Reduction – Oxidation Reactions "REDOX"

- Is a chemical reaction in which electrons are transferred
- Must have both **reduction** and **oxidation** happening for the reaction to occur
  - **REDUCTION** – a process in which electrons are gained by an entity
  - **OXIDATION** – a process in which electrons are lost by an entity

  - How can you remember this?

"LEO the lion says GER"

LEO = Losing Electrons = Oxidation

GER = Gaining Electrons = Reduction

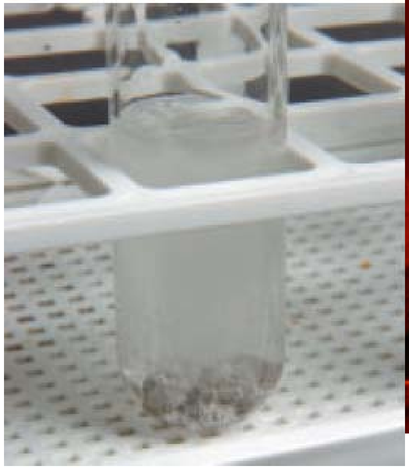
Other memory devices:

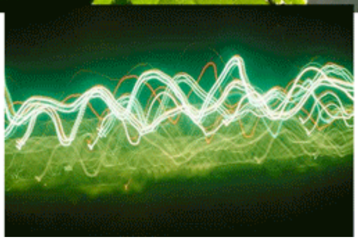
OIL RIG (**O**xidation **I**s **L**osing electrons, **R**eduction **I**s **G**aining electrons)

REGOLE (**R**eduction **E**lectron **G**ain **O**xidation **L**oss of **E**lectron)

Reduction – Oxidation Reactions “REDOX”

- Examples of Redox Reactions:
  - *Synthesis, decomposition, combustion, single displacement, cellular respiration, photosynthesis,*
    (NOT double displacement)



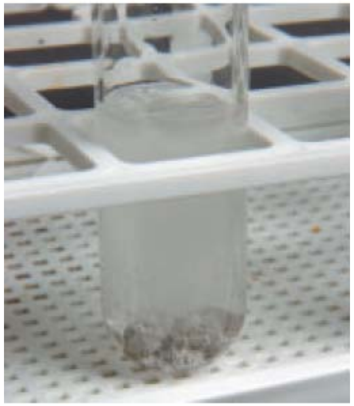


An Introduction to Redox

- Imagine that a reaction is a combination of two parts called *half-reactions.*
  - A half reaction represents what is happening to one reactant, it tells one part of the story.
  - Another half-reaction is required to complete the description of the reaction.

- Example: When metal is placed into hydrochloric acid solution, gas bubbles form as the zinc slowly disappears.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g}$$



- What happens to the zinc? To the $HCl_{(aq)}$? *Look at the half-reactions.*

$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2\ e^-$$

$$2\ H^+{}_{(aq)} + 2\ e^- \rightarrow H_{2\ (g)}$$

Notice that both of these half-reactions are balanced by <u>mass</u> (same number of atoms/ions of each element on both sides) and by <u>charge</u> (same total charge on both sides)

  - A **half reaction** is a balanced chemical equation that represents either a loss or gain of electrons by a substance

An Introduction to Redox

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$$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2\,e^{-}$$

OXIDATION - entity loses electrons

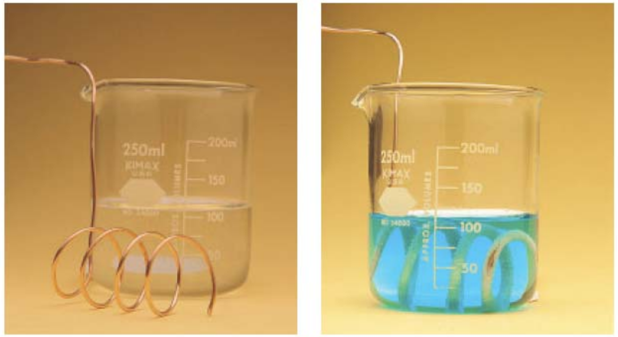
REDUCTION - entity gains electrons

$$2\,H^{+}{}_{(aq)} + 2\,e^{-} \rightarrow H_{2\,(g)}$$

  - Where is **oxidation** occurring?? (LEO)

  - Where is **reduction** occurring?? (GER)

An Introduction to Redox



- Example: When a piece of copper is placed into a beaker of silver nitrate, the following

$$Cu_{(s)} + AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + Ag_{(s)}$$

- Write the balanced half-reaction equations:
    - *To show that the number of electrons gained* ***equals*** *the number of electrons lost in two half-equations, it may be necessary to* ***multiply*** *one or both half-reaction equations by a coefficient to balance the electrons. I.e. Ag half reaction must be multiplied by 2*

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$

OXIDATION

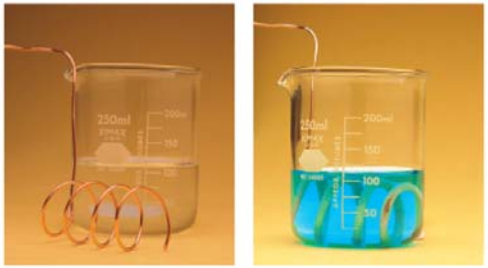
$$2\,[Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}]$$

REDUCTION

- Where is Oxidation occurring?

- Where is Reduction occurring?

An Introduction to Redox



OXIDATION $Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2\,e^-$

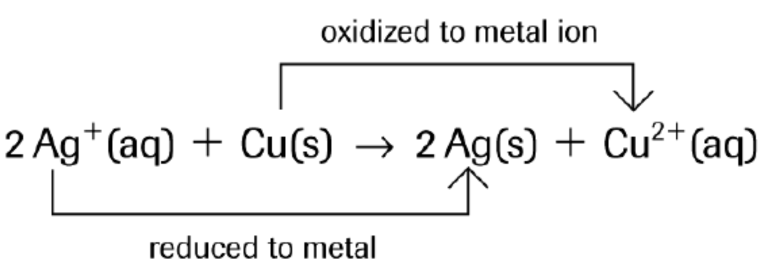
REDUCTION $2\,[Ag^+{}_{(aq)} + e^- \rightarrow Ag_{(s)}]$

- Now add the half-reactions and cancel the terms that appear on both sides of the equation to obtain the **net-ionic equation**

$$2\,Ag^+{}_{(aq)} + \cancel{2\,e^-} + Cu_{(s)} \rightarrow 2\,Ag_{(s)} + Cu^{2+}{}_{(aq)} + \cancel{2\,e^-}$$

$$2\,Ag^+{}_{(aq)} + Cu_{(s)} \rightarrow 2\,Ag_{(s)} + Cu^{2+}{}_{(aq)}$$

  - Silver ions are **reduced** to silver metal by reaction with copper metal. Simultaneously, copper metal is **oxidized** to copper(II) ions by reaction with silver ions.



An Introduction to Redox

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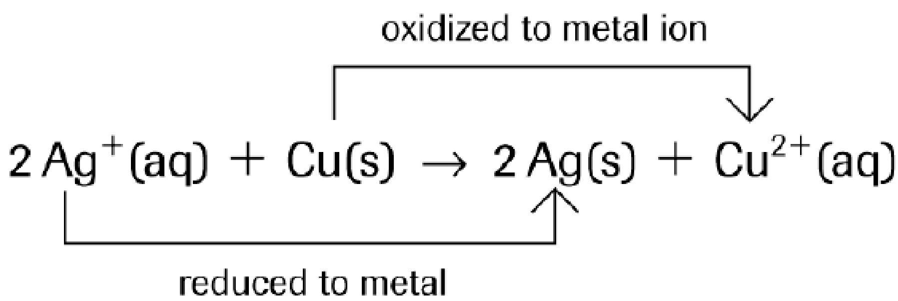
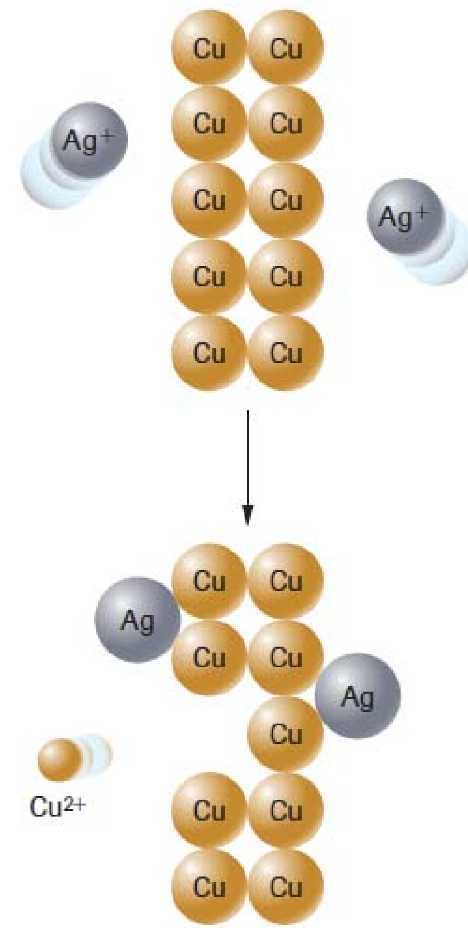




An Introduction to Redox

- There are two methods for developing net ionic equations:

  1) **½ reaction method we just learned**

$$2\,Ag^{+}(aq) + \cancel{2e^{-}} + Cu(s) \rightarrow 2\,Ag(s) + Cu^{2+}(aq) + \cancel{2e^{-}}$$

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

OR

2) **Using the net-ionic equation method from Chem 20**

$$Cu_{(s)} + 2AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$$ NON-IONIC

$$Cu_{(s)} + 2Ag^{+}_{(aq)} + \cancel{2\,NO_3^{-}}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + \cancel{2NO_3^{-}}_{(aq)} + 2Ag_{(s)}$$ TOTAL IONIC

$$2\,Ag^{+}_{(aq)} + Cu_{(s)} \rightarrow 2\,Ag_{(s)} + Cu^{2+}_{(aq)}$$ NET-IONIC

Summary "Electron Transfer Theory"

- A ***redox reaction*** is a chemical reaction in which electrons are transferred between entities
- The total number of electrons gained in the reduction ***equals*** the total number of electrons lost in the oxidation
- ***Reduction*** is a process in which electrons are gained by an entity
- ***Oxidation*** is a process in which electrons are lost by an entity
- Both reduction and oxidation are represented by ***balanced half-reaction equations.***

REDOX Reactions…. so far

Reduction

- Historically, the formation of a metal from its "ore" (or oxide)
  - *I.e. nickel(II) oxide is reduced by hydrogen gas to nickel metal*

$$NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(l)}$$

$$Ni^{+2} \rightarrow Ni^{o}$$

- A gain of electrons occurs (so the entity becomes more negative)
- Electrons are shown as the reactant in the half-reaction

Oxidation

- Historically, reactions with oxygen
  - *I.e. iron reacts with oxygen to produce iron(III) oxide*

$$4\ Fe_{(s)} + O_{2(g)} \rightarrow Fe_2O_{3(s)}$$

$$Fe^{0} \rightarrow Fe^{+3}$$

- A loss of electrons occurs (so the entity becomes more positive)
- Electrons are shown as the product in the half-reaction

Oxidation States

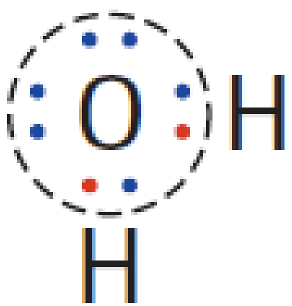
Learning Tip

Although the meaning of the terms *oxidation state* and *oxidation number* are slightly different, some people use these terms interchangeably.

- An **oxidation state** is defined as the *apparent* net electric charge an atom would have if the electron pairs in a covalent bond belonged *entirely* to the most electronegative atom.
- An **oxidation number** is a positive or negative number corresponding to the oxidation state of the atom in a compound. (These are NOT charges!)
- Example: In water, which is the most electronegative atom, H or O?
  - Oxygen, so we act as if the oxygen owns both electrons in the electron pair.

Learning Tip

Oxidation numbers are simply positive or negative numbers assigned on the basis of a set of arbitrary rules. It is important for you to realize that these are not electric charges. For this reason, chemists use the term *oxidation number*. For example, we assign oxidation numbers of −2 and +1 to the oxygen and hydrogen atoms in a water molecule.



Each oxygen atom has 8 p^+ and 8 e^-. But if the oxygen atom gets to count the two hydrogen electrons (red dots) in the two shared pairs, as its own, then it has 8 p^+ but 10 e^-, leaving an apparent net charge of -2

Each hydrogen atom has 1 p+, but with no additional electron (since oxygen has already counted it), that leaves hydrogen with an apparent net charge of +1

Oxidation States

Table 1 Common Oxidation Numbers

Atom or ion	Oxidation number	Examples
all atoms in elements	0	Na is 0 Cl in Cl_2 is 0
hydrogen in all compounds, except hydrogen in hydrides	+1 −1	H in HCl is +1 H in LiH is −1
oxygen in all compounds, except oxygen in peroxides	−2 −1	O in H_2O is −2 O in H_2O_2 is −1
all monatomic ions	charge on ion	Na^+ is +1 S^{2-} is −2

Tip:

- The sum of the oxidation numbers for a neutral compound = 0
- The sum of the oxidation numbers for a polyatomic ion = ion charge

*** This method only works if there is only one unknown after referring to the above table*

Oxidation States

- Example: What is the oxidation number of carbon in methane CH_4?
  - After referring to **Table 1**, we assign an oxidation number of +1 to hydrogen
  - **So now we have some simple math…**
  - Since a methane molecule is electrically neutral, then the oxidation number of the one carbon atom and the four hydrogen atoms 4(+1) must equal zero.

$$x \quad + \quad 4(+1) \quad = \quad 0$$

- So the oxidation number of carbon is = **-4**
- **How do we write this?**

$$\overset{-4}{C}\overset{+1}{H}_4$$

Oxidation States

- Example: What is the oxidation number of mangan
  MnO_4^- ?
  - After referring to **Table 1**, we assign an oxidation num
  - Since a permanganate ion has a charge of 1-, then the c
    manganese atom and the four oxygen atoms 4(-2) mu

$$x + 4(-2) = -1$$

$$x + -8 = -1$$

- So the oxidation number of manganese is = **-7**

Learning Tip

Alternatively, you can always split an ionic formula into the cation and anion before solving for an unknown oxidation number.

For example, if you want to know the oxidation number for sulfur in sodium sulfate, start with the sulfate ion:

$$\overset{x}{S}\overset{-2}{O}{}_4^{2-}$$

$$x + 4(-2) = -2 \qquad x = +6$$

- Example: What is the oxidation number of sulfur in sodium sulfate?
  - We know the oxidation numbers of both Na and O, and solve algebraically

$$\overset{+1}{Na_2}\overset{x}{S}\overset{-2}{O_4}$$

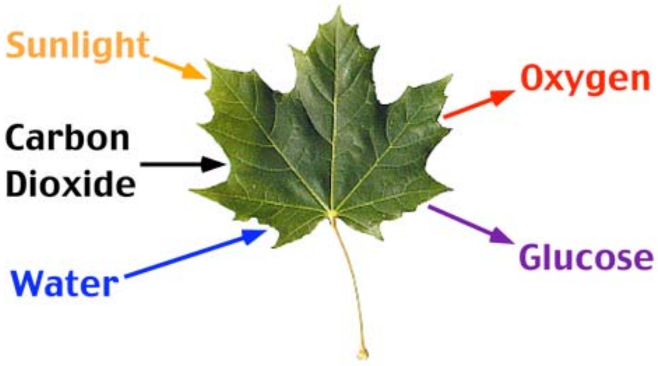
$$2(+1) + x + 4(-2) = 0$$

$$2 + x + -8 = 0$$

So the oxidation number of sulfur is **+6**

Redox in Living Organisms

- The ability of carbon to take on different oxidation states is essential to life on Earth. Photosynthesis involves a series of reduction reactions in which the oxidation number of carbon changes from +4 in carbon dioxide to an average of 0 in sugars such as glucose.



- The smell of a skunk is caused by a thiol compound (R-SH). To deodorize a pet sprayed by a skunk, you need to convert the smelly thiol to an odourless compound. Hydrogen peroxide in a basic solution acts as an oxidizing agent to change the thiol to a disulfide compound (RS-SR), which is odourless.

Determining Oxidation Numbers Summary

1. Assign common oxidation numbers (**Table 1** on page 658)

2. The total of the oxidation numbers of atoms in a molecule or ion equals the value of the net electric charge of the molecule or ion.

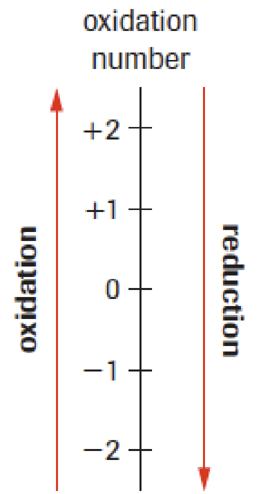
   a) The sum of the oxidation numbers for a compound is zero.

   b) The sum of the oxidation numbers for a polyatomic ion equals the charge of the ion.

3. Any unknown oxidation number is determined algebraically from the sum of the known oxidation numbers and the net charge on the entity.

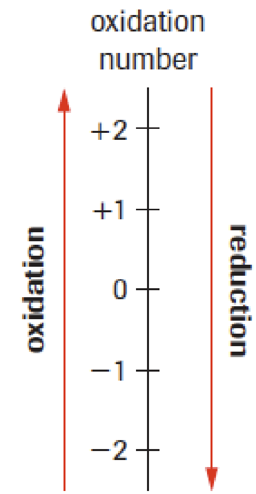
Oxidation Numbers and Redox

- Although the concept of oxidation states is somewhat arbitrary, because it is based on assigned charges, it is self-consistent and allows predictions of electron transfer.
  - Chemists believe that if the oxidation number of an atom or ion changes during a chemical reaction, then an electron transfer (oxidation-reduction reaction) occurs.
  - Based on oxidation numbers,
    - If the oxidation numbers do not change = no transfer of e^-'s = not a redox rxn
    - An **increase** in the oxidation number = **oxidation**
    - A **decrease** in the oxidation number = **reduction**



Oxidation Numbers and Redox

- Example: Identify the oxidation and reduction in the reaction of zinc metal with hydrochloric acid.



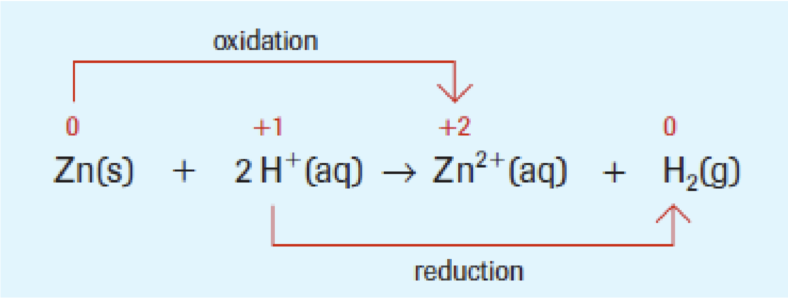
  - First write the chemical equation (as it is not provided)

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

  - Determine all of the oxidation numbers

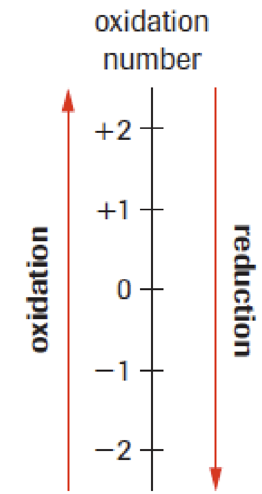
$$\overset{0}{Zn}(s) + 2\,\overset{+1}{H^{+}}(aq) \rightarrow \overset{+2}{Zn^{2+}}(aq) + \overset{0}{H_2}(g)$$

  - Now look for the oxidation number of an atom/ion that **increases** as a result of the reaction and label the change as **oxidation.** There must also be an atom/ion whose oxidation number **decreases.** Label this change as **reduction.**



Oxidation Numbers and Redox

- Example: When natural gas burns in a furnace, carbon dioxide and water form. Identify oxidation and reduction in this reaction.



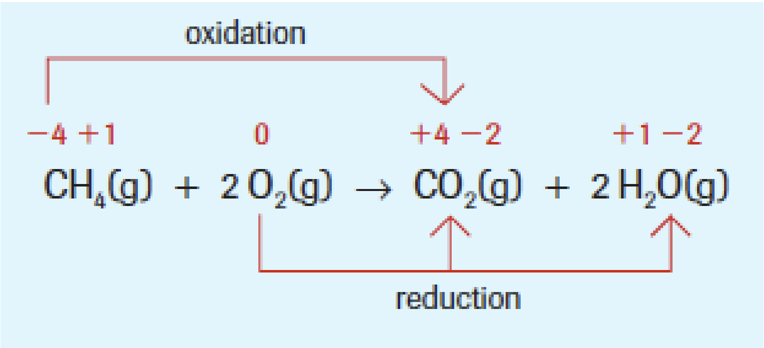
  - First write the chemical equation (as it is not provided)

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

  - Determine all of the oxidation numbers

$$\overset{-4\;+1}{CH_4}(g) + 2\,\overset{0}{O_2}(g) \rightarrow \overset{+4\;-2}{CO_2}(g) + 2\,\overset{+1\;-2}{H_2O}(g)$$

  - Now look for the oxidation number of an atom/ion that **increases** as a result of the reaction and label the change as **oxidation.** There must also be an atom/ion whose oxidation number **decreases.** Label this change as **reduction.**



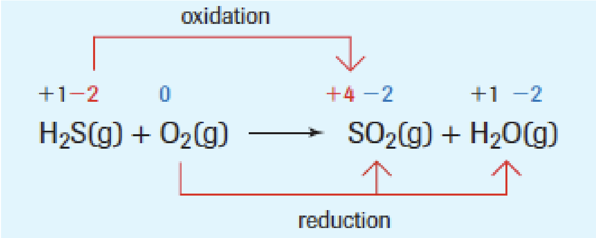
Balancing Redox Equations using Oxidation Numbers

1. Assign **oxidation numbers** and identify the atoms/ions whose oxidation numbers change
2. Using the **change** in oxidation numbers, write the number of **electrons** transferred per **atom**.
3. Using the chemical formulas, determine the number of **electrons** transferred per **reactant**. (Use formula subscripts to do this)
4. Calculate the simplest whole number coefficients for the reactants that will **balance** the total number of electrons transferred. Balance the reactants and products.
5. Balance the O atoms using $H_2O_{(l)}$, and then balance the H atoms using $H^+_{(aq)}$

Balancing Redox Equations using Oxidation Numbers #1

Example: When hydrogen sulfide is burned in the presence of oxygen, it is converted to sulfur dioxide and water vapour. Use oxidation numbers to balance this equation. $H_2S_{(g)} + O_{2(g)} \rightarrow SO_{2(g)} + H_2O_{(g)}$

1. Assign oxidation numbers to all atoms/ions and look for the numbers that change. Highlight these.
   - Notice that a sulfur atom is oxidized from -2 to +4. This is a change of 6 meaning 6 e^- have been transferred.
   - An oxygen atom is reduced from 0 to -2. This is a change of 2 or $2e^-$ transferred.
   - Because the substances are molecules, not atoms, we need to specify the change in the number of e^-'s per molecule



$\overset{+1\ -2}{H_2S(g)}$	+	$\overset{0}{O_2(g)}$	$\rightarrow$	$\overset{+4\ -2}{SO_2(g)}$	+	$\overset{+1\ -2}{H_2O(g)}$
$6\ e^-$/S atom		$2\ e^-$/O atom				
$6\ e^-/H_2S$		$4\ e^-/O_2$				

2. The next step is to determine the simplest whole numbers that will balance the number of electrons transferred for each reactant. The numbers become the coefficients of the reactants

$$2\ H_2S(g) + 3\ O_2(g) \rightarrow SO_2(g) + H_2O(g)$$

1. The coefficients for the products can be obtained by balancing the atoms whose oxidation numbers have changed and then any other atoms.

$$2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ SO_2(g) + 2\ H_2O(g)$$

Balancing Redox Equations using Oxidation Numbers #2

Example: Chlorate ions and iodine react in an **acidic** solution to produce chloride ions and iodate ions. Balance the equation for this reactions. $\mathbf{ClO_3^-{}_{(aq)} + I_{2(aq)} \rightarrow Cl^-{}_{(aq)} + IO_3^-{}_{(aq)}}$

1. Assign oxidation numbers to all atoms/ions and look for the numbers that change. Highlight these.

Remember to record the change in the number of electrons per atom and per molecule or polyatomic ion.

+5 −2		0		−1		+5 −2
$ClO_3^-(aq)$	+	$I_2(aq)$	$\rightarrow$	$Cl^-(aq)$	+	$IO_3^-(aq)$
$6\ e^-/Cl$		$5\ e^-/I$				
$6\ e^-/ClO_3^-$		$10\ e^-/I_2$				

1. The next step is to determine the simplest whole numbers that will balance the number of electrons transferred for each reactant. The numbers become the coefficients of the reactants. The coefficients for the products can be obtained by balancing the atoms whose oxidation numbers have changed and then any other atoms.

$$5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq)$$

2. Although Cl and I atoms are balanced, oxygen is not. Add $H_2O_{(l)}$ molecules to balance the O atoms.

$$3\ H_2O(l) + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq)$$

3. Add $H^+_{(aq)}$ to balance the hydrogen. The redox equation should now be completely balanced. Check your work by checking the total numbers of each atom/ion on each side and checking the total electric charge, which should also be balanced.

$$3\ H_2O(l) + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq) + 6\ H^+(aq)$$

Balancing Redox Equations using Oxidation Numbers #3

Example: Methanol reacts with permanganate ions in a basic solution. The main reactants and products are shown below. Balance the equation for this reaction.

- Assign oxidation numbers to all atoms/ions and look for the numbers that change. Highlight these.

- Remember to record the change in the number of electrons per atom and per molecule or polyatomic ion.

- Determine the simplest whole numbers that will balance the number of electrons transferred for each reactant. The numbers become the coefficients of the reactants. The coefficients for the products can be obtained by balancing the atoms whose oxidation numbers have changed and then any other atoms.

$$\overset{-2\ +1\ -2\ +1}{1\ CH_3OH(aq)} + \overset{+7\ -2}{6\ MnO_4^-(aq)} \rightarrow \overset{+4\ -2}{1\ CO_3^{2-}(aq)} + \overset{+6\ -2}{6\ MnO_4^{2-}(aq)}$$

$6\ e^-/C$	$1\ e^-/Mn$
$6\ e^-/CH_3OH$	$1\ e^-/MnO_4^-$

- Add $H_2O_{(l)}$ to balance the oxygen, add $H^+_{(aq)}$ to balance the hydrogen.

$$2\ H_2O(l) + CH_3OH(aq) + 6\ MnO_4^-(aq) \rightarrow CO_3^{2-}(aq) + 6\ MnO_4^{2-}(aq) + 8\ H^+(aq)$$

Balancing Redox Equations using Oxidation Numbers #4

Example: Household bleach contains sodium hypochlorite. Some of the hypochlorite ions disproportionate (react with themselves) to produce chloride ions and chlorate ions. Write the balanced redox equation for the disproportionation.

For disproportionation reactions, start with two identical entities on the reactant side and follow the usual procedure for balancing equations.

$$\overset{+1\;-2}{2\,ClO^-(aq)} + \overset{+1\;-2}{ClO^-(aq)} \rightarrow \overset{-1}{2\,Cl^-(aq)} + \overset{+5\;-2}{ClO_3^-(aq)}$$

$2\,e^-/Cl$ $\quad$ $4\,e^-/Cl$

$$3\,ClO^-(aq) \rightarrow 2\,Cl^-(aq) + ClO_3^-(aq)$$

Balancing Redox Equations using Oxidation Numbers #5

- Example: A person suspected of being intoxicated blows into this device and the alcohol in the person's breath reacts with an acidic dichromate ion solution to produce acetic acid (ethanoic acid) and aqueous chromium(III) ions. Balance the equation for this reaction.

−2+1 −2 +1   +6 −2   0 +1 0 −2 −2 +1   +3

$$C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow CH_3COOH(aq) + Cr^{3+}(aq)$$

$2\ e^-/C$	$3\ e^-/Cr$
$4\ e^-/C_2H_5OH$	$6\ e^-/Cr_2O_7^{2-}$

- Remember to balance the C and Cr first, then add $H_2O_{(l)}$ to balance O, $H^+_{(aq)}$ to balance H and then stop because this is an *acidic* solution

$$16\ H^+(aq) + 2\ Cr_2O_7^{2-}(aq) + 3\ C_2H_5OH(aq) \rightarrow 4\ Cr^{3+}(aq) + 3\ CH_3COOH(aq) + 11\ H_2O(l)$$

Balancing Redox Reactions using Half-Reactions

Rules for Writing Half-Reactions

1. Write an unbalanced ½ reaction showing formulas for reactants and products
2. Balance all atoms except H and O
3. Balance O by adding $H_2O_{(l)}$
4. Balance H by adding $H^+_{(aq)}$
5. Balance the charge by adding e^- and cancel anything that is the same on both sides

For basic solutions only:

6. Add OH-(aq) to both sides to equal the number of H+(aq) present
7. Combine $H^+_{(aq)}$ and $OH^-_{(aq)}$ on the same side to form $H_2O_{(l)}$. Cancel equal amounts of $H_2O_{(l)}$ from both sides.

Balancing Redox Reactions by Constructing Half-Reactions

SUMMARY

1. Use the information provided to start two half-reaction equations.
2. Balance each half-reaction equation.
3. Multiply each half-reaction by simple whole numbers to balance electrons lost and gained.
4. Add the two half-reaction equations, cancelling the electrons and anything else that is exactly the same on both sides of the equation.

Balancing Redox Reactions by Constructing Half Reactions

- Example: A person suspected of being intoxicated blows into this device and the alcohol in the person's breath reacts with an acidic dichromate ion solution to produce acetic acid (ethanoic acid) and aqueous chromium(III) ions. Predict the balanced redox reaction equation.

- Create a skeleton equation from the information provided:

$$C_2H_5OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow CH_3COOH(aq) + Cr^{3+}(aq)$$

- Separate the entities into the start of two half-reaction equations

$$C_2H_5OH(aq) \rightarrow CH_3COOH(aq)$$
$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

- Now use the steps you learned for balancing half reactions

$$H_2O(l) + C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4\,H^+(aq) + 4\,e^-$$

$$6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

- Now, balance the electrons lost and gained, and add the half reactions. Cancel the electrons and anything else that is exactly the same on both sides of the equation.

$$3\,[H_2O(l) + C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4\,H^+(aq) + 4\,e^-]$$
$$2\,[6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)]$$

$$3\,C_2H_5OH(aq) + 2\,Cr_2O_7^{2-}(aq) + 16\,H^+(aq) \rightarrow 3\,CH_3COOH(aq) + 4\,Cr^{3+}(aq) + 11\,H_2O(l)$$

Redox Terms

- Review: **"LEO the lion says GER"**
  - Loss of electrons = entity being oxidized
  - Gain of electrons = entity being reduced
  - **BUT….** Chemists don't say "*the reactant being oxidized*" or "*the reactant being reduced*"
  - Rather, they use the terms **OXIDIZING AGENT (OA)** and **REDUCING AGENT (RA)**
    - **OXIDIZING AGENT**: *causes oxidation* by removing (gaining) electrons from another substance in a redox reaction
    - **REDUCING AGENT**: *causes reduction* by donating (losing) electrons to another substance in a redox reaction

What does this mean? Let's revisit our first example when zinc and hydrochloric acid reacted.

Which reactant was reduced? *Which was oxidized?*

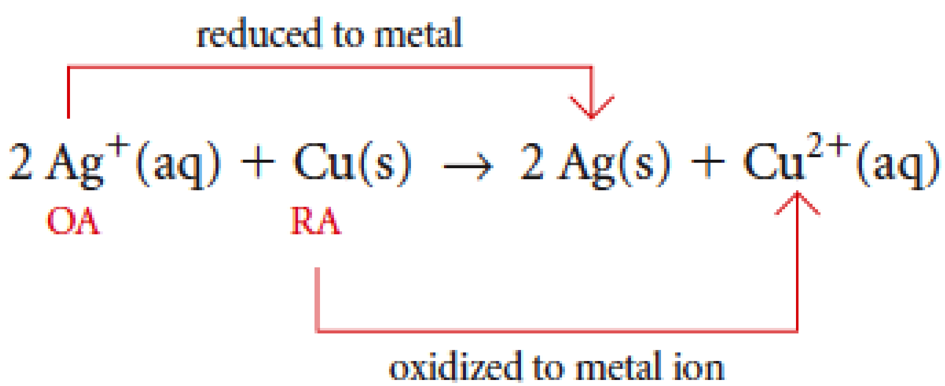
So…. *Which is the Oxidizing Agent (OA)?* *Which is the Reducing Agent (RA)*

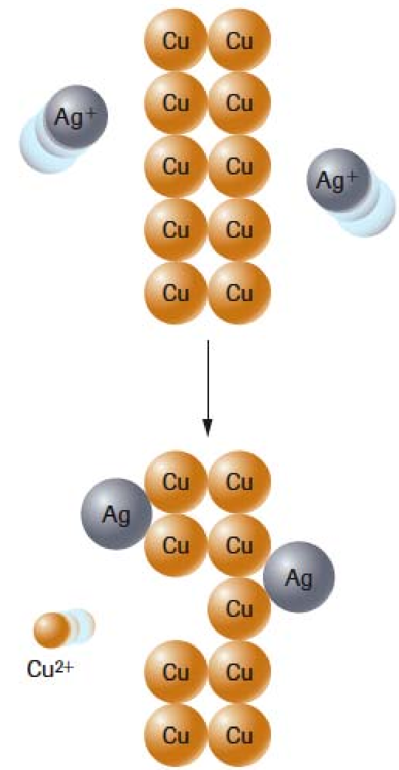
LEO = Oxidized $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ Reducing Agent

GER = Reduced $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ Oxidizing Agent

Redox Terms

- Silver ions were **reduced** to silver metal **by** reaction with copper metal. Simultaneously, copper metal was **oxidized** to copper(II) ions **by** reaction with silver ions.





- If .

- If $Cu_{(s)}$ is oxidized it is the:

OXIDIZING AGENT (OA)

REDUCING AGENT (RA)

It is important to note that oxidation and reduction are *processes*, and oxidizing agents and reducing agents are *substances*.

REDOX Reactions … so far

Reduction	Oxidation
• Historically, the formation of a metal from its "ore" (or oxide) ▫ *I.e. nickel(II) oxide is reduced by hydrogen gas to nickel metal* $NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(l)}$ *$Ni^{+2} \rightarrow Ni^{o}$*	• Historically, reactions with oxygen ▫ *I.e. iron reacts with oxygen to produce iron(III) oxide* $4\ Fe_{(s)} + O_{2(g)} \rightarrow Fe_2O_{3(s)}$ *$Fe^{0} \rightarrow Fe^{+3}$*
• A gain of electrons occurs (so the entity becomes more negative)	• A loss of electrons occurs (so the entity becomes more positive)
• Electrons are shown as the reactant in the half-reaction	• Electrons are shown as the product in the half-reaction
• A species undergoing reduction will be responsible for the oxidation of another entity – and is therefore classified as an oxidizing agent (OA)	• A species undergoing oxidation will be responsible for the reduction of another entity – and is therefore classified as an reducing agent (RA)

Redox Terms

- Summary so far:
    - The substance that is reduced (gains electrons) is also known as the oxidizing agent
    - The substance that is oxidized (loses electrons) is also knows as the reducing agent

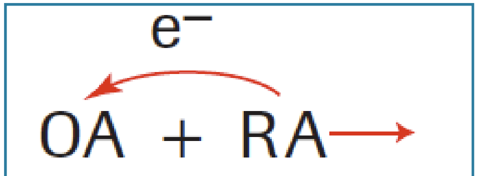


Figure 3
In all redox reactions, electrons are transferred from a reducing agent (RA) to an oxidizing agent (OA).

- **Question**: If a substance is a very strong oxidizing agent, what does this mean in terms of electrons?

The substance has a very strong attraction for electrons.

- **Question**: If a substance is a very strong reducing agent, what does this mean in terms of electrons?

The substance has a weak attraction for its electrons, which are easily removed

Redox Table

- A reaction is considered **spontaneous** if it occurs on its own
- A reduction ½ reaction table is useful in predicting the spontaneity of a reaction
  - Reduction Tables show reduction ½ reactions in the forward direction, therefore all the reactants will be **oxidizing agents**
  - If we list the OA's from an experiment in decreasing order of strength, we create a reduction ½ reaction table:

decreasing reactivity of oxidizing agents

SOA ↓

$$Ag^{+}_{(aq)} + 1\,e^{-} \rightarrow Ag_{(s)}$$
$$Cu^{2+}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)}$$
$$Zn^{2+}_{(aq)} + 2\,e^{-} \rightarrow Zn_{(s)}$$
$$Mg^{2+}_{(aq)} + 2\,e^{-} \rightarrow Mg_{(s)}$$

↑ SRA

decreasing reactivity of reducing agents

Building Redox Tables #1

- Consider the following experimental information and add half-reactions to the redox table you have created

	$Hg^{2+}_{(aq)}$	$Cu^{2+}_{(aq)}$	$Ag^{+}_{(aq)}$	$Au^{3+}_{(aq)}$
$Hg_{(s)}$	✗	✗	✗	✓
$Cu_{(s)}$	✓	✗	✓	✓
$Ag_{(s)}$	✓	✗	✗	✓
$Au_{(s)}$	✗	✗	✗	✗

SOA

$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$

$Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_{(s)}$

$Ag^{+}_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$

SRA

Building Redox Tables #1

SOA ↓

$Au^{3+}_{(aq)}$	+	$3\ e^-$	→	$Au_{(s)}$
$Hg^{2+}_{(aq)}$	+	$2\ e^-$	→	$Hg_{(s)}$
$Ag^{+}_{(aq)}$	+	$1\ e^-$	→	$Ag_{(s)}$
$Cu^{2+}_{(aq)}$	+	$2\ e^-$	→	$Cu_{(s)}$
$Zn^{2+}_{(aq)}$	+	$2\ e^-$	→	$Zn_{(s)}$
$Mg^{2+}_{(aq)}$	+	$2\ e^-$	→	$Mg_{(s)}$

SRA ↑

- The **spontaneity rule!**
  - **A reaction will be spontaneous if on a redox table:**

OA above RA = Spontaneous Reaction

RA below OA = Non-spontaneous Reaction

Building Redox Tables #2

- Example 2: Use the following information to create a table of reduction ½ reactions

OA RA

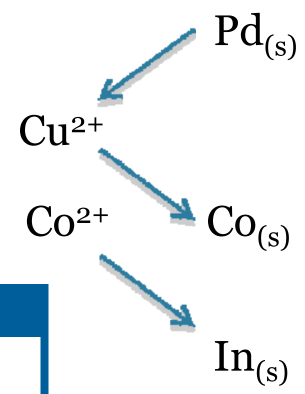
$3\,Co^{2+}_{(aq)} + 2\,In_{(s)} \rightarrow 2\,In^{3+}_{(aq)} + 3\,Co_{(s)}$

OA RA

$Cu^{2+}_{(aq)} + Co_{(s)} \rightarrow Co^{2+}_{(aq)} + Cu_{(s)}$

OA RA

$Cu^{2+}_{(aq)} + Pd_{(s)} \rightarrow$ no reaction



Learning Tip

The nonspontaneity of a reaction is communicated in several ways: “no evidence of reaction,” “nonspontaneous,” “no reaction,” or “nonspont,” written over the equation arrow.

SOA

$Pd^{2+}_{(aq)} + 2\,e^- \rightarrow Pd_{(s)}$

$Cu^{2+}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)}$

$Co^{2+}_{(aq)} + 2\,e^- \rightarrow Co_{(s)}$

$In^{3+}_{(aq)} + 3\,e^- \rightarrow In_{(s)}$

SRA

Building Redox Tables #3

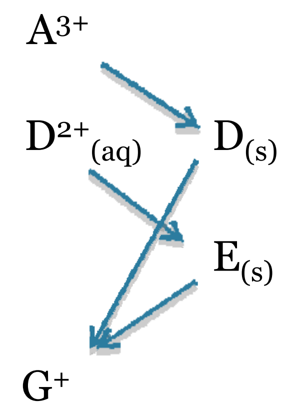
- Example 3: Use the following information to create a table of reduction ½ reactions

OA RA
$2\,A^{3+}{}_{(aq)} + 3\,D_{(s)} \rightarrow 3\,D^{2+}{}_{(aq)} + 2\,A_{(s)}$

OA RA
$G^{+}{}_{(aq)} + D_{(s)} \rightarrow$ no reaction

OA RA
$3\,D^{2+}{}_{(aq)} + 2\,E_{(s)} \rightarrow 3\,D_{(s)} + 2\,E^{3+}{}_{(aq)}$

OA RA
$G^{+}{}_{(aq)} + E_{(s)} \rightarrow$ no reaction



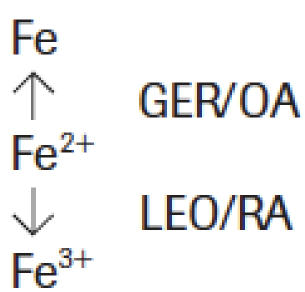
SOA

$A^{3+}{}_{(aq)} + 3\,e^{-} \rightarrow A_{(s)}$
$D^{2+}{}_{(aq)} + 2\,e^{-} \rightarrow D_{(s)}$
$E^{3+}{}_{(aq)} + 3\,e^{-} \rightarrow E_{(s)}$
$G^{+}{}_{(aq)} + 1\,e^{-} \rightarrow G_{(s)}$

SRA

Building Redox Tables

- So far we have been using examples where the oxidizing agents are metal ions and the reducing agents are metal atoms. What else could gain or lose electrons?
  - Non-metal atoms I.e. $Cl_{2(g)} + 2e^- \rightarrow 2\ Cl^-_{(aq)}$ ($Cl_{2(g)}$ could act as a Reducing Agent)
  - Non-metal ions I.e. $2\ Br^-_{(aq)} \rightarrow Br_{2(l)} + 2\ e^-$ ($2Br^-_{(aq)}$ could act as an Oxidizing Agent)
- Redox Table Trend
  - OA's tend to be **metal ions** and **non-metal atoms**
  - RA's tend to be **metal atoms** and **non-metal ions**
- Also, are there any entities that could act as both OA or RA?
  - Multivalent metals



Iron(II) ions can either lose or gain electrons and, therefore, can act as either reducing agents or oxidizing agents.

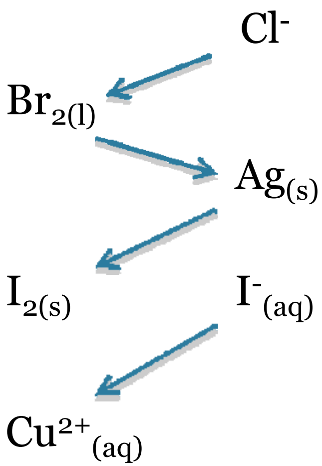
- Example 4: Use the following information to create a table of reduction ½ reactions

RA: $Ag_{(s)}$ + OA: $Br_{2(l)}$ → $AgBr_{(s)}$

RA: $Ag_{(s)}$ + OA: $I_{2(s)}$ → no evidence of reaction

OA: $Cu^{2+}_{(aq)}$ + RA: $I^-_{(aq)}$ → no redox reaction

OA: $Br_{2(l)}$ + RA: $Cl^-_{(aq)}$ → no evidence of reaction



SOA ↓

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$

$Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$

$Ag^+_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

SRA ↑

Predicting Redox Reactions

- Now that you know what redox reactions are, you will be responsible for determining if a reaction will occur (is **spontaneous**) and if so, what the **reaction equation** will be. How do we do this?

1. The first step is to determine all the entities that are present.
   - Helpful reference: Table 5 pg. 680
   - *Remember: In solutions, molecules and ions behave independently of each other.*
   - Example: When a solution of **potassium permanganate** is slowly poured through **acidified iron(II) sulfate** solution.
   - Does a redox reaction occur and what is the reaction equation?

Table 6 Hints for Listing and Labelling Entities

• Aqueous solutions contain $H_2O(l)$ molecules.
• Acidic solutions contain $H^+(aq)$ ions.
• Basic solutions contain $OH^-(aq)$ ions.
• Some oxidizing and reducing agents are combinations, for example, $MnO_4^-(aq)$ and $H^+(aq)$.
• $H_2O(l)$, $Fe^{2+}(aq)$, $Cu^+(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either oxidizing or reducing agents. Label both possibilities in your list.

$K^+(aq)$ $MnO_4^-(aq)$ $H^+(aq)$ $Fe^{2+}(aq)$ $SO_4^{2-}(aq)$ $H_2O(l)$

Predicting Redox Reactions

2. The second step is to determine all possible OA's and RA's

- This is a crucial step!! Things to watch out for:
  - Combinations
    - (i.e. $MnO_4^-{}_{(aq)}$ is an oxidizing agent only in an acidic solution)
    - To indicate this draw an arc between the permanganate and hydrogen ion
  - Species that can act as both OA and RA
    - Any lower charge multivalent metal i.e. Fe^{2+}, Cu^{+}, Sn^{2+}, Cr^{2+}
    - Water ($H_2O_{(l)}$)
    - Label both possibilities in your list

Table 6 Hints for Listing and Labelling Entities

- Aqueous solutions contain $H_2O(l)$ molecules.
- Acidic solutions contain $H^+(aq)$ ions.
- Basic solutions contain $OH^-(aq)$ ions.
- Some oxidizing and reducing agents are combinations, for example, $MnO_4^-(aq)$ and $H^+(aq)$.
- $H_2O(l)$, $Fe^{2+}(aq)$, $Cu^+(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either oxidizing or reducing agents. Label both possibilities in your list.

OA		OA (combination)	OA	OA		OA (combination)	OA
$K^+(aq)$	$MnO_4^-(aq)$		$H^+(aq)$	$Fe^{2+}(aq)$	$SO_4^{2-}(aq)$		$H_2O(l)$
				RA			RA

- Before we move on, let's practice Step 1 and 2
  - Pg. 680 #23

Practice

25. List all entities initially present in the following mixtures, and identify all possible oxidizing and reducing agents.

(a) A lead strip is placed in a copper(II) sulfate solution.
(b) A gold coin is placed in a nitric acid solution.
(c) A potassium dichromate solution is added to an acidic iron(II) nitrate solution.
(d) An aqueous chlorine solution is added to a phosphorous acid solution.
(e) A potassium permanganate solution is mixed with an acidified tin(II) chloride solution.
(f) Iodine solution is added to a basic mixture containing manganese(IV) oxide.

- Pg. 680 #23

(a)

OA $Cu^{2+}(aq)$

$Pb(s)$ **RA**

RA

OA $SO_4^{2+}(aq)$

OA $H_2O(l)$ **RA**

(b)

$Au(s)$ **RA**

OA $H^{+}(aq)$

OA

$NO_3^{-}(aq)$

OA $H_2O(l)$ **RA**

(c)

OA $K^{+}(aq)$

$Cr_2O_7^{2-}(aq)$

OA

$H^{+}(aq)$

OA

OA

$NO_3^{-}(aq)$

OA $Fe^{2+}(aq)$ **RA**

OA $H_2O(l)$ **RA**

- Pg. 680 #23

(d)

OA				OA
$Cl_2(aq)$	$H_2SO_3(aq)$			$H_2O(l)$
	╲	RA	╱	RA

(e)

OA		╱ OA ╲		OA	OA				OA
$K^+(aq)$	$MnO_4^-(aq)$			$H^+(aq)$	$Sn^{2+}(aq)$	$Cl^-(aq)$			$H_2O(l)$
					RA	RA ╲	RA	╱	RA

(f)

			OA			OA
$OH^-(aq)$		$MnO_2(s)$	$I_2(aq)$			$H_2O(l)$
RA ╲	RA	╱	╲	RA	╱	RA

Predicting Redox Reactions

3. The third step is to identify the SOA and SRA using Appendix C11 (page 805)

OA	SOA	OA	OA	OA	OA
$K^+(aq)$	$MnO_4^-(aq)$	$H^+(aq)$	$Fe^{2+}(aq)$	$SO_4^{2-}(aq)$	$H_2O(l)$
			SRA		RA

3. The fourth step is to show the ½ reactions (from the redox table) and balance
   - SOA equation straight from table. SRA equation read from **right to left**

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

$$5\,[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-]$$

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Fe^{2+}(aq) \rightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

- Are these equations balanced? Do the number of electrons lost = electrons gained
- If not, multiply one or both equations by a number then add the balanced equations

Predicting Redox Reactions

3. The last step is to predict the spontaneity. Does the net ionic equation represent a spontaneous or non-spontaneous redox reaction?

If the SOA
above → Spontaneous
SRA??

If the SRA
below → Nonspontaneous
SOA

Figure 9
A solution of potassium permanganate is being added to an acidic solution of iron(II) ions. The dark purple colour of $MnO_4^-(aq)$ ions instantly disappears. The interpretation is that $MnO_4^-(aq)$ ions react with $Fe^{2+}(aq)$ ions to produce the yellow-brown $Fe^{3+}(aq)$ and $Mn^{2+}(aq)$ ions.

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Fe^{2+}(aq) \xrightarrow{\text{spont.}} 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Predicting Redox Reactions #2

Could copper pipe be used to transport a hydrochloric acid solution?

1. List all entities

$Cu(s)$ $H^+(aq)$ $Cl^-(aq)$ $H_2O(l)$

1. Identify all possible OA's and RA's

1. Identify the SOA and SRA

RA	OA	RA	OA, RA
$Cu(s)$	$H^+(aq)$	$Cl^-(aq)$	$H_2O(l)$

(RA combination of $Cl^-(aq)$ and $H_2O(l)$)

2. Show ½ reactions and balance

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$

3. Predict spontaneity

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$

$$2\,H^+(aq) + Cu(s) \xrightarrow{\text{nonspont.}} H_2(g) + Cu^{2+}(aq)$$

Since the reaction is nonspontaneous, it should be possible to use a copper pipe to carry hydrochloric acid

Table 6 Hints for Listing and Labelling Entities

- Aqueous solutions contain $H_2O(l)$ molecules.
- Acidic solutions contain $H^+(aq)$ ions.
- Basic solutions contain $OH^-(aq)$ ions.
- Some oxidizing and reducing agents are combinations, for example, $MnO_4^-(aq)$ and $H^+(aq)$.
- $H_2O(l)$, $Fe^{2+}(aq)$, $Cu^+(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either oxidizing or reducing agents. Label both possibilities in your list.

REDOX Reactions … the end

Reduction

- Historically, the formation of a metal from its "ore" (or oxide)
  - *I.e. nickel(II) oxide is reduced by hydrogen gas to nickel metal*

$$NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(l)}$$

$$Ni^{+2} \rightarrow Ni^{o}$$

- A gain of electrons occurs (so the entity becomes more negative)
- Electrons are shown as the reactant in the half-reaction
- A species undergoing reduction will be responsible for the oxidation of another entity – and is therefore classified as an oxidizing agent (OA)
- Decrease in oxidation number

Oxidation

- Historically, reactions with oxygen
  - *I.e. iron reacts with oxygen to produce iron(III) oxide*

$$4\ Fe_{(s)} + O_{2(g)} \rightarrow Fe_2O_{3(s)}$$

$$Fe^{0} \rightarrow Fe^{+3}$$

- A loss of electrons occurs (so the entity becomes more positive)
- Electrons are shown as the product in the half-reaction
- A species undergoing oxidation will be responsible for the reduction of another entity – and is therefore classified as an reducing agent (RA)
- Increase in oxidation number