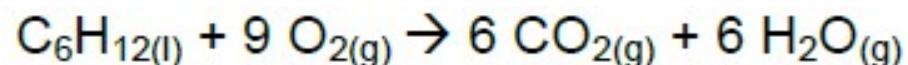
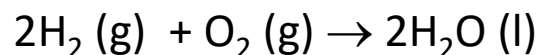


Types of chemical reactions with special reference to redox reactions. The concept of oxidation number, Reducing and oxidizing agents.

Chemical reactions are processes in which the atoms of one or more substances are rearranged to form different chemical compounds



Chemical reaction a process that results in a chemical bond or the breaking of chemical bond

Reaction can include ions, molecule or atom

How to tell if a chemical reaction has occurred (recap):

- **Temperature changes** that can't be accounted for.
 - **Exothermic** reactions give off energy (as in fire).
 - **Endothermic** reactions absorb energy (as in a cold pack).
- **Spontaneous color change.**
 - This happens when things rust, when they rot, and when they burn.
- **Appearance of a solid** when two liquids are mixed.
 - This solid is called a **precipitate**.
- **Formation of a gas / bubbling**, as when vinegar and baking soda are mixed.

Type of chemical reaction

Many chemical reactions can be classified as one of five basic types. Having a thorough understanding of these types of reactions will be useful for predicting the products of an unknown reaction.

The five basic types of chemical reactions

- (i) Combination
- (ii) Decomposition
- (iii) single-replacement
- (iv) double-replacement
- (v) combustion

By analyzing the reactants and products of a given reaction we will be able to place it in any of the five categories

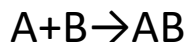
Some reactions will fit into more than one category.

Combination Reactions

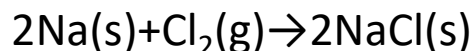
A **combination reaction**, also known as a **synthesis reaction**, is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

Combination Reactions

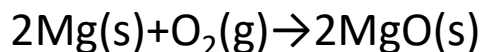
The general form of a combination reaction is:



One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

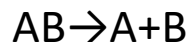


Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide.



Decomposition Reactions

A **decomposition reaction** *is a reaction in which a compound breaks down into two or more simpler substances.* The general form of a decomposition reaction is:

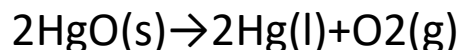


Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Decomposition Reactions

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements.

Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas

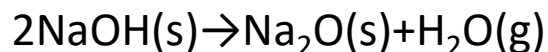


A reaction is also considered to be a decomposition reaction even when one or more of the products is still a compound. A metal carbonate decomposes into a metal oxide and carbon dioxide gas.

For example, calcium carbonate decomposes into calcium oxide and carbon dioxide.

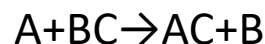


Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water.

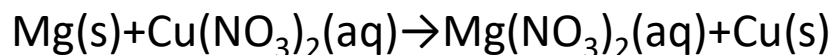


Single-Replacement Reactions

A **single-replacement reaction** is a reaction in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

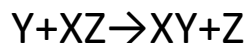


In this general reaction, element A is a metal and replaces element B, also a metal, in the compound.



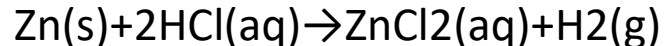
Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:



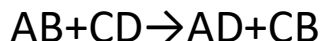
Y is a nonmetal and replaces the nonmetal Z in the compound with X.

Many metals react easily with acids, and, when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (see figure below).



Double-Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

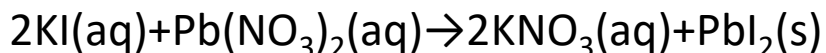


In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions.

Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

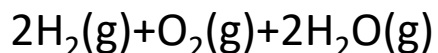
A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound.

When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs.



Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve O_2 as one reactant. The combustion of hydrogen gas produces water vapor (see figure below).

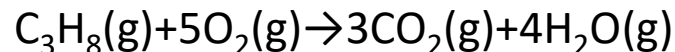


This reaction also qualifies as a combination reaction.

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen

The products of the combustion of hydrocarbons are always carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amount of heat energy.

Propane (C_3H_8) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.



4.5 OXIDATION-REDUCTION (REDOX) REACTIONS

Redox reactions are the third and, perhaps, most important type of chemical process. They include the formation of a compound from its elements (and vice versa), all combustion reactions, the reactions that generate electricity in batteries, the reactions that produce cellular energy, and many others. In this section, we examine the process and introduce some essential terminology.

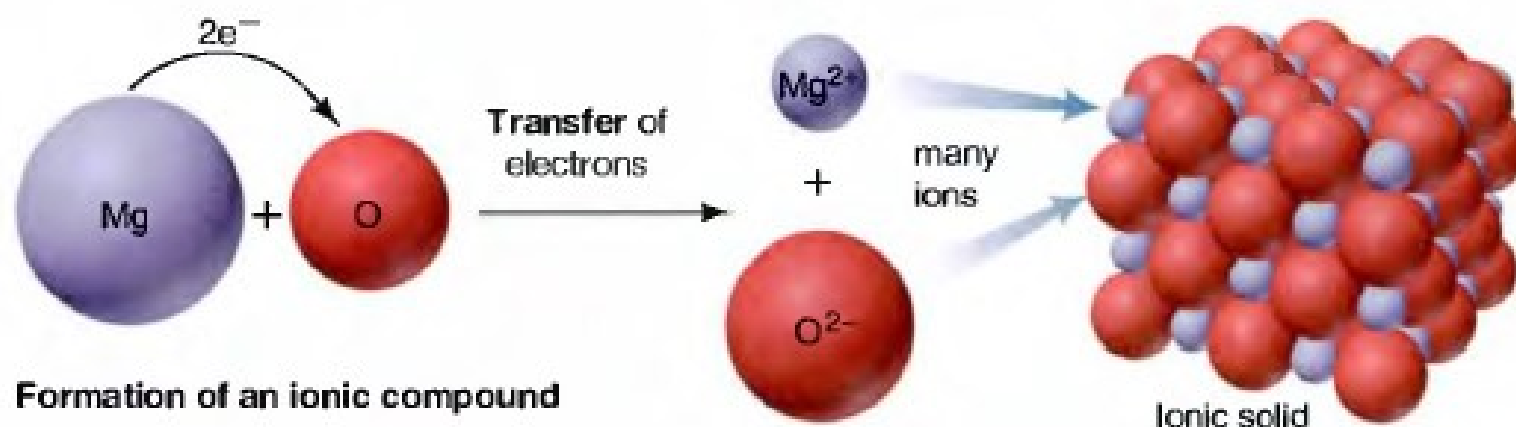
The Key Event: Movement of Electrons Between Reactants

In **oxidation-reduction** (or **redox**) reactions, the key chemical event is the *net movement of electrons from one reactant to the other*. This movement of electrons occurs *from the reactant (or atom in the reactant) with less attraction for electrons to the reactant (or atom) with more attraction for electrons*.

Such movement of electron charge occurs in the formation of both ionic and covalent compounds. As an example, let's reconsider the flashbulb reaction (see Figure 3.7), in which an ionic compound, MgO, forms from its elements:



Figure 4.9A shows that during the reaction, each Mg atom loses two electrons and each O atom gains them; that is, two electrons move from each Mg atom to each O atom. This change represents a *transfer of electron charge* away from each Mg atom toward each O atom, resulting in the formation of Mg^{2+} and O^{2-} ions. The ions aggregate and form an ionic solid.

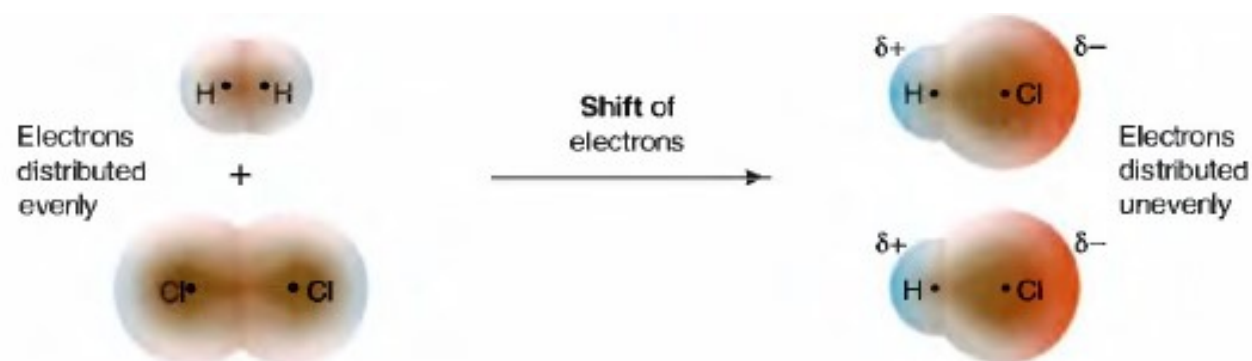


A Formation of an ionic compound

During the formation of a covalent compound from its elements, there is again a net movement of electrons, but it is more of a *shift* in electron charge than a full transfer. Thus, *ions do not form*. Consider the formation of HCl gas:



To see the electron movement here, compare the electron charge distributions in the reactant bonds and in the product bonds. As Figure 4.9B shows, H_2 and Cl_2 molecules are each held together by covalent bonds in which the electrons are shared equally between the atoms (the tan shading is symmetrical). In the HCl molecule, the electrons are shared unequally because the Cl atom attracts them more strongly than the H atom does. Thus, in HCl, the H has less electron charge (*blue shading*) than it had in H_2 , and the Cl has more charge (*red shading*) than it had in Cl_2 . In other words, in the formation of HCl, there has been a relative *shift of electron charge* away from the H atom toward the Cl atom. This electron *shift* is not nearly as extreme as the electron *transfer* during MgO formation. In fact, in some reactions, the net movement of electrons may be very slight, but the reaction is still a redox process.

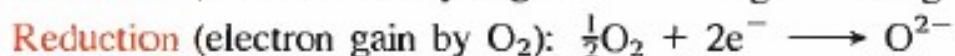
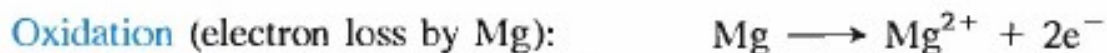


B Formation of a covalent compound

Some Essential Redox Terminology

Chemists use some important terminology to describe the movement of electrons in oxidation-reduction reactions. **Oxidation** is the *loss* of electrons, and **reduction** is the *gain* of electrons. (The original meaning of *reduction* comes from the process of reducing large amounts of metal ore to smaller amounts of metal, but you'll see shortly why we use the term "reduction" for the act of gaining.)

For example, during the formation of magnesium oxide, Mg undergoes oxidation (electron loss) and O₂ undergoes reduction (electron gain). The loss and gain are simultaneous, but we can imagine them occurring in separate steps:



One reactant acts on the other. Thus, we say that O₂ *oxidizes* Mg, and that O₂ is the **oxidizing agent**, the species doing the oxidizing. Similarly, Mg *reduces* O₂, so Mg is the **reducing agent**, the species doing the reducing.

Note especially that O₂ takes the electrons that Mg loses or, put the other way around, Mg gives up the electrons that O₂ gains. This give-and-take of electrons means that *the oxidizing agent is reduced* because it takes the electrons (and thus gains them), and *the reducing agent is oxidized* because it gives up the electrons (and thus loses them). In the formation of HCl, Cl₂ oxidizes H₂ (H loses some electron charge and Cl gains it), which is the same as saying that H₂ reduces Cl₂. The reducing agent, H₂, is oxidized and the oxidizing agent, Cl₂, is reduced.

Using Oxidation Numbers to Monitor the Movement of Electron Charge

Chemists have devised a useful “bookkeeping” system to monitor which atom loses electron charge and which atom gains it. Each atom in a molecule (or ionic compound) is assigned an **oxidation number (O.N.)**, or *oxidation state*, the charge the atom would have *if* electrons were not shared but were transferred completely. Oxidation numbers are determined by the set of rules in Table 4.3. [Note that an oxidation number has the sign *before* the number (+2), whereas an ionic charge has the sign *after* the number (2+).]

Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

General Rules

1. For an atom in its elemental form (Na, O₂, Cl₂, etc.): O.N. = 0
2. For a monatomic ion: O.N. = ion charge
3. The sum of O.N. values for the atoms in a molecule or formula unit of a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1A(1): O.N. = +1 in all compounds
2. For Group 2A(2): O.N. = +2 in all compounds
3. For hydrogen: O.N. = +1 in combination with nonmetals
O.N. = -1 in combination with metals and boron
4. For fluorine: O.N. = -1 in all compounds
5. For oxygen: O.N. = -1 in peroxides
O.N. = -2 in all other compounds (except with F)
6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals (except O), and other halogens lower in the group

		<div> <div>+1</div> <div>-1</div> </div>						
1		H		Group number Highest O.N./Lowest O.N.				
		1A	2A	3A	4A	5A	6A	7A
		+1	+2	+3	+4	+5	+6	+7
Period	2	Li	Be	B	C	N	O	F
	3	Na	Mg	Al	Si	P	S	Cl
	4	K	Ca	Ga	Ge	As	Se	Br
	5	Rb	Sr	In	Sn	Sb	Te	I
	6	Cs	Ba	Tl	Pb	Bi	Po	At
	7	Fr	Ra					
					114		116	

SAMPLE PROBLEM 4.6 Determining the Oxidation Number of an Element

Problem Determine the oxidation number (O.N.) of each element in these compounds:

(a) Zinc chloride (b) Sulfur trioxide (c) Nitric acid

Plan We apply Table 4.3, noting the general rules that the O.N. values in a compound add up to zero, and the O.N. values in a polyatomic ion add up to the ion's charge.

Solution (a) ZnCl_2 . The sum of O.N.s for the monatomic ions in the compound must equal zero. The O.N. of the Zn^{2+} ion is +2. The O.N. of each Cl^- ion is -1, for a total of -2. The sum of O.N.s is $+2 + (-2)$, or 0.

(b) SO_3 . The O.N. of each oxygen is -2, for a total of -6. The O.N.s must add up to zero, so the O.N. of S is +6.

(c) HNO_3 . The O.N. of H is +1, so the O.N.s of the NO_3 group must add up to -1 to give zero for the compound. The O.N. of each O is -2 for a total of -6. Therefore, the O.N. of N is +5.

FOLLOW-UP PROBLEM 4.6 Determine the O.N. of each element in the following:

(a) Scandium oxide (Sc_2O_3) (b) Gallium chloride (GaCl_3)
(c) Hydrogen phosphate ion (d) Iodine trifluoride

The periodic table is a great help in learning the highest and lowest oxidation numbers of most main-group elements, as Figure 4.10 shows:

- For most main-group elements, the A-group number (1A, 2A, and so on) is the *highest* oxidation number (always positive) of any element in the group. The exceptions are O and F (see Table 4.3).
- For main-group nonmetals and some metalloids, the A-group number minus 8 is the *lowest* oxidation number (always negative) of any element in the group.

For example, the highest oxidation number of S (Group 6A) is +6, as in SF_6 ,

		Group number						
		Highest O.N./Lowest O.N.						
		1A	2A	3A	4A	5A	6A	7A
		+1	+2	+3	+4	+5	+6	+7
				-4	-3	-2	-1	
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Ga	Ge	As	Se	Br	
5	Rb	Sr	In	Sn	Sb	Te	I	
6	Cs	Ba	Tl	Pb	Bi	Po	At	
7	Fr	Ra						

For example, the highest oxidation number of S (Group 6A) is +6, as in SF_6 , and the lowest is $(6 - 8)$, or -2 , as in FeS and other metal sulfides.

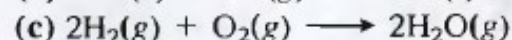
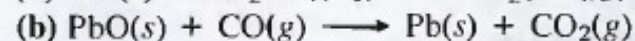
Thus, another way to define a redox reaction is one in which *the oxidation numbers of the species change*, and the most important use of oxidation numbers is to monitor these changes:

- If a given atom has a higher (more positive or less negative) oxidation number in the product than it had in the reactant, the reactant species that contains the atom was oxidized (lost electrons). Thus, *oxidation is represented by an increase in oxidation number*.
- If an atom has a lower (more negative or less positive) oxidation number in the product than it had in the reactant, the reactant species that contains the atom was reduced (gained electrons). Thus, *the gain of electrons is represented by a decrease (a "reduction") in oxidation number*.

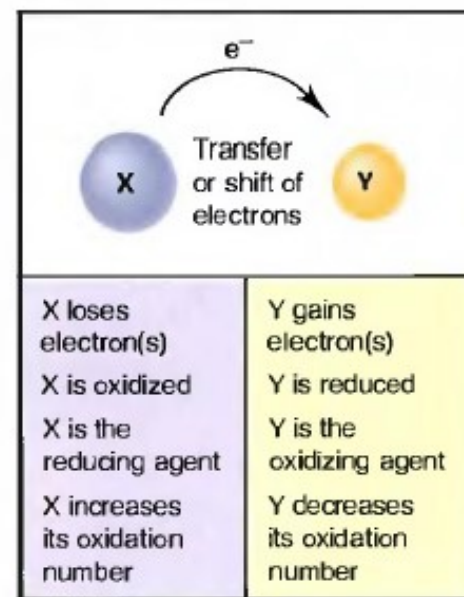
Figure 4.11 summarizes redox terminology. Oxidation numbers are assigned according to the relative attraction of an atom for electrons, so they are ultimately based on atomic properties, as you'll see in Chapters 8 and 9. (For the remainder of this section, **blue** oxidation numbers represent **oxidation**, and **red** oxidation numbers indicate **reduction**.)

SAMPLE PROBLEM 4.7 Recognizing Oxidizing and Reducing Agents

Problem Identify the oxidizing agent and reducing agent in each of the following:



Plan We first assign an oxidation number (O.N.) to each atom (or ion) based on the rules in Table 4.3. The reactant is the reducing agent if it contains an atom that is oxidized (O.N. increased from left side to right side of the equation). The reactant is the oxidizing



4.6 ELEMENTS IN REDOX REACTIONS

As we saw in Sample Problem 4.7, *whenever atoms appear in the form of a free element on one side of an equation and as part of a compound on the other, there must have been a change in oxidation state, and the reaction is a redox process.*

And, while there are many redox reactions that do *not* involve free elements, we'll focus here on the many others that do. One way to classify these is by comparing the numbers of reactants and products. By that approach, we have three types:

- *Combination reactions:* two or more reactants form one product:



- *Decomposition reactions:* one reactant forms two or more products:

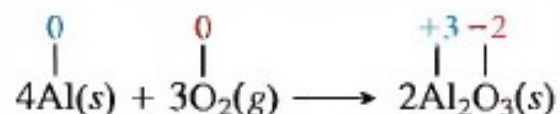


- *Displacement reactions:* the number of substances is the same but atoms (or ions) exchange places:

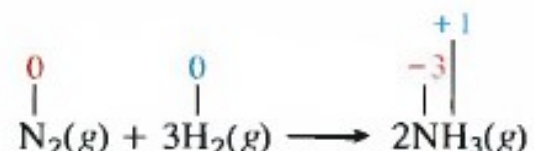


Combining Two Elements Two elements may react to form binary ionic or covalent compounds. Here are some important examples:

1. *Metal and nonmetal form an ionic compound.* A metal, such as aluminum, reacts with a nonmetal, such as oxygen. The change in O.N.'s shows that the metal is oxidized, so it is the reducing agent; the nonmetal is reduced, so it is the oxidizing agent.



2. *Two nonmetals form a covalent compound.* In one of thousands of examples, ammonia forms from nitrogen and hydrogen in a reaction that occurs in industry on an enormous scale:



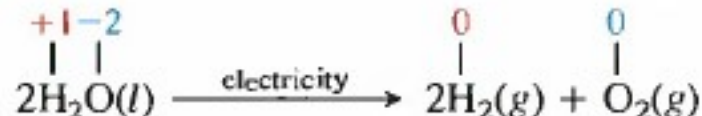
Decomposing Compounds into Elements A decomposition reaction occurs when a reactant absorbs enough energy for one or more of its bonds to break. The energy can take many forms; we'll focus in this discussion on heat and electricity. The products are either elements or elements and smaller compounds. Following are several common examples:

1. *Thermal decomposition.* When the energy absorbed is heat, the reaction is a thermal decomposition. (A Greek *delta*, Δ , above a reaction arrow indicates that heat is required for the reaction.) Many metal oxides, chlorates, and perchlorates release oxygen when strongly heated. Heating potassium chlorate is a method for forming small amounts of oxygen in the laboratory; the same reaction occurs in some explosives and fireworks:

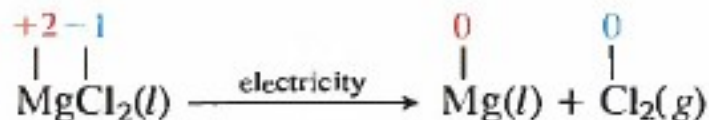


Notice that the lone reactant is the oxidizing *and* the reducing agent.

2. *Electrolytic decomposition.* In the process of *electrolysis*, a compound absorbs electrical energy and decomposes into its elements. Observing the electrolysis of water was crucial in the establishment of atomic masses:



Many active metals, such as sodium, magnesium, and calcium, are produced industrially by electrolysis of their molten halides:



(We'll examine the details of electrolysis in Chapter 21.)

Displacing One Element by Another; Activity Series As we said, displacement reactions have the same number of reactants as products. We mentioned double-displacement (metathesis) reactions in discussing precipitation and acid-base reactions. The other type, *single-displacement* reactions, are all oxidation-reduction processes. They occur when one atom displaces the ion of a different atom from solution. When the reaction involves metals, the atom reduces the ion; when it involves nonmetals (specifically halogens), the atom oxidizes the ion. Chemists rank various elements into activity series—one for metals and one for halogens—in order of their ability to displace one another.

1. *The activity series of the metals.* Metals can be ranked by their ability to displace H_2 (actually reduce H^+) from various sources or by their ability to displace one another from solution.

- *A metal displaces H_2 from water or acid.* The most reactive metals, such as those from Group 1A(1) and Ca, Sr, and Ba from Group 2A(2), displace H_2 from water, and they do so vigorously. Figure 4.12 shows this reaction for

lithium. Heat is needed to speed the reaction of slightly less reactive metals, such as Al and Zn, so these metals displace H_2 from steam:



Still less reactive metals, such as nickel and tin, do not react with water but *do* react with acids. Because the concentration of H^+ is higher in acid solutions than in water, H_2 is displaced more easily. Here is the net ionic equation:



Notice that in all such reactions, the metal is the reducing agent (O.N. of metal increases), and water or acid is the oxidizing agent (O.N. of H decreases). The least reactive metals, such as silver and gold, cannot displace H_2 from any source.

- *A metal displaces another metal ion from solution.* Direct comparisons of metal reactivity are clearest in these reactions. For example, zinc metal displaces copper(II) ion from (actually reduces Cu^{2+} in) copper(II) sulfate solution, as the total ionic equation shows:

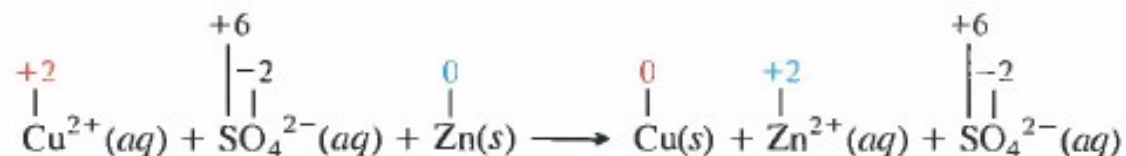
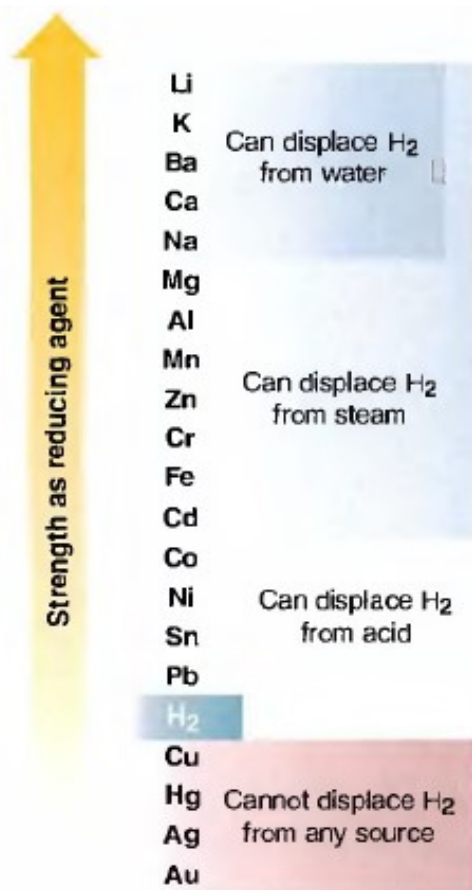


Figure 4.13 demonstrates in atomic detail that copper metal can displace silver ion from solution. Thus, zinc is more reactive than copper, which is more reactive than silver.

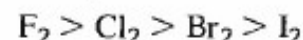


The diagram shows a vertical list of metals from Li at the top to Au at the bottom. A yellow arrow on the left points upwards, labeled 'Strength as reducing agent'. The list is divided into three horizontal regions: a light blue region at the top (Li to Ni), a light blue region in the middle (Sn to Pb), and a light red region at the bottom (Cu to Au). H₂ is positioned between Pb and Cu. Text annotations indicate that metals above H₂ can displace H₂ from water, those between H₂ and Pb can displace H₂ from steam, those between Pb and Cu can displace H₂ from acid, and metals below Cu cannot displace H₂ from any source.

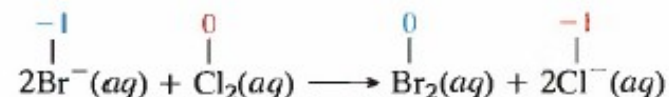
Element	Notes
Li	Can displace H ₂ from water
K	
Ba	
Ca	
Na	
Mg	Can displace H ₂ from steam
Al	
Mn	
Zn	
Cr	
Fe	Can displace H ₂ from acid
Cd	
Co	
Ni	
Sn	
Pb	Cannot displace H ₂ from any source
H ₂	
Cu	
Hg	
Ag	
Au	

The results of many such reactions between metals and water, aqueous acids, and metal-ion solutions form the basis of the **activity series of the metals**. In Figure 4.14 elements higher on the list are stronger reducing agents than elements lower down; that is, for those that are stable in water, elements higher on the list can reduce aqueous ions of elements lower down. The list also shows whether the metal can displace H₂ (reduce H⁺) and, if so, from which source. Look at the metals in the equations we've just discussed. Note that Li, Al, and Ni lie above H₂, while Ag lies below it; also, Zn lies above Cu, which lies above Ag. The most reactive metals on the list are in Groups 1A(1) and 2A(2) of the periodic table, and the least reactive lie at the right of the transition elements in Groups 1B(11) and 2B(12).

2. *The activity series of the halogens.* Reactivity decreases down Group 7A(17), so we can arrange the halogens into their own activity series:

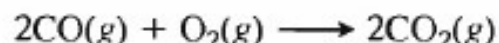


A halogen higher in the periodic table is a stronger oxidizing agent than one lower down. Thus, chlorine can oxidize bromide ions or iodide ions from solution, and bromine can oxidize iodide ions. Here, chlorine displaces bromine:



Combustion Reactions *Combustion* is the process of combining with oxygen,

Combustion Reactions *Combustion* is the process of combining with oxygen, often with the release of heat and light, as in a flame. Combustion reactions do not fall neatly into classes based on the number of reactants and products, but *all are redox processes* because elemental oxygen is a reactant:



The combustion reactions that we commonly use to produce energy involve organic mixtures such as coal, gasoline, and natural gas as reactants. These mixtures consist of substances with many carbon-carbon and carbon-hydrogen bonds. During the reaction, these bonds break, and each C and H atom combines with oxygen. Therefore, the major products are CO_2 and H_2O . The combustion of the hydrocarbon butane, which is used in camp stoves, is typical:



Biological *respiration* is a multistep combustion process that occurs within our cells when we “burn” organic foodstuffs, such as glucose, for energy:



SAMPLE PROBLEM 4.8 Identifying the Type of Redox Reaction

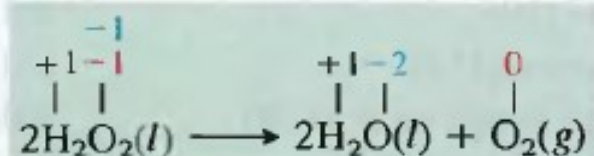
Problem Classify each of the following redox reactions as a combination, decomposition, or displacement reaction, write a balanced molecular equation for each, as well as total and net ionic equations for part (c), and identify the oxidizing and reducing agents:

- (a) Magnesium(s) + nitrogen(g) \longrightarrow magnesium nitride(s)
- (b) Hydrogen peroxide(l) \longrightarrow water + oxygen gas
- (c) Aluminum(s) + lead(II) nitrate(aq) \longrightarrow aluminum nitrate(aq) + lead(s)

Plan To decide on reaction type, recall that combination reactions produce fewer products than reactants, decomposition reactions produce more products, and displacement reactions have the same number of reactants and products. The oxidation number (O.N.) becomes more positive for the reducing agent and less positive for the oxidizing agent.

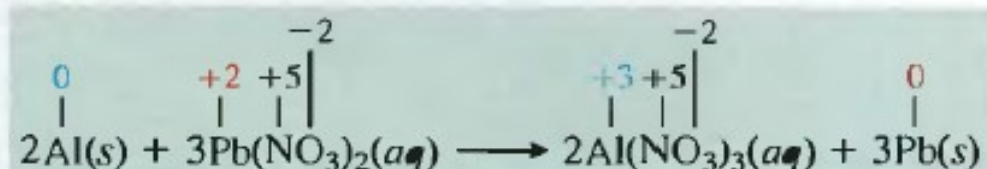
Solution (a) Combination: two substances form one. This reaction occurs along with

(b) **Decomposition:** one substance forms two. This reaction occurs within every bottle of this common household antiseptic. Hydrogen peroxide is very unstable and breaks down from heat, light, or just shaking:



H_2O_2 is both the oxidizing *and* the reducing agent. The O.N. of O in peroxides is -1 . It increases to 0 in O_2 and decreases to -2 in H_2O .

(c) **Displacement:** two substances form two others. As Figure 4.14 shows, Al is more active than Pb and, thus, displaces it from aqueous solution:



Al is the reducing agent; $\text{Pb}(\text{NO}_3)_2$ is the oxidizing agent.

The total ionic equation is



The net ionic equation is

