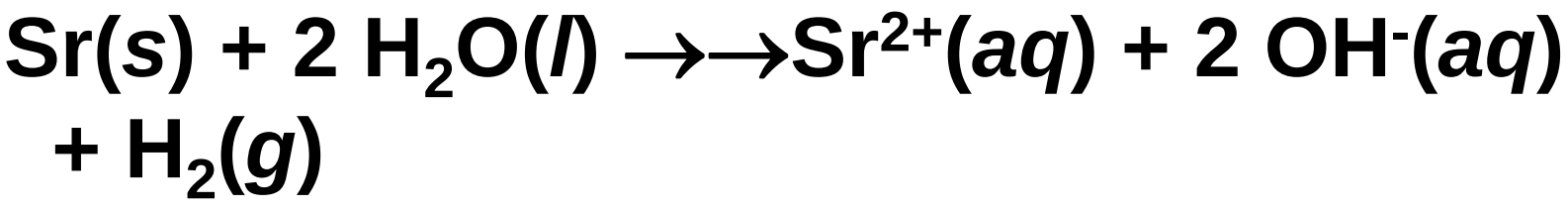
STRENGTH OF OXIDIZING AND REDUCING AGENTS

- Different substances compared and rated on relative potential as reducing/oxidizing agents
- Ex. Activity series – related to each element's tendency to lose electrons
- Elements lose electrons to positively charged ions of any element below them in series



Practice Problem 2:

- **Determine which atom is oxidized and which is reduced in the following reaction**



Learning Check

Identify each of the following as
1) oxidation or 2) reduction.

__A. $Sn(s) \longrightarrow Sn^{4+}(aq) + 4e^-$

__B. $Fe^{3+}(aq) + 1e^- \longrightarrow Fe^{2+}(aq)$

__C. $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$

Writing Oxidation and Reduction Reactions

Write the separate oxidation and reduction reactions for the following equation.

$$2Cs(s) + F_2(g) \longrightarrow 2CsF(s)$$

A cesium atom loses an electron to form cesium ion.

$$Cs(s) - 1e^- \longrightarrow Cs^+(s)$$ **oxidation**

Fluorine atoms gain electrons to form fluoride ions.

$$F_2(s) + 2e^- \longrightarrow 2F^-(s)$$ **reduction**

What is a Half-Reaction?

- A half-reaction is simply one which shows either reduction OR oxidation, but not both. Here is an example redox reaction:
- $Ag^{+} + Cu \rightarrow Ag + Cu^{2+}$
- It has BOTH a reduction and an oxidation in it. That is why we call it a redox reaction, from **RED**uction and **OX**idation.

Separate out the two half-reactions

To do that, identify the atoms which get reduced and get oxidized. Here are the two half-reactions from the example:

$$Ag^{+} \text{ ---> } Ag$$

$$Cu \text{ ---> } Cu^{2+}$$

- The silver is being reduced, its oxidation number going from +1 to zero. The copper's oxidation number went from zero to +2, so it was oxidized in the reaction. In order to figure out the half-reactions, you MUST be able to calculate the oxidation number of an atom.

- When you look at the two half-reactions, you will see they are already balanced for atoms with one Ag on each side and one Cu on each side. So, all we need to do is balance the charge.
- To do this you add electrons to the more positive side. You add enough to make the total charge on each side become EQUAL.
- To the silver half-reaction, we add one electron:

$$Ag^{+} + e^{-} \text{---> } Ag$$

- To the copper half-reaction, we add two electrons:

$$Cu - 2e^{-} \text{---> } Cu^{2+}$$

Half-reactions NEVER occur alone

- notice that each half-reaction wound up with a total charge of zero on each side. This is not always the case. You need to strive to get the total charge on each side EQUAL, not zero.

Half-Reactions Practice Problems

- Balance each half-reaction for atoms and charge:
- 1) Cl_2 ---> Cl^-
- 2) Sn ---> Sn^{2+}
- 3) Fe^{2+} ---> Fe^{3+}
- 4) I_3^- ---> I^-
- 5) ICl_2^- ---> I^-
- 6) Sn + NO_3^- ---> SnO_2 + NO_2
- 7) HClO + Co ---> Cl_2 + Co^{2+}
- 8) NO_2 ---> NO_3^- + NO

Answers

- 1) $Cl_2 + 2e^- \rightarrow 2Cl^-$
- 2) $Sn \rightarrow Sn^{2+} + 2e^-$
- 3) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- 4) $I_3^- + 2e^- \rightarrow 3I^-$
- 5) $ICl_2^- + 2e^- \rightarrow I^- + 2Cl^-$
- 6) $Sn \rightarrow SnO_2$ and $NO_3^- \rightarrow NO_2$
- 7) $HClO \rightarrow Cl_2$ and $Co \rightarrow Co^{2+}$
- 8) $NO_2 \rightarrow NO_3^-$ and $NO_2 \rightarrow NO$

What is oxidized and reduced?
What are the oxidizing and reducing agents?

$Mg + CuSO_4 \rightarrow MgSO_4 + Cu$

$2K + Br_2 \rightarrow 2KBr$

$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

NOTE:
Atoms in a polyatomic ion DO NOT change in charge!

$$\overset{0}{Mg} + \overset{+2}{CuSO_4} \longrightarrow \overset{+2}{MgSO_4} + \overset{0}{Cu}$$

Mg oxidized (reducing agent)

Cu^{+2} reduced (oxidizing agent)

$$2\overset{0}{K} + \overset{0}{Br_2} \longrightarrow 2\overset{+1\ -1}{KBr}$$

K oxidized (reducing agent)

Br_2 reduced (oxidizing agent)

$$\overset{0}{Cu} + 2\overset{+1}{AgNO_3} \longrightarrow \overset{+2}{Cu(NO_3)_2} + \overset{0}{2Ag}$$

Cu oxidized (reducing agent)

Ag^{+1} reduced (oxidizing agent)

Writing Half Reactions

$$\overset{0}{2Na} + \overset{0}{F_2} \longrightarrow \overset{+1\ -1}{2NaF}$$

Oxidation: $Na \rightarrow Na^{+1} + 1e^-$

or $2Na \rightarrow 2Na^{+1} + 2e^-$

Note: e- are "lost" (on the right of arrow)

Reduction: $F + 1e^- \rightarrow F^{-1}$

or $F_2 + 2e^- \rightarrow 2F^{-1}$

Note: e- are "gained" (on the left of arrow)

The Chemistry of Photography

1. For photographic film that contains AgBr, light causes loss of an electron by bromide (Br^-) and gain of that electron by silver ion (Ag^+).
2. Grains of reduced metallic silver (Ag) form the photographic image.

Learning Check

In light-sensitive sunglasses, UV light initiates an oxidation-reduction reaction.

$$Ag^{+} + Cl^{-} \xrightarrow{\text{uv light}} Ag + Cl$$

A. Which reactant is oxidized?

B. Which reactant is reduced?

Solution

In light-sensitive sunglasses, UV light initiates an oxidation-reduction reaction.

$$Ag^+ + Cl^- \xrightarrow{\text{uv light}} Ag + Cl$$

A. Which reactant is oxidized? $Cl^- \longrightarrow Cl + 1e^-$

B. Which reactant is reduced? $Ag^+ + 1e^- \longrightarrow Ag$

Learning Check

Identify the substances that are oxidized and reduced in each of the following reactions:

A. $Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$

B. $2Al(s) + 3Br_2(g) \longrightarrow 2AlBr_3(s)$

Solution

A. Mg is oxidized $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$

H^+ is reduced $2H^+ + 2e^- \longrightarrow H_2$

B. Al is oxidized $Al \longrightarrow Al^{3+} + 3e^-$

Br is reduced $Br + e^- \longrightarrow Br^-$

Common uses of the terms oxidization and reduction

Term	Meaning
Oxidation	To combine with oxygen To lose hydrogen To lose electrons To increase in oxidation number
Reduction	To lose oxygen To combine with hydrogen To gain electrons To decrease in oxidation number

Galvanic elements

- Oxidation-Reduction Reactions
  - c. The Chemistry of Batteries
    1. Combining a readily oxidized substance with an easily reduced substance can create a battery.
    2. The oxidized material is the anode and the reduced material is the cathode of the battery.

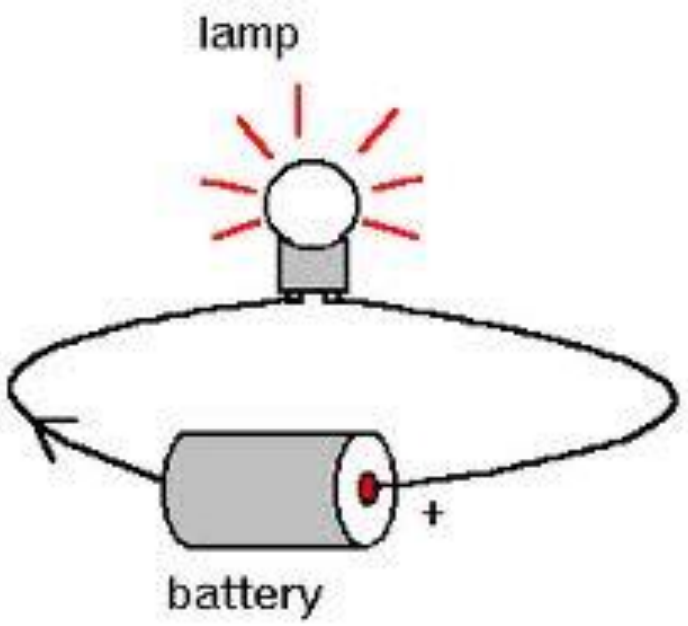
Electrochemical Cells (Batteries)

Chemical reaction that produces electricity.
Called “voltaic cells” as they produce voltage
This happens SPONTANEOUSLY.

Moving Electrons = Electricity

Electrons given off by oxidized substance travel towards substance being reduced.

Traveling electrons move through “external circuit” where they do work.



How do the Electrons Move?

Batteries often contain 2 metals.

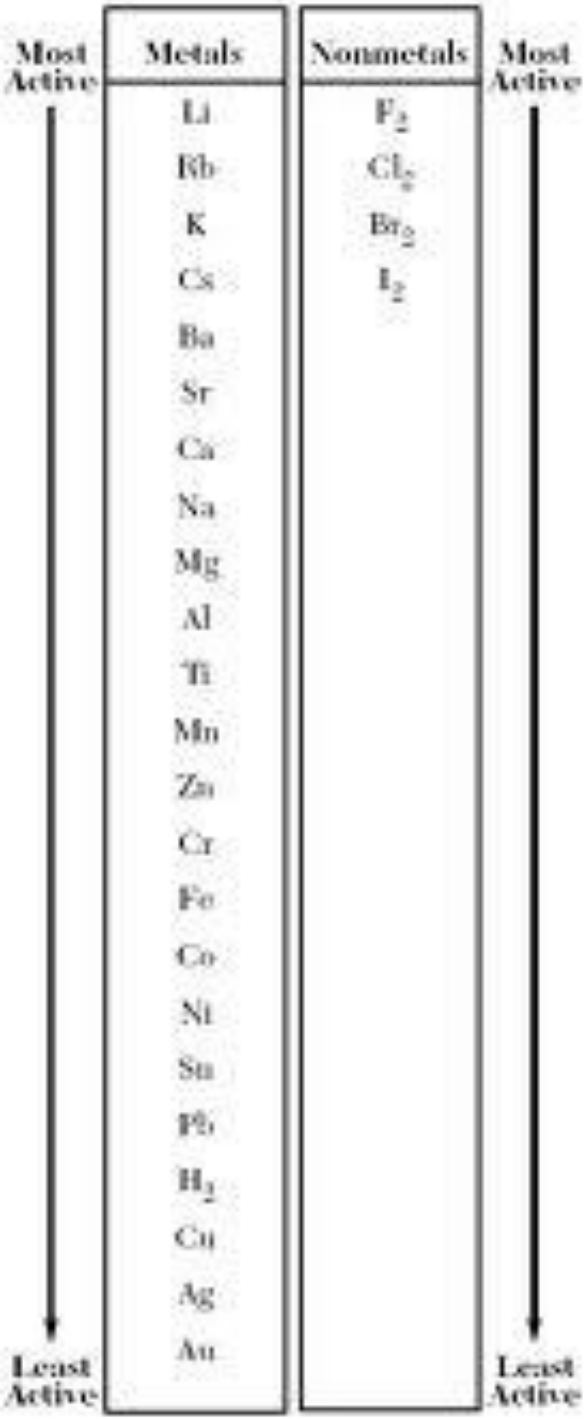
<u>Start with Table of metal activity</u>
Electrons travel from the more “Active metal”
toward the less active metal.

Metal above = oxidized
Ion on Metal below = reduced

Electrons flow

From metal above to ion of metal below

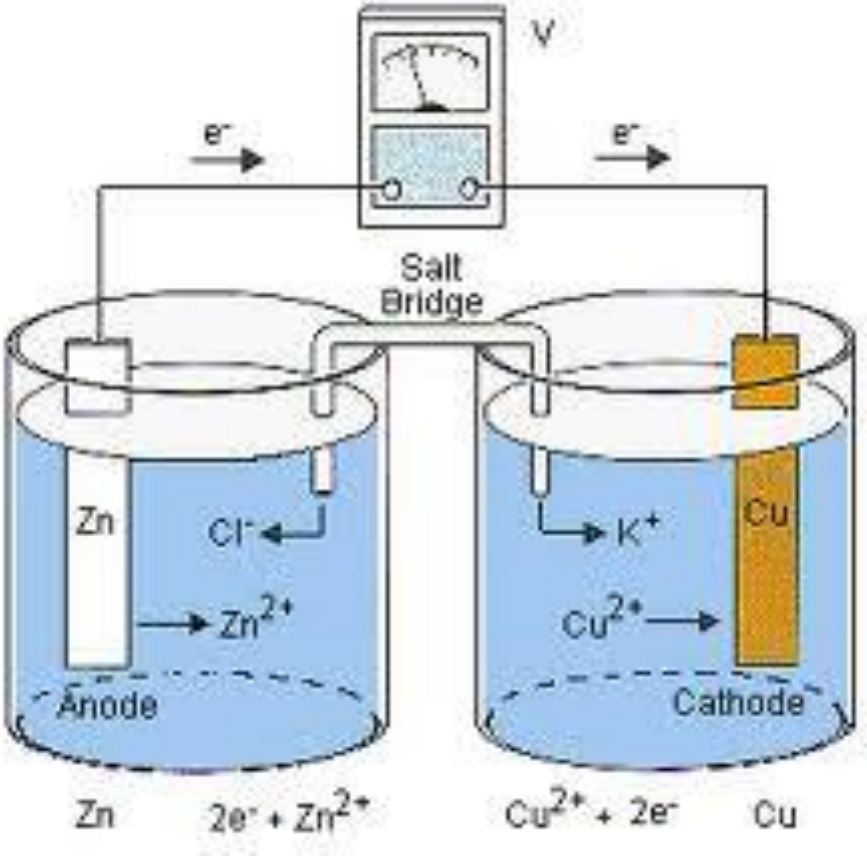
e-



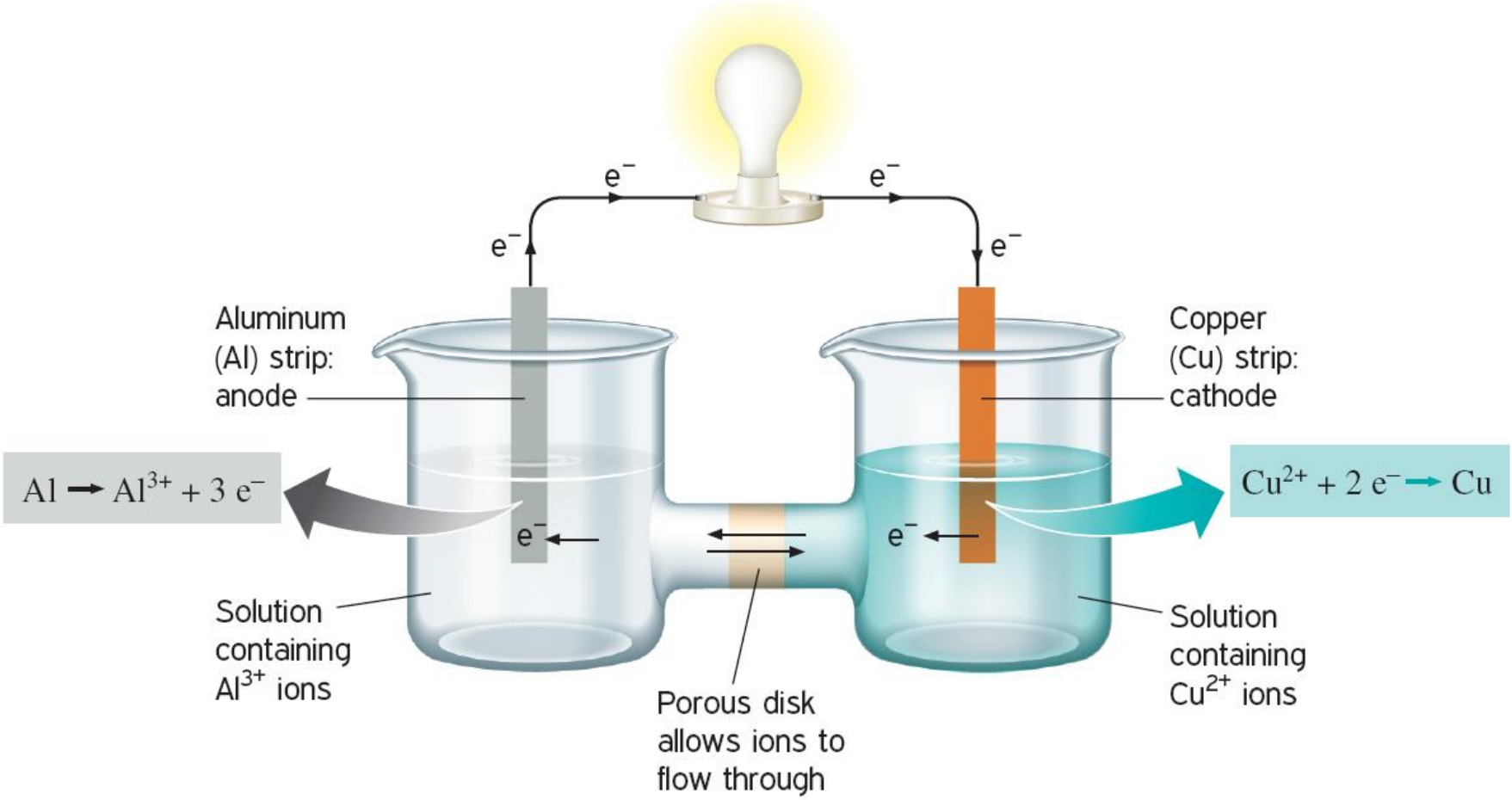
Parts of a Simple Battery (Voltaic Cell)

Made of Two “Half Cells” containing:

2 Metal Electrodes
2 Solutions of Ions
External Wire
Salt Bridge

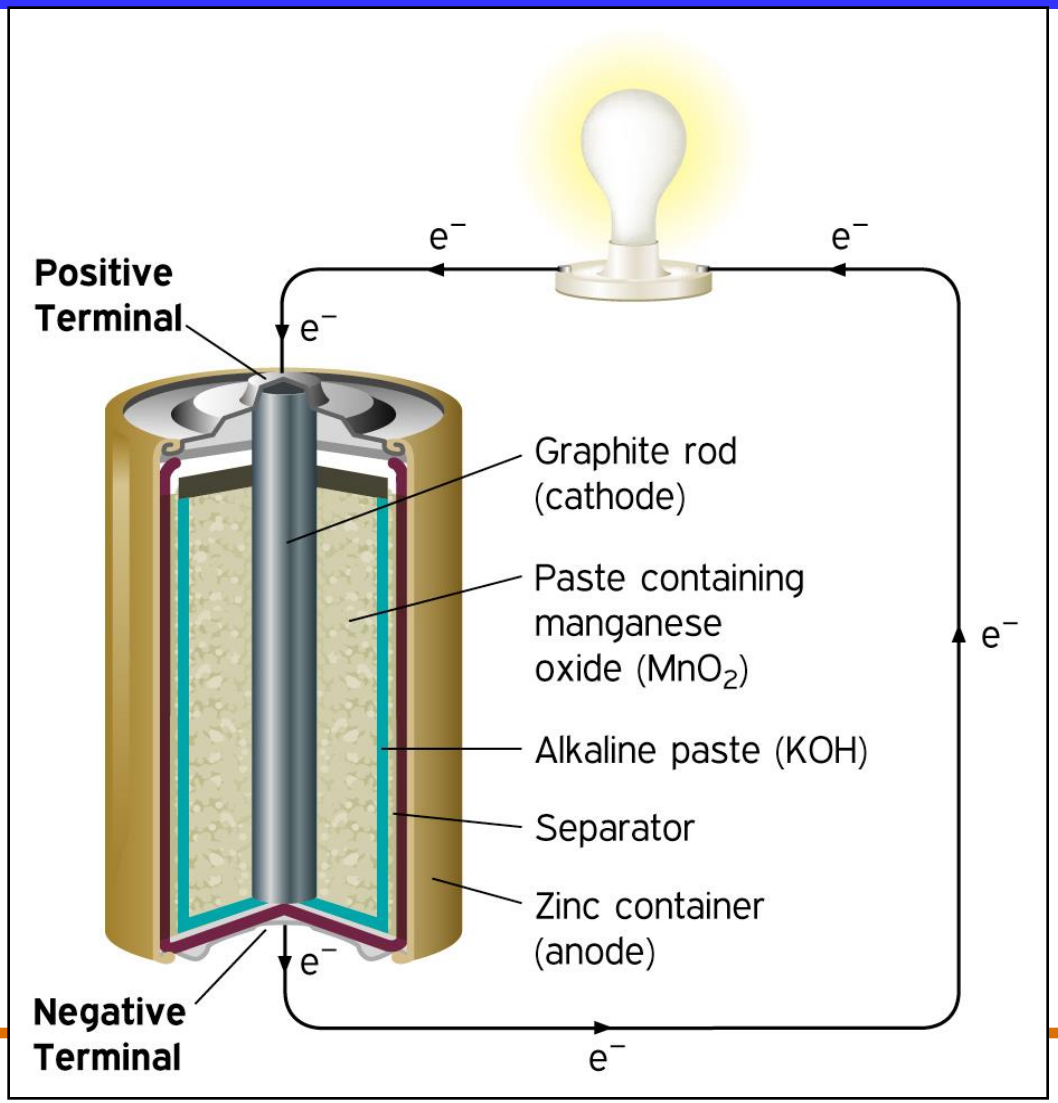


Batteries



Electrons from the Al metal flow through a wire to reduce Cu^{2+} in solution, resulting in a current that can do work.

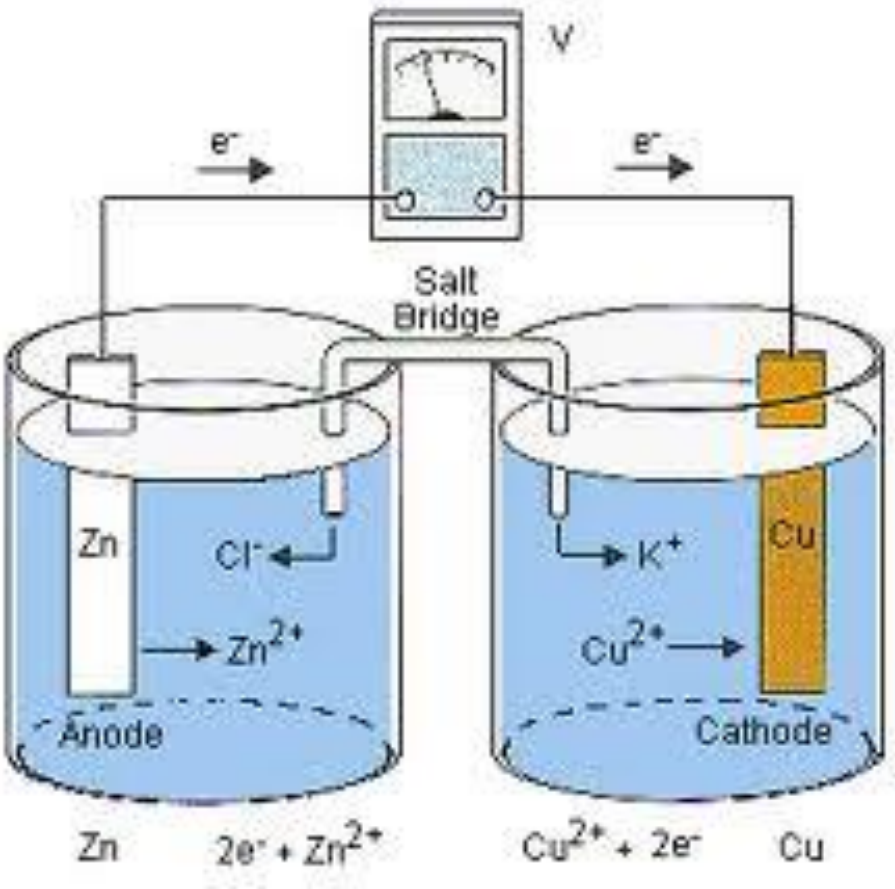
An alkaline "dry cell" in circuit with a lightbulb



Electrons need to flow in a “circuit” that is connected.

<u>External Wire</u>:
allows electrons to flow between metal electrodes

<u>Salt Bridge:</u> allows ions to flow between solutions



$Zn/Zn^{+2}//Cu^{+2}/Cu$

What is Ox/Red?

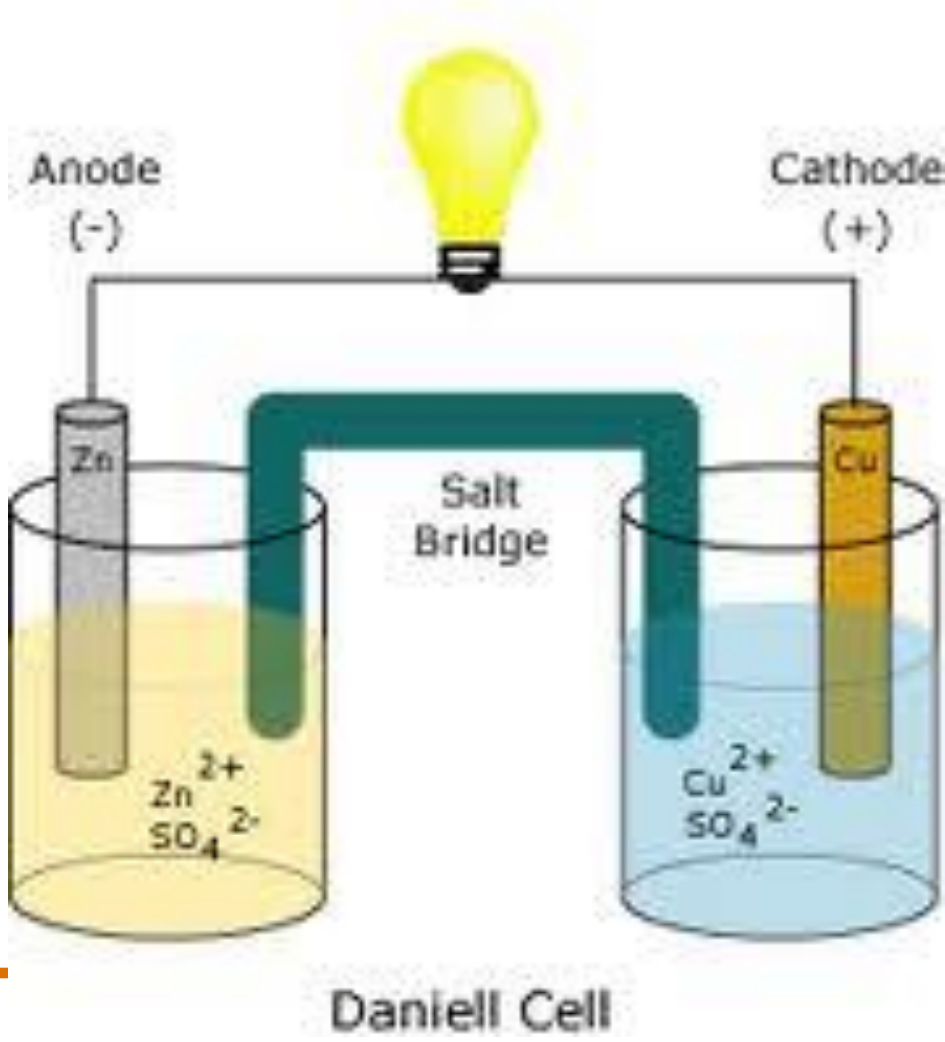
See Table

Metal above is oxidized

Zn

Ion of metal below

reduced Cu^{+2}



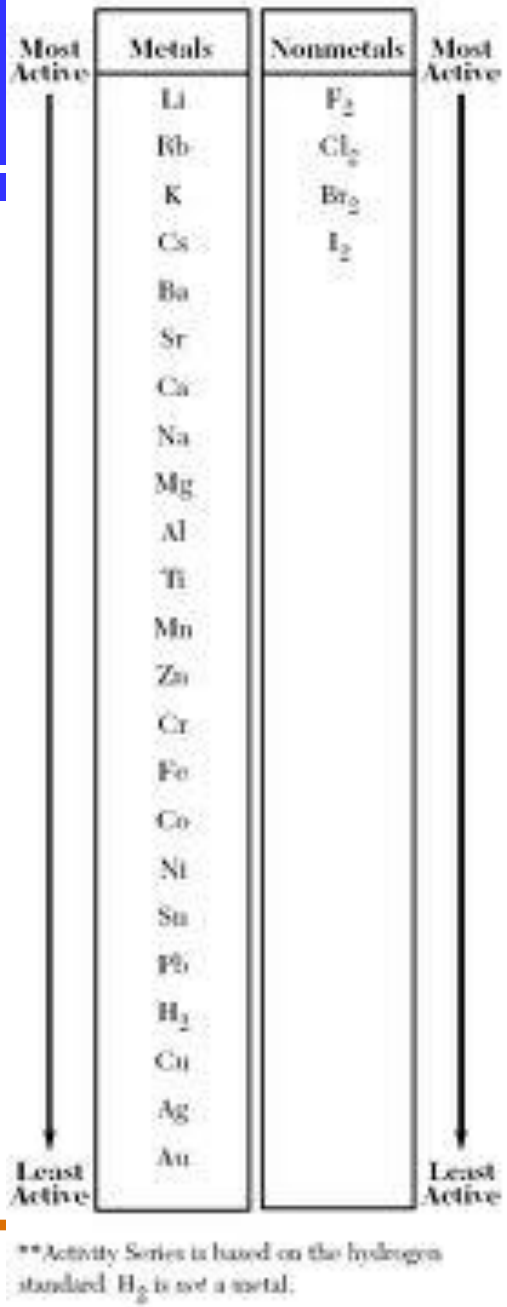
Which way do electrons flow in the external wire?

See Table

Electrons flow “Down” the table from what is oxidized towards what is reduced.

from Zn to Cu

e-

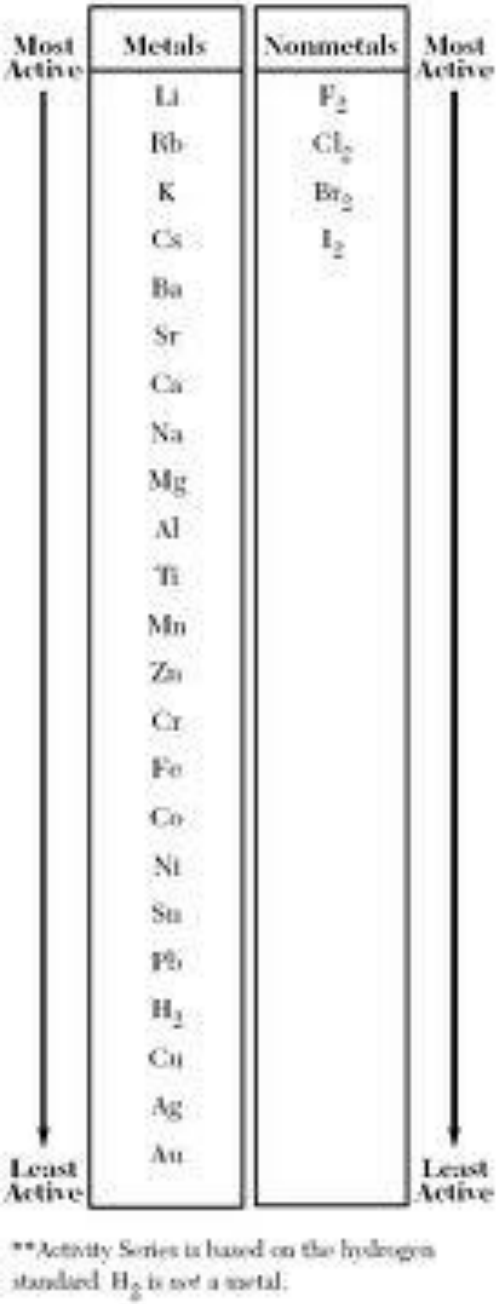


Which electrode is negative?
Which electrode is positive?

Electrons flow from negative to positive electrode.

Negative electrode: Zn
Positive electrode: Cu

e-



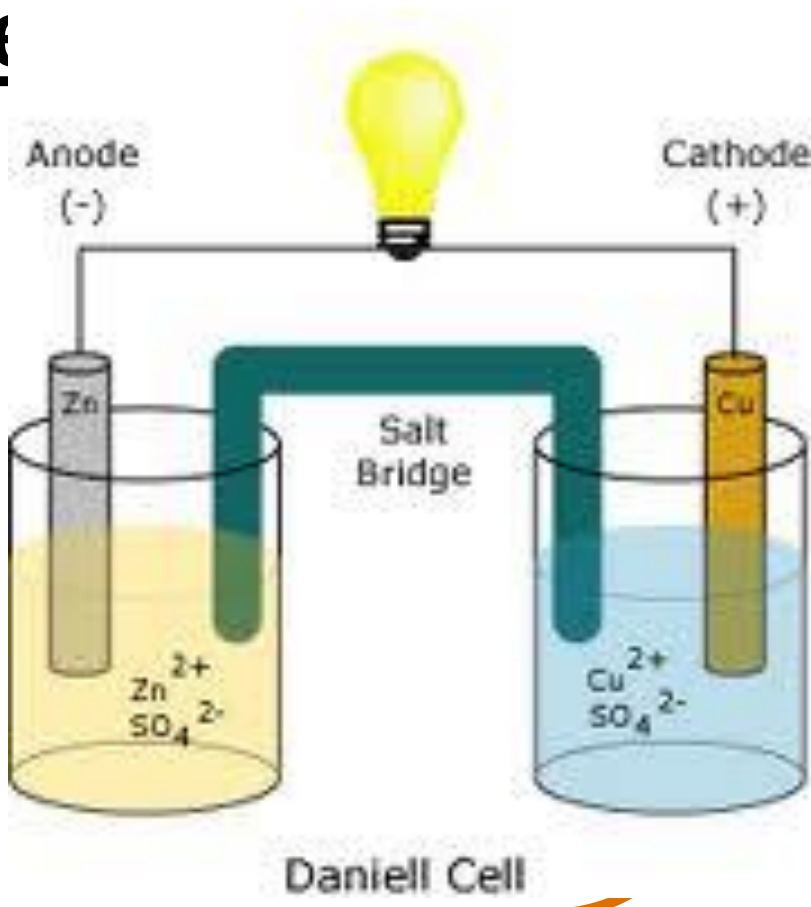
Which electrode is the anode and cathode?

Anode: metal electrode where oxidation occurs

Zn

Cathode: metal electrode where reduction occurs

Cu



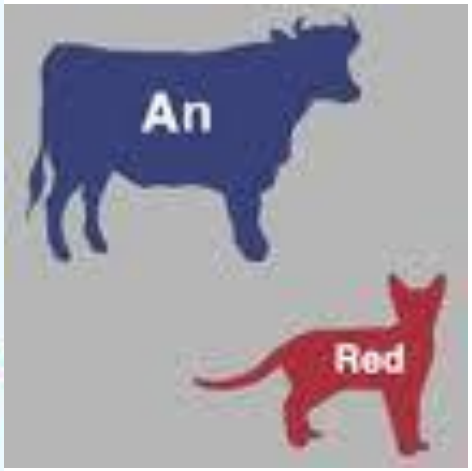
Remember

AN OX

RED CAT

Anode is where oxidation happens

Cathode is where reduction happens



- Oxidation-Reduction Reactions

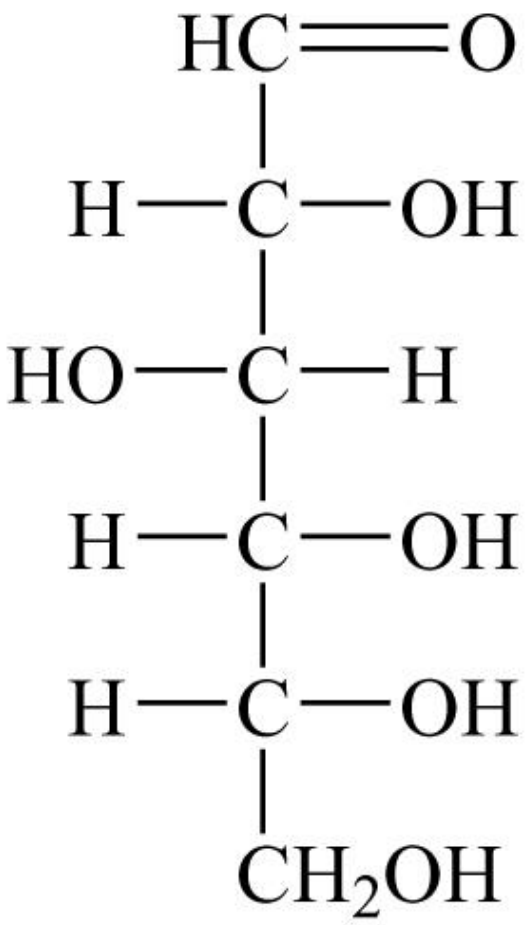
d. Role in Metabolism

1. Oxidation can also be considered to be gain of oxygen or loss of hydrogen in a molecule.
2. Reduction can also be considered to be loss of oxygen or gain of hydrogen in a molecule.
3. Respiration is a redox process whereby living organisms oxidize food to release energy.

Oxidizing food molecules via respiration yields energy

Credit: Patrick Groleau. Photo courtesy of Julie Millard

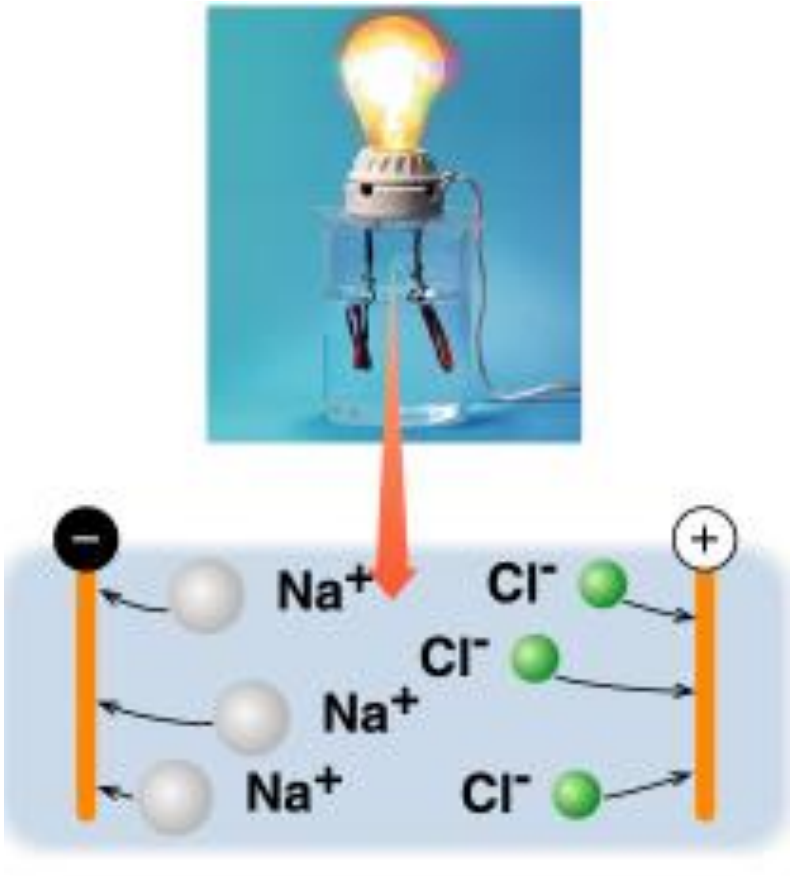
Glucose and CO_2



$C_6H_{12}O_6$ (glucose)

CO_2 (carbon dioxide)

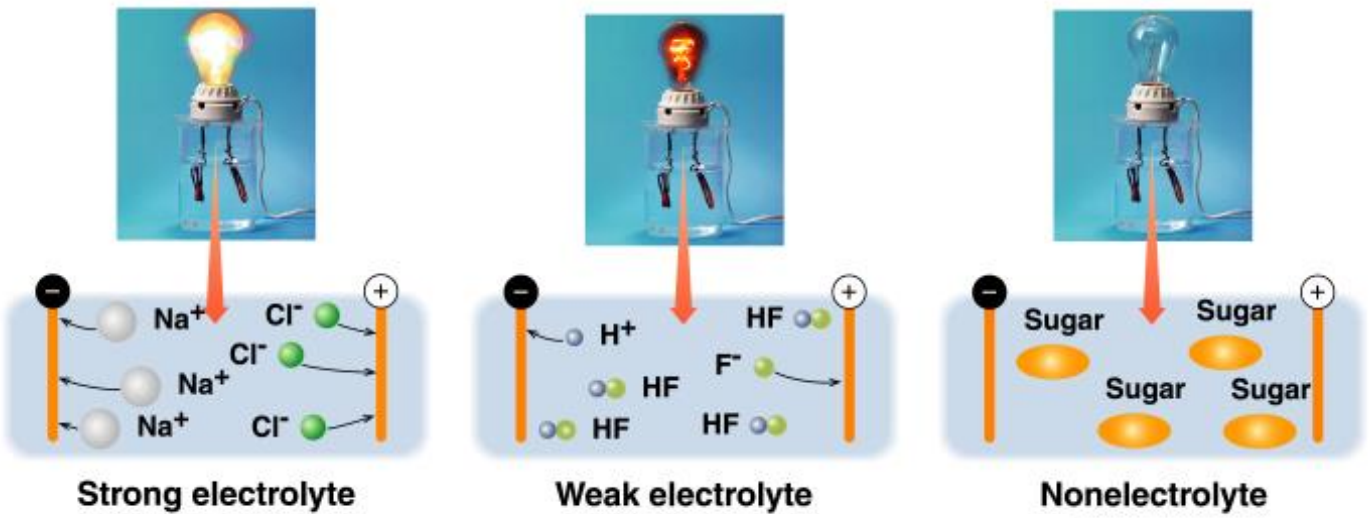
Electrolytes and Nonelectrolytes



Solutes and Ionic Charge

In water,

- **strong electrolytes** produce ions and conduct an electric current.
- **weak electrolytes** produce a few ions.
- **nonelectrolytes** do not produce ions.



Strong Electrolytes

Strong electrolytes

- dissociate in water producing positive and negative ions.
- conduct an electric current in water.
- equations show the formation of ions in aqueous (*aq*) solutions.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq) \quad \text{100\% ions}$$

$$CaBr_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Br^-(aq)$$

Learning Check

Complete each of the following equations for strong electrolytes in water.

A. $CaCl_2\,(s) \xrightarrow{H_2O}$

1) $CaCl_2(s)$

2) $Ca^{2+}(aq) + Cl_2^{-}(aq)$

3) $Ca^{2+}(aq) + 2\ Cl^{-}(aq)$

B. $K_3PO_4\,(s) \xrightarrow{H_2O}$

1) $3\ K^{+}(aq) + PO_4^{3-}(aq)$

2) $K_3PO_4(s)$

3) $K_3^{+}(aq) + P^{3-}(aq) + O_4^{-}(aq)$

Solution

Complete each of the following equations for strong electrolytes in water:

A. $CaCl_2\,(s) \xrightarrow{H_2O}$

3) $Ca^{2+}(aq) + 2\ Cl^{-}(aq)$

B. $K_3PO_4\,(s) \xrightarrow{H_2O}$

1) $3\ K^{+}(aq) + PO_4^{3-}(aq)$

Weak Electrolytes

A **weak electrolyte**

- dissociates only slightly in water.
- in water forms a solution of a few ions and mostly undissociated molecules.

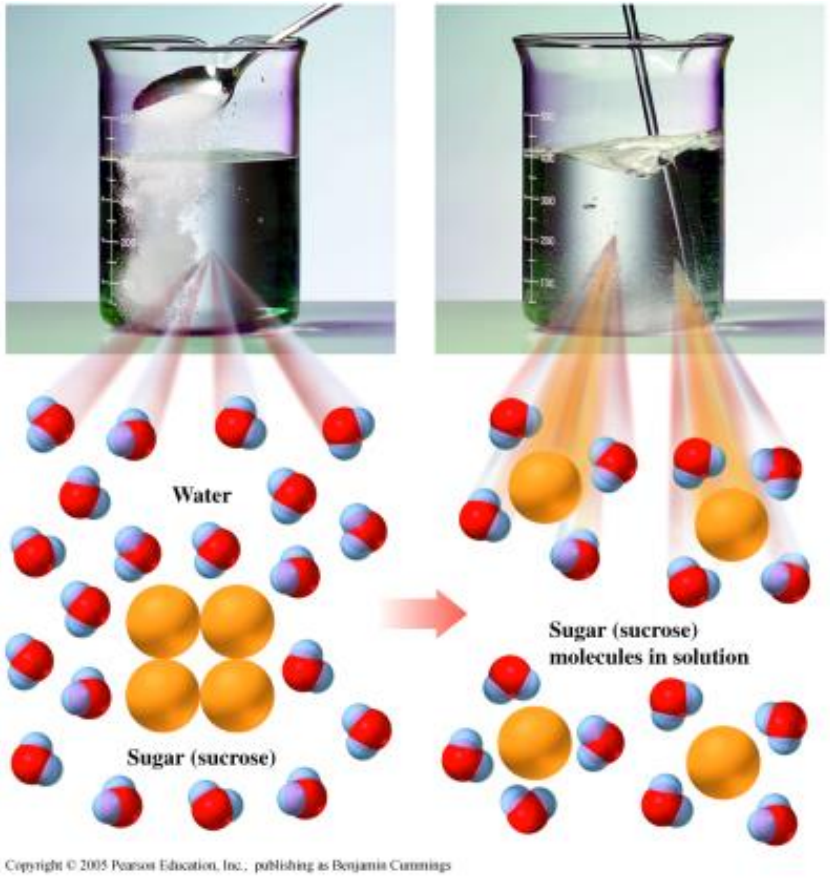
$$HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Nonelectrolytes

Nonelectrolytes

- dissolve as molecules in water.
- do not produce ions in water.
- do not conduct an electric current.



Equivalents

An equivalent (Eq) is the amount of an electrolyte or an ion that provides 1 mole of electrical charge (+ or -).

1 mole Na^+	=	1 equivalent
1 mole Cl^-	=	1 equivalent
1 mole Ca^{2+}	=	2 equivalents
1 mole Fe^{3+}	=	3 equivalents

Electrolytes in Body Fluids

In replacement solutions for body fluids, the electrolytes are given in milliequivalents per liter (mEq/L).

Ringer's Solution

Na^+	147 mEq/L	Cl^-	155 mEq/L
K^+	4 mEq/L		
Ca^{2+}	4 mEq/L		

The milliequivalents per liter of cations must equal the milliequivalents per liter of anions.

Learning Check

A. In 1 mole of Fe^{3+}, there are

1) 1 Eq. 2) 2 Eq. 3) 3 Eq.

B. In 2.5 mole SO_4^{2-}, there are

1) 2.5 Eq. 2) 5.0 Eq. 3) 1.0 Eq.

C. An IV bottle contains NaCl. If the Na^+ is 34 mEq/L, the Cl^- is

1) 34 mEq/L. 2) 0 mEq/L. 3) 68 mEq/L.

Solution

A. 3) 3 equiv

B. 2) 5.0 Eq

$$2.5 \text{ mole } SO_4^{2-} \times \frac{2 \text{ Eq}}{1 \text{ mole } SO_4^{2-}} = 5.0 \text{ Eq}$$

C. 1) 34 mEq/L