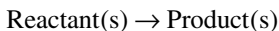

CHEMICAL REACTIONS

5.1 DEFINITION OF CHEMICAL REACTIONS AND BALANCING OF CHEMICAL EQUATIONS

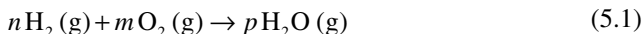
The concept of molecules and compounds was introduced in Chapter 4. Chemists and chemical engineers manipulate compounds to form new materials that achieve a specific goal or purpose. It is of crucial importance that compounds be mixed in the proper ratios so that the desired reaction can be achieved. The relationship between the compound and its atoms is displayed through the molecular formula, and the chemist uses this information to develop a balanced chemical equation that can properly describe the breaking and forming of bonds in chemical reactions.

As mentioned in Chapter 4, a chemical reaction is “a process in which substances (reactants) change into other substances (products) by rearrangement, combination, or separation of atoms.” A chemical reaction is represented by a chemical equation with two sides: one for the reactants and one for the products.



The arrow means “forms,” “yields,” “changes to,” or “is/are converted into.”

The law of conservation of matter, “matter is neither destroyed nor created,” applies to all atoms in a chemical reaction. As a result, a balanced chemical reaction requires that there must be an equivalent number of atoms of each type on both sides of the equation. Consider the reaction between hydrogen and oxygen to form water, as shown in Equation 5.1.

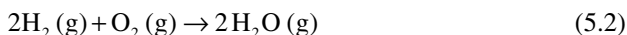


In Equation 5.1, we have placed a letter in front of each molecule to represent the stoichiometric coefficient, a multiplying number assigned to the species in a chemical equation in order to balance the equation. Now the challenge is to determine what number each letter in Equation 5.1 represents.

Let’s suppose we were producing one molecule of water. In this case, there would be one oxygen atom on the right-hand side of the equation, and to have a balanced chemical equation would require that we have one oxygen atom on the left side. But diatomic oxygen is shown on the left side, and it is not possible to have fractional numbers of molecules. So the smallest number of oxygen molecules on the left side would be one. Based on this analysis, let’s tentatively state that $m=1$.

Now, let’s go back to the right-hand side. We have two oxygen atoms on the left side (since there is one molecule of O_2), so we need two oxygen atoms on the right side. That means we need two water molecules on the right side, or $p=2$. Now the equation is balanced in terms of oxygen.

What about hydrogen? There are two water molecules on the right side, and each one has two hydrogen atoms, which means there are four hydrogen atoms total. When a stoichiometric coefficient is placed in front of a molecular formula, the stoichiometric coefficient acts as a multiplying number and applies to ALL subscripts present in the molecular formula. Hydrogen is present as diatomic hydrogen on the left side, so each molecule of H_2 contains two hydrogen atoms. That means we need two hydrogen molecules (H_2), or $n=2$. Therefore, the equation is balanced in terms of hydrogen atoms.



One must keep in mind that the molecular formula for each molecule MUST NOT be changed, because that would change the nature of the molecule. In other words, a water molecule can never be changed to H_2O_2 to balance the equation. It would not be the molecule of water anymore but a completely different species, hydrogen peroxide, used as a powerful bleaching agent. The only route to balance Equation 5.1 is to use a stoichiometric coefficient in front of each molecule to make sure that the number of atoms of each type is equal on both sides of the equation (Highlight 5.1).

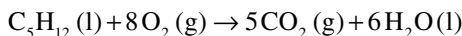
Highlight 5.1 Balancing Chemical Equations

Balance the following typical equations:

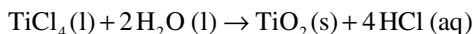
- The combustion of pentane (liquid) in air.
- The synthesis of titanium dioxide from titanium tetrachloride and water.
- The reaction of ammonia gas with oxygen to produce gaseous nitrogen monoxide and water vapor.

Solutions:

(a) Pentane is an important component of some fuels and is mostly used as a laboratory solvent. Its molecular formula is C_5H_{12} . Pentane is a volatile hydrocarbon that is liquid at room temperature. It burns in air by reacting with oxygen and forms carbon dioxide and water, the two products of combustion reactions.

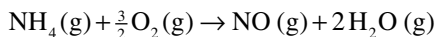


(b) Titanium dioxide, TiO_2 , is produced from the purification of titanium tetrachloride, $TiCl_4$, and is accompanied by the release of hydrochloric acid:

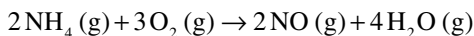


TiO_2 is one of the most prominent photocatalysts and has been used for the oxidation of numerous hazardous materials in either air or water. New technology places a very thin layer of TiO_2 on the outside of glass, which causes soot that would otherwise build up on the surface to be oxidized in sunlight, keeping the window clean.

(c) Ammonia gas reacts with oxygen to produce gaseous nitrogen monoxide and water vapor:



While this is properly balanced, it is preferable to have whole numbers instead of fractions for stoichiometric coefficients, because it is not possible to have fractional molecules. Let's multiply all coefficients by 2:



When all atoms are accounted for in a chemical equation, the masses represented by the equation are also balanced (remember the law of conservation of mass). The second section illustrates this concept.

5.2 CHEMICAL REACTIONS AND QUANTITIES OF REACTANTS AND PRODUCTS

Equation 5.2 shows that two diatomic molecules of hydrogen and one diatomic molecule of oxygen react to produce two molecules of water. But chemists and engineers don't work with individual molecules; rather, we work with large quantities of substances. In order to relate the number of molecules to mass quantities, we first start by defining the quantity of matter as a mole, which is identically equal to 6.022×10^{23} molecules (or atoms). Then, to determine the quantities of reactants and products, we know that each mole of atoms has an atomic weight expressed in g/mol. By adding the atomic weight of each atom in a molecule, we can deduce the molecular weight or molar mass of the molecule.

For example, the molar mass of the diatomic molecule of hydrogen would be

$$2 \times \text{atomic weight of an atom of hydrogen} = 2 \times (1.0079 \text{ g/mol}) = 2.0158 \text{ g/mol}$$

Remember, a hydrogen molecule contains two hydrogen atoms, as indicated by the subscript 2, and thus the molar mass is two times the atomic mass of a hydrogen atom (as written in the periodic table).

We can do the same with the diatomic molecule of oxygen:

$$2 \times \text{atomic weight of an atom of oxygen} = 2 \times (15.9994 \text{ g/mol}) = 31.9988 \text{ g/mol}$$

As well as for the molecule of water:

$$\begin{aligned} 2 \times \text{atomic weight of an atom of hydrogen} + 1 \times \text{atomic weight of an atom of oxygen} \\ = 2 \times (1.0079 \text{ g/mol}) + 1 \times (15.9994 \text{ g/mol}) = 18.0152 \text{ g/mol} \end{aligned}$$

The molar masses show that 1 mol of H_2 is equivalent to 2.0152 g of H_2 , that 1 mol of O_2 is equivalent to 31.9988 g of O_2 , and 1 mol of water is equivalent to 18.0152 g of H_2O .

However, in the *balanced* equation, 2 diatomic molecules of hydrogen react with 1 diatomic molecule of oxygen to produce 2 molecules of water. We can also say 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O .

$$\begin{aligned} \text{Total mass of reactants in g} &= (2 \text{ mol } \text{H}_2 \times \text{molar mass of } \text{H}_2) \\ &\quad + (1 \text{ mol } \text{O}_2 \times \text{molar mass of } \text{O}_2) \\ &= (2 \text{ mol} \times 2.0158 \text{ g/mol}) + (1 \text{ mol} \times 31.9988 \text{ g/mol}) \\ &= \mathbf{36.0304 \text{ g}} \end{aligned}$$

Let's calculate the total mass of products and confirm that the conservation of mass is respected:

$$\begin{aligned} \text{Total mass of products in g} &= 2 \text{ mol H}_2\text{O} \times \text{molar mass of H}_2\text{O} \\ &= 2 \text{ mol} \times 18.0152 \text{ g/mol} \\ &= \mathbf{36.0304 \text{ g}} \end{aligned}$$

Note that when using metric units, atomic weight, molecular weight, and molar mass are expressed in grams per mole (g/mol) and then the mass of the species comes out in grams (g). When looking at the units, it makes sense:

$$\text{mol} \times \text{g/mol} = \text{g}$$

We will need these conversions between molar quantities and mass quantities to measure the efficiency of chemical reactions in Section 5.4.

For Highlights 5.2 and 5.3, you will need a periodic table.

Highlight 5.2 Calculations of Molecular Weights

Consider the following compounds and calculate their molecular weights.

- (a) PCl_5
- (b) NaH_2PO_4
- (c) $\text{C}_6\text{H}_{12}\text{O}_6$
- (d) $\text{Mg}_3(\text{PO}_4)_2$
- (e) $\text{Mg}(\text{NO}_3)_2$

Solutions:

- (a) PCl_5

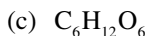
$$\text{M.W.} = (1\text{P} \times 30.9738 \text{ g/mol}) + (5\text{Cl} \times 35.453 \text{ g/mol}) = 208.2388 \text{ g/mol}$$

The answer should be expressed with five significant figures (since there are five significant figures in the measure of the molecular weight of the chlorine atom): 208.24 g/mol.

- (b) NaH_2PO_4

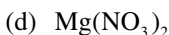
$$\begin{aligned} \text{M.W.} &= (1\text{Na} \times 22.9898 \text{ g/mol}) + (2\text{H} \times 1.0079 \text{ g/mol}) \\ &\quad + (1\text{P} \times 30.9738 \text{ g/mol}) + (4\text{O} \times 15.9994 \text{ g/mol}) \\ &= 119.977 \text{ g/mol} \end{aligned}$$

The answer should be expressed with five significant figures: 119.98 g/mol.



$$\begin{aligned} \text{M.W.} &= (6\text{C} \times 12.0107 \text{ g/mol}) + (12\text{H} \times 1.0079 \text{ g/mol}) \\ &\quad + (6\text{O} \times 15.9994 \text{ g/mol}) \\ &= 180.1554 \text{ g/mol} \end{aligned}$$

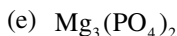
The answer should be expressed with five significant figures: 180.16 g/mol.



$$\begin{aligned} \text{M.W.} &= (1\text{Mg} \times 24.3050 \text{ g/mol}) + (2\text{N} \times 14.0067 \text{ g/mol}) \\ &\quad + (6\text{O} \times 15.9994 \text{ g/mol}) \\ &= 148.3148 \text{ g/mol} \end{aligned}$$

The answer should be expressed with six significant figures: 148.315 g/mol.

Attention: $Mg(NO_3)_2$ is a compound containing 2 anions of nitrate NO_3^- to balance the 2+ charge from Mg^{2+} . Thus, there are 2 N and (3×2) O total.



$$\begin{aligned} \text{M.W.} &= (3\text{Mg} \times 24.3050 \text{ g/mol}) + (2\text{P} \times 30.9738 \text{ g/mol}) \\ &\quad + (8\text{O} \times 15.9994 \text{ g/mol}) \\ &= 262.8578 \text{ g/mol} \end{aligned}$$

The answer should be expressed with six significant figures: 262.858 g/mol.

Highlight 5.3 Calculations of Masses

Calculate the mass (in g) for the following:

- (a) 0.5 mol of aspirin[®], acetylsalicylic acid with the molecular formula $C_9H_8O_4$
- (b) 1.1×10^{-3} mol of vitamin C also known as L-ascorbate with the molecular formula $C_6H_8O_6$

Solutions:

(a) In this example we know the number of moles and we have the molecular formula of aspirin. The goal is to find the mass in grams of aspirin. We know that by multiplying the number of mol by the molecular weight, $\text{mol} \times \text{g/mol}$, we get a mass in g. The molecular weight of aspirin, $C_9H_8O_4$, is calculated as we did in the previous examples above:

$$\begin{aligned} \text{M.W.} &= (9\text{C} \times 12.0107 \text{ g/mol}) + (8\text{H} \times 1.0079 \text{ g/mol}) \\ &\quad + (4\text{O} \times 15.9994 \text{ g/mol}) \\ &= 180.1571 \text{ g/mol} \end{aligned}$$

$$\begin{aligned}\text{Mass of aspirin} &= 180.1571 \text{ g/mol of } \text{C}_9\text{H}_8\text{O}_4 \times 0.5 \text{ mol} \\ &= 90.07855 \text{ g of } \text{C}_9\text{H}_8\text{O}_4\end{aligned}$$

With only one significant figure (as present in 0.5 mol) the answer is expressed correctly as 90 g.

(b) We will proceed the same way we did for example (a).

$$\begin{aligned}\text{M.W. of vitamin C} &= (6\text{C} \times 12.0107 \text{ g/mol}) + (8\text{H} \times 1.0079 \text{ g/mol}) \\ &\quad + (6\text{O} \times 15.9994 \text{ g/mol}) \\ &= 176.1238 \text{ g/mol of vitamin C}\end{aligned}$$

Knowing the molecular weight of vitamin C and the number of moles, we can determine its mass.

$$\begin{aligned}\text{Mass of vitamin C} &= (1.1 \times 10^{-3} \text{ mol}) \times 176.1238 \text{ g/mol} \\ &= 0.193736 \text{ g of vitamin C}\end{aligned}$$

With only two significant figures as present in 1.1×10^{-3} , the answer is expressed correctly as 0.19 g.

5.3 PATTERNS OF CHEMICAL REACTIONS

The most common patterns of chemical reactions are summarized in this section. Examples of typical reactions involving inorganic and organic compounds are discussed and the concept of atom economy (introduced in Chapter 2) is used to describe the efficiency of the reaction.

5.3.1 Combination, Synthesis, or Addition Reactions



Combination or addition reactions involve the addition of a compound B to a compound A (or the addition of a reagent to a substrate) and results in the complete consumption of both compounds (or both reagent and substrate). Therefore, this type of reaction is 100% atom economical and efficient with no generation of waste or by-product.

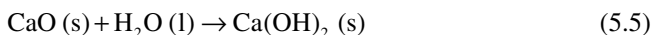
5.3.1.1 Examples with Inorganic Compounds

These three examples illustrate the different types of combination reactions.

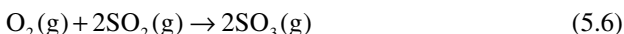
1. Two elements can combine to form a compound:



2. Two compounds can combine to form a different one:



3. One element and one compound can combine to form a different compound:

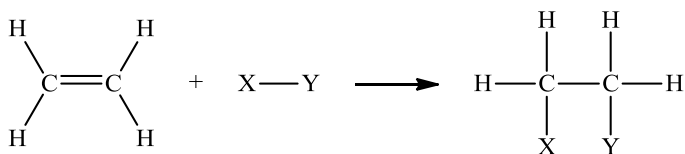


Recall from Chapter 2 the definition of atom economy, the ratio of the mass of the species in the desired product relative to the mass of all of the reactants. In all of these reactions the atoms present in the reactants are also present in the products. In this case it is implied that these reactions are 100% atom economical. Remember from Chapter 2 that atom economy is a mass utilization number only; it does not take into account the energy usage, the toxicity of the products, or whether the feedstocks are derived from renewable materials.

5.3.1.2 Examples with Organic Compounds

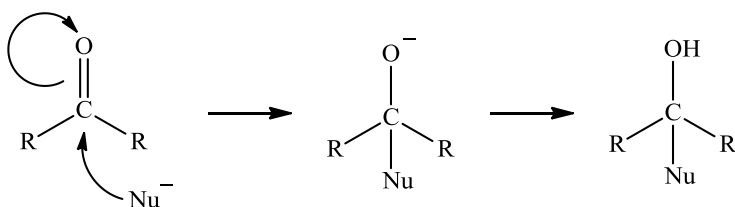
There are two main types of addition reactions, involving either an electrophile or a nucleophile as one of the starting compounds. All addition reactions of organic compounds involve the breaking of a double bond (π bond) and the formation of two new single covalent bonds (σ bonds).

In electrophilic addition, one of the starting compounds must have a double or a triple bond; in other words, it must possess an electron-rich unsaturated $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bond. An electrophile seeks out an unshared electron pair. The reaction in Scheme 5.1 shows an electrophilic addition to ethylene.



Scheme 5.1. Electrophilic addition to ethylene.

Nucleophilic addition involves the addition of a nucleophile across a double bond. The nucleophile can be any negative ion or any neutral molecule that has at least one unshared electron pair. The reaction in Scheme 5.2 shows nucleophilic addition to a ketone.



Scheme 5.2. Nucleophilic addition to a ketone.

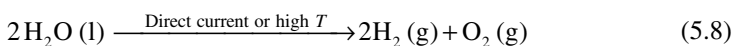
Lewis bases are nucleophiles whereas Lewis acids are electrophiles.

5.3.2 Decomposition Reactions

Decomposition reactions should be 100% economical but the environmental impact of the decomposition products should be examined closely.



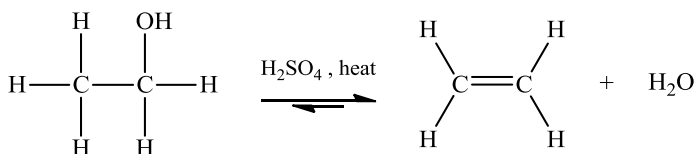
A typical example of a decomposition reaction is the electrolysis of water, which is the decomposition of water into hydrogen and oxygen gases using an electric current passing through the water or using very high temperatures.



This reaction has significance as a clean way to produce hydrogen for use in fuel cells. However, a broader analysis of the reaction requires one to consider the source of energy used to produce the current. Many researchers are experimenting with photovoltaics, which convert sunlight into electricity, as a means of creating the current needed to drive the reaction. Some researchers at the University of Berkeley in California are looking at the use of hydrogenase, an enzyme that can split water into oxygen and hydrogen.

5.3.3 Elimination Reactions

Elimination reactions are the opposite of addition reactions. This type of reaction generates unsaturation of the starting material and two substituents are usually removed from the starting molecule. A typical example is a dehydration reaction where there is a loss of a water molecule from the starting reagent. Alcohols can be dehydrated to alkenes accompanied by the production of a molecule of water, as shown in Scheme 5.3.



Scheme 5.3. Dehydration of alcohols to alkenes.

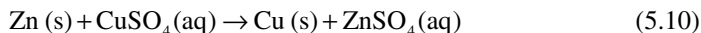
In this example, if the alcohol is propanol then the alkene is propene. The atom economy can be obtained as the mass of a propene molecule (42 g/mol) divided by the original mass of the propanol molecule (60 g/mol) for an atom economy of 70%. However, in this case the undesired product is water, which is innocuous, so except for the effort required to recover the alkene product, the atom economy less than 100% is not as significant from a green standpoint.

5.3.4 Displacement Reactions

This very common type of reaction is one in which a portion of one molecule is replaced with another species, as shown here:

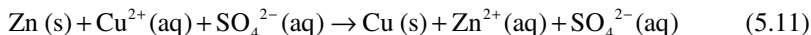


Typical displacement reactions encompass oxidation–reduction (redox) reactions:

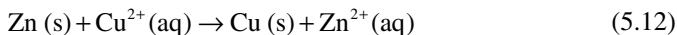


Note that all soluble ionic compounds such as CuSO_4 and ZnSO_4 dissociate into their respective ions in aqueous solution. When dissolved in water, CuSO_4 (aq) ionizes to produce Cu^{2+} (aq) and SO_4^{2-} (aq). Likewise, ZnSO_4 (aq) dissociates to form Zn^{2+} (aq) and SO_4^{2-} (aq) when immersed in water.

If the displacement reaction displayed in Equation 5.10 is carried out in water (as it must be, since two solids sitting next to each other would not react), then recognizing that each of the species dissociates provides



Note that the sulfate anion appears on both sides of the reaction. In this case, sulfate is called a spectator ion and is not involved in the overall process. This allows us to rewrite Equation 5.10 in terms of only the Zn and the Cu:



The net effect of an oxidation–reduction reaction is a transfer of electrons from one reactant to another. The substance that accepts electrons incurs a reduction of the electric charge on an atom of the substance and is said to be reduced. The other substance loses electrons, has an increase of the electric charge on an atom of the substance, and is oxidized. In all oxidation–reduction reactions, one reactant is oxidized and another is reduced.

Because there is a transfer of electrons between two species, oxidation–reduction reactions can be divided into two half-reactions, one for each of the species undergoing a transfer of electrons. In these cases, it is important that we keep track not only of the number of atoms but also of the number of electrons, since the conservation of mass law also requires that charge is conserved. We designate an electron as e^- , and thus we can write an oxidation reaction as



Likewise, we can express the reduction reaction by recognizing that the electrons are on the reactants side:



Now we can go back to the specific redox reaction between CuSO_4 and ZnSO_4 that we were considering previously.

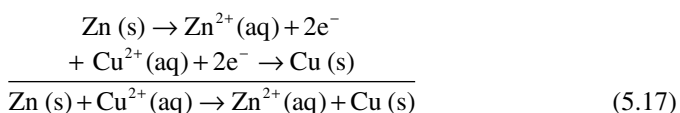
The oxidation reaction occurs for the zinc atom, as it goes from solid Zn with a charge of zero to the aqueous Zn ion with a charge of +2. In this case, the half-reaction is written as



The reduction reaction occurs for the copper, which is reduced from Cu ion with a charge of +2 to solid copper with no charge. The reduction reaction can be written as



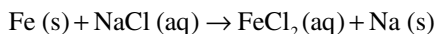
If we add these two half-reactions together, we recombine to obtain the entire redox reaction,



The 2e^{-} appear on both sides of the equation and cancel out when adding the two half-reactions together to recover the full redox reaction. In some cases, the half-reactions don't balance precisely, and it is important to consider that one half-reaction occurs multiple times for every time the other half-reaction occurs. That will ensure that the electrons always balance, and charge is conserved. Highlight 5.4 explains what to do in case of unbalanced numbers of electrons.

Highlight 5.4 Balancing Redox Reactions

Consider the following equation:

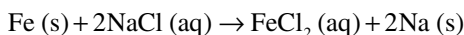


- Balance this equation in terms of atoms and calculate the atom efficiency.
- Determine which element is reduced and which one is oxidized.
- Write the overall redox reaction.

Solutions:

(a) In this equation, the number of Fe atoms and the number of Na atoms are correctly balanced. However, there are 2 Cl atoms in the iron(II) chloride molecule, FeCl_2 , whereas there is only 1 Cl in sodium chloride, NaCl. When adding a stoichiometric coefficient of 2 in front of the NaCl molecule to obtain 2 Cl atoms, we are also changing the number of Na atoms to 2. Remember when balancing a chemical

equation, we cannot change the intrinsic formula of the compound and when adding a stoichiometric coefficient in front of a formula, it applies to all atoms in the formula. So we now have 2 Na atoms on the reactants side. We need to add a stoichiometric coefficient of 2 in front of Na (s) in the products.

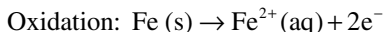


This equation is now balanced with respect to all atoms.

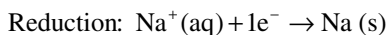
Assuming that the FeCl_2 is the desired product, we can calculate its molecular weight as 126.751 g/mol. The reactants are Fe and 2 moles of NaCl, which has a total mass of 172.73 g/mol. Taking the ratio of the desired product to the total mass of reactants provides an atom efficiency of 73.4%.

(b) When looking at the above equation, it looks like a displacement reaction. Let's see if it is a redox reaction. Remember in a redox reaction, there must be a transfer of electrons.

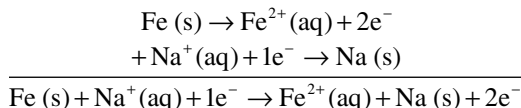
On the reactants side, Fe has a charge of 0. On the product side FeCl_2 (aq) is an ionic compound consisting of Fe^{2+} (aq) and 2 Cl^- (aq). So Fe switches from a charge of 0 to a charge of +2 on the products side, which means that Fe loses 2 electrons and is oxidized. We can write that as an oxidation half-reaction, as follows:



On the reactants side, NaCl (aq) is an ionic compound consisting of Na^+ (aq) and Cl^- (aq). Na^+ has a charge of +1 on the reactants side; on the product side the charge of Na in Na (s) is 0. So Na switches from a charge of +1 to a charge of 0, which means that Na gains 1 e^- and is reduced to Na (s). We can write this as a reduction half-reaction, as follows:



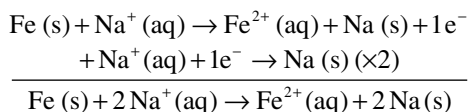
(c) In a redox reaction, the number of electrons lost should be equal to the number of electrons gained. If we add the two half-reactions above, we get



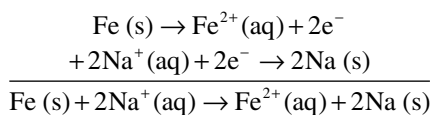
which could be rewritten as



This looks different from what we've seen before, because we still have an electron remaining on the right-hand side. If we do one more reduction reaction, we can eliminate the remaining electron:



Now the equation is properly balanced, and the electrons do not appear in the final equation. We can get to the same end result, without the intermediate equation, simply by multiplying all of the stoichiometric coefficients in the reduction reaction by 2, giving the following single set of redox reactions:



This allows for the number of electrons to cancel out so that both atoms and charges are balanced correctly.

Many students have a difficult time remembering which reaction is oxidation and which is reduction. If you recall that reduction reduces the charge of the ion, that will be helpful, as long as you can remember that zero is less than +2, and -2 is less than zero. A useful mnemonic to remember the definitions of oxidation and reduction is the following:

OIL RIG (Oxidation is Loss; Reduction is Gain)

One can also remember that oxidation starts with an O and there is an "o" in loss.

Another problem that is frequently encountered is to know what the appropriate charge can be on the ions under consideration. For *monoatomic* cations and anions, the common charges are called oxidation numbers, and they can often be identified on a periodic table (see Chapter 4). Polyatomic ions are more challenging and often must be derived from the oxidation numbers of the underlying monatomic components. Knowing some rules to determine the oxidation numbers of elements will allow you to calculate the charge for polyatomic ions.

Rule 1: The oxidation number of an atom of a pure element is zero.

Example: Oxygen in O₂, sulfur in S₈, iron in metallic Fe, or chlorine in Cl₂ all have an oxidation number of zero.

Rule 2: Because atoms want to have a complete outside electron shell, they will normally donate electrons if they have only a few extra in the outside shell, or acquire some to complete the shell. As a result, the oxidation number of many elements can be determined from their placement in the periodic table.

Example: Alkali metals in group 1(A) have an oxidation state of +1, and metals in group 2A have an oxidation state of +2. Specifically, Na^+ has an oxidation number of +1; Ca^{2+} has an oxidation number of +2.

Likewise, the oxidation number of elements in groups 6A and 7A are generally -2 and -1 , respectively.

Example: Cl^- has an oxidation number of -1 ; Se^{2-} has an oxidation number of -2 .

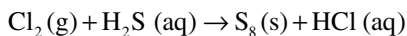
One needs to use Rule 2 with caution, since elements of higher periods may have multiple oxidation states. In addition, the transition elements usually have multiple oxidation states and can accept or donate electrons in multiple arrangements. In such cases, the oxidation state of the unknown element can be determined based on the oxidation state of a known species.

Rule 3: The sum of the oxidation numbers in a neutral compound is zero.

For example, to calculate the oxidation number of P in PCl_5 , one starts from knowing that the oxidation state for Cl is -1 . PCl_5 is a neutral molecule. There are 5 Cl atoms, which contributes a total charge of -5 . Thus, the oxidation state of P in this molecule must be $+5$, in order for the charges to balance. See Highlight 5.5.

Highlight 5.5 Balancing Redox Reactions

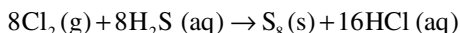
Chlorine (Cl_2) as an oxidizing agent used in water and sewage treatment plants. Consider the following equation, which demonstrates how chlorine can be used to eliminate hydrogen sulfide coming from the decay of organic matter:



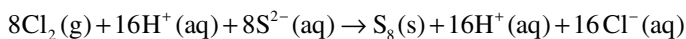
- Balance this equation in terms of atoms.
- Determine which element is reduced and which one is oxidized.
- Write the overall redox reaction.

Solutions:

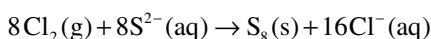
(a) Since elemental sulfur takes the form of S_8 , the balanced equation requires 8 molecules of H_2S , which means 16 molecules of HCl on the right-hand side and finally 8 chlorine molecules on the reactant side. In summary, the balanced equation is written as



(b) In a redox reaction, one element is oxidized (it loses electrons) and one is reduced (it gains electrons). In the balanced equation, we first look at the reactants. Both Cl_2 and H_2S are neutral molecules. The H_2S can dissociate in water, and since the oxidation state of hydrogen is +1, then the oxidation state of sulfur must be -2 . Likewise, looking at the products, we know the oxidation states of hydrogen and chlorine are +1 and -1 , respectively. As a result, we can write the complete ionic equation:

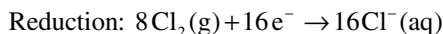


After canceling the spectator ions, the net ionic equation is the following:

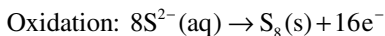


Chlorine goes from zero as a reactant to -1 as a product, so it is reduced. Similarly, sulfur goes from -2 as a reactant to zero as a product, so it must be oxidized.

(c) To write the overall redox equation, let's write the two half-equations first.

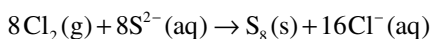
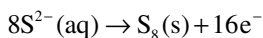
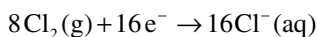


(Because there are 16Cl^- on the products side and there are 8Cl_2 on the reactants side, the number of electrons gained also needs to be multiplied by 8.)



(Because there are 8S^{2-} , the number of electrons also needs to be multiplied by 8, which gives a total of 16.)

In the two half-reactions the number of electrons lost is equal to the number of electrons gained. The 16e^- cancel each other out. We can add the two half-reactions to obtain the overall redox equation:



This equation is balanced with respect to the atoms and the charges.

All the examples above involved inorganic compounds; oxidation and reduction reactions can also take place with organic compounds. For example, methane can be oxidized to carbon dioxide (CO_2) (effectively the oxidation number of C changes from -4 to $+4$). As mentioned in Chapter 4 primary alcohols can be oxidized to aldehydes

(the oxidation number of C changes from -2 to 0). Typical reductions include the conversion of an alkene to an alkane. In organic reactions, an oxidation involves the removal of hydrogen atoms whereas the reverse reduction adds hydrogen atoms to an organic molecule.

5.3.5 Exchange or Substitution Reactions

Substitution reactions can involve inorganic or organic compounds and follow the typical chemical path:



5.3.5.1 Examples with Inorganic Compounds

Typical exchange reactions result in three possible products:

1. The formation of a precipitate or insoluble ionic compound (case for precipitation reactions).
2. The formation of a molecular compound remaining in aqueous solution (case for the production of H_2O (l) in acid–base neutralization reactions).
3. The formation of a gaseous molecular compound.

PRECIPITATION REACTIONS. Exchange reactions involve ionic compounds. Some ionic compounds are soluble in water and others are not. When an ionic compound dissolves in water, it dissociates into ions; when an ionic compound is completely converted to ions and forms an aqueous solution, it is referred to as a strong electrolyte. An electrolyte is a substance whose aqueous solution contains ions and conducts electricity.

The solubility of a compound in water depends on the relative force of attraction between the ions that make up the compound and the counteracting force between the water molecules and the ions. Since it is very difficult to estimate these relationships, one commonly refers to a set of rules that describe which compounds are soluble, slightly soluble, and insoluble. Table 5.1 provides these rules [1, p. 165].

When a compound contains at least one ion that is not soluble (insoluble), the compound does not dissociate and remains in its solid state. When the chemical reaction is written with the phase designation(s) included, this indicates the formation of a precipitate or that the product is a solid; it does *not* signify that it is soluble.

For example, let's look at the reaction between ammonium sulfide, $(NH_4)_2S$, and copper nitrate $Cu(NO_3)_2$. Will a precipitate form?

The first step in working through this reaction is to determine what products will be formed, independent of whether they are soluble. Since this is an exchange reaction, the cation of the first compound reacts with the anion of the second compound and vice versa. Two compounds are formed: ammonium nitrate NH_4NO_3 and copper

TABLE 5.1. Solubility Rules

Usually Soluble Ions	Exceptions
Group 1A alkali metals Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ , and ammonium NH ₄ ⁺	None
Nitrates, NO ₃ ⁻	None
Chlorates, ClO ₃ ⁻	None
Perchlorates, ClO ₄ ⁻	None
Acetates, CH ₃ COO ⁻	None
Sulfates, SO ₄ ²⁻	CaSO ₄ , SrSO ₄ , BaSO ₄ , and PbSO ₄ are <i>insoluble</i>
Chlorides, Cl ⁻ , bromides, Br ⁻ , and iodides, I ⁻	AgCl, Hg ₂ Cl ₂ , PbCl ₂ , AgBr, Hg ₂ Br ₂ , PbBr ₂ , AgI, Hg ₂ I ₂ , and PbI ₂ are <i>insoluble</i>
Usually Insoluble Ions	Exceptions
Phosphates, PO ₄ ³⁻	Phosphates of group 1A alkali metals and of ammonium are <i>soluble</i>
Carbonates, CO ₃ ²⁻	Carbonates of group 1A alkali metals and of ammonium are <i>soluble</i>
Hydroxides, OH ⁻	Hydroxides of group 1A alkali metals and of ammonium are <i>soluble</i> ; Sr(OH) ₂ , Ba(OH) ₂ , and Ca(OH) ₂ are <i>slightly soluble</i>
Oxalates, C ₂ O ₄ ²⁻	Oxalates of group 1A alkali metals and of ammonium are <i>soluble</i>
Sulfides, S ²⁻	Sulfides of group 1A alkali metals and of ammonium are <i>soluble</i> ; sulfides of group 2A, MgS, CaS, and BaS, are <i>sparingly soluble</i>

sulfide CuS. Without regard to the phase state of the compounds, the overall balanced chemical reaction looks like this:



Note that the stoichiometric coefficient for the ammonium nitrate product must be two, since there are two ammonium ions and two nitrate ions present in the reacting species.

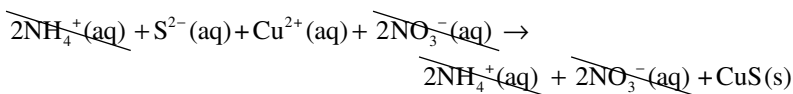
Next, we can determine which of these products is soluble. According to the solubility rules, all nitrates are soluble, so the ammonium nitrate product will dissolve in water and we designate its phase as aqueous (aq). On the other hand, sulfides are insoluble, and copper sulfide is not an exception. Thus, copper sulfide will precipitate and the phase designation is listed as solid (s). Now, combining the phase designations with the balanced overall equation provides



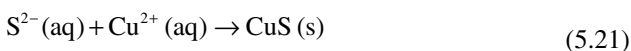
This equation is commonly referred to as the molecular equation.

As we demonstrated in the case of displacement reactions, it is possible to write the equation involving compounds that dissociate. It consists in dissociating all aqueous compounds into their respective ions and leaving solids as they are. This constitutes the complete ionic equation. Common ions that appear in both reactants and products will cancel each other out; they are spectator ions. The resulting equation is the net ionic equation.

The complete ionic equation is

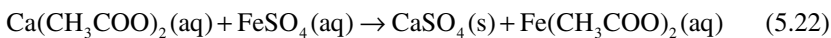


Remember that the number 2 in front of NH_4NO_3 is a stoichiometric coefficient, and upon dissociation, it generates two ammonium ions and two nitrate ions. The ammonium and nitrate ions are spectator ions, which appear on both sides of the reaction equation. They cancel each other out, leaving the following net ionic equation:

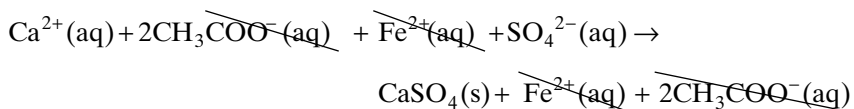


While some of this discussion brings back memories of the redox analysis described in the previous section, you should be careful to note that the current case is not redox chemistry. The sulfur ion in the reactant has a charge of -2 , as described in the equation. The sulfur in the product CuS also has a charge of -2 , but it is not shown that way since it is an element in a neutral molecule. Thus, there is no change in the oxidation of the sulfur, and this is not a redox reaction.

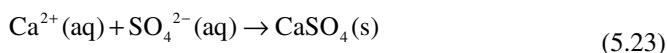
Another example looks at the reaction between calcium acetate, $\text{Ca}(\text{CH}_3\text{COO})_2$, and iron sulfate, FeSO_4 . The exchange reaction between calcium acetate and iron(II) sulfate results in the formation of calcium sulfate, CaSO_4 , and iron(II) acetate, $\text{Fe}(\text{CH}_3\text{COO})_2$. According to the solubility rules, calcium sulfate is an exception and is insoluble. Iron(II) acetate is soluble. So the molecular equation can be written as



Dissociation of soluble ionic compounds into their respective ions gives the complete ionic equation:



Fe^{2+} and CH_3COO^- are spectator ions; the net ionic equation can be written as follows:



See Highlight 5.6.

Highlight 5.6 Precipitation Reactions

In each of the following cases predict if a precipitate would form and justify your answer. In the case of precipitation, write the molecular, complete ionic, and net ionic equations. Only the names of the compounds will be given. Make sure the ionic formula is correct before you start balancing the molecular equation.

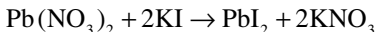
- Reaction between lead nitrate and potassium iodide.
- Reaction between calcium nitrate and potassium chloride.
- Reaction between nickel chlorate and barium phosphate.

Solutions:

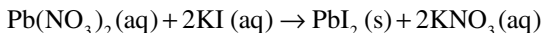
(a) Lead nitrate has the following ionic formula: $\text{Pb}(\text{NO}_3)_2$. Two nitrate ions are necessary to balance the +2 charge from Pb^{2+} . Potassium iodide is KI.

If an exchange reaction occurs, lead would react with iodide to form lead iodide, PbI_2 , and potassium would react with nitrate to form potassium nitrate, KNO_3 .

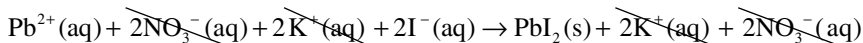
The balanced molecular equation, without regard to the phase of the compounds, is the following:



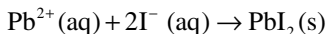
According to the solubility rules, all nitrates are soluble and all iodides are soluble but PbI_2 is an exception and will therefore form a precipitate:



The complete ionic equation shows the dissociation of all soluble species into their respective ions:

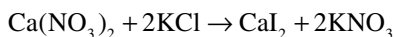


The net ionic equation eliminates all the spectator ions:

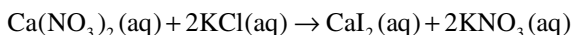


(b) Calcium nitrate has the following ionic formula: $\text{Ca}(\text{NO}_3)_2$. Two nitrate ions are necessary to balance the +2 charge from Ca^{2+} . Potassium chloride is KCl.

If an exchange reaction occurs, calcium would react with iodide to form calcium iodide, CaI_2 , and potassium would react with nitrate to form potassium nitrate, KNO_3 . Thus, the balanced reaction, without regard to phase, can be written as



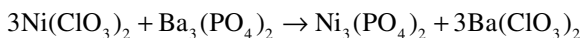
According to the solubility rules, all nitrates are soluble and all iodides are soluble. CaI_2 is *not* an exception and therefore *no precipitation* will occur. Thus, the final reaction expression is written as



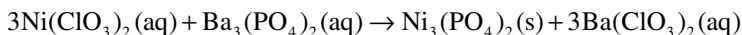
(c) Nickel chlorate has the following ionic formula: $\text{Ni}(\text{ClO}_3)_2$. Two chlorate ions are necessary to balance the +2 charge from Ni^{2+} . Barium phosphate has the following formula: $\text{Ba}_3(\text{PO}_4)_2$. Barium cation has a +2 charge. The polyatomic anion, phosphate, is PO_4^{3-} . To balance the positive and negative charges, we need three barium cations (total charge of +6) and two phosphate anions (total charge of -6).

If an exchange reaction occurs, nickel would react with phosphate to form nickel phosphate, $\text{Ni}_3(\text{PO}_4)_2$ (the reasoning is the same as for barium phosphate). Barium would react with chlorate to form barium chlorate, $\text{Ba}(\text{ClO}_3)_2$. Two chlorate anions are necessary to balance the +2 charge from the barium cation.

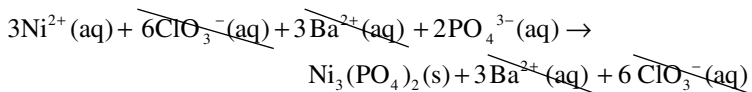
The balanced molecular equation, without regard to phase, is the following:



According to the solubility rules, all phosphates are insoluble (nickel is not a group 1A element) and all chlorates are soluble. Thus, the solubility definition provides the following result:



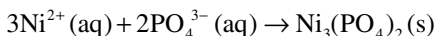
The complete ionic equation looks like this:



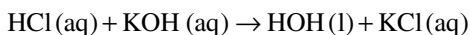
Remember:

1. When there is a stoichiometric coefficient in front of the formula for a compound, the stoichiometric coefficient is multiplied by the subscript to get the total number of ions.
2. Polyatomic anions do not dissociate further. Thus, phosphates stay as PO_4^{3-} and chlorates remain as ClO_3^{-} .

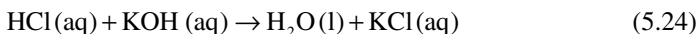
The net ionic equation is the following:



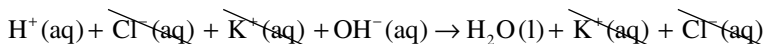
ACID–BASE NEUTRALIZATION REACTIONS. As defined in Chapter 4, acids and bases can either be weak or strong. In the case of the reaction between a strong acid and a strong base, an exchange reaction occurs. For example, hydrochloric acid and potassium hydroxide react in an exchange manner to form hydrogen hydroxide (WATER!!!!) and potassium chloride. Potassium chloride is not an exception and is therefore soluble. The molecular equation can be written as



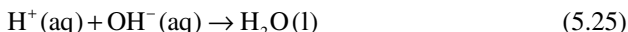
or



Since both hydrochloric acid and potassium hydroxide are strong electrolytes, they dissociate completely in solution, allowing one to write the following complete ionic equation:

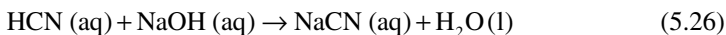


Recognizing that the chloride and the potassium ions are spectator ions, the net ionic equation can be written as follows:

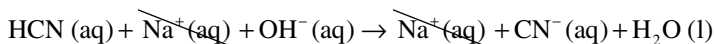


This net ionic equation represents the formation of water from its respective ions, hydrogen and hydroxide. The formation of water results from the neutralization of the strong acid with the strong base. Only in the case of the reaction between a strong acid and a strong base will this neutralization occur. The ability to reduce the net ionic reaction into the formation reaction for water is an indication that the reaction is a neutralization reaction.

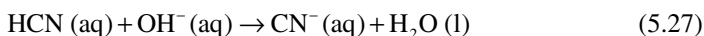
The reaction between a weak acid, HCN, and a strong base, NaOH, also results in the formation of water and a soluble salt, in this case, sodium cyanide, NaCN (aq):



The strong base of NaOH completely dissociates into Na^+ and OH^- . HCN is a weak acid, and recalling that the definition of a weak acid is one which does not completely dissociate, it is written in the reaction equation in its molecular form. Thus, the complete ionic equation is written as



Now, canceling the Na^+ spectator ions gives the net ionic equation:



See Highlight 5.7.

Highlight 5.7 Acids and Bases and Neutralization Reactions

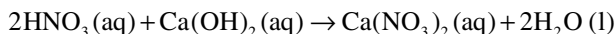
In the following examples, identify the strength of acids and bases and derive the molecular, complete ionic, and net ionic equations.

- (a) Reaction between nitric acid and calcium hydroxide. (*Note:* Even if calcium hydroxide is slightly soluble, it is considered as completely ionized.)
- (b) Reaction between acetic acid and barium hydroxide. (*Note:* Even if barium hydroxide is slightly soluble, it is considered as completely ionized.)

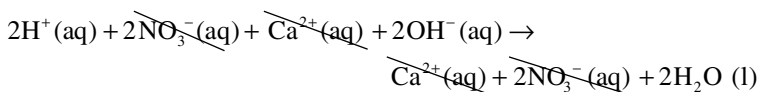
Solutions:

(a) Nitric acid, HNO_3 , is a strong acid and calcium hydroxide, $\text{Ca}(\text{OH})_2$, is a strong base. This reaction is therefore a neutralization reaction, which produces a salt, calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, and water.

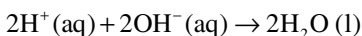
The balanced molecular equation is



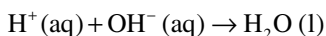
The complete ionic equation is



The net ionic equation is the formation of water from its respective ions:

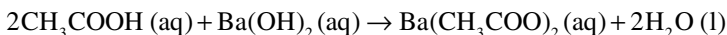


Simplifying the equation by dividing all stoichiometric coefficients by 2 gives

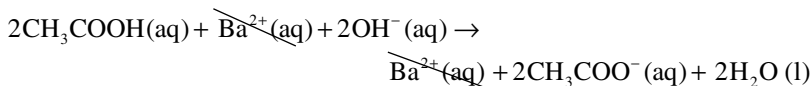


(b) Acetic acid, CH_3COOH , is a weak acid whereas barium hydroxide, $\text{Ba}(\text{OH})_2$, is a strong base. The products are a salt, barium acetate, $\text{Ba}(\text{CH}_3\text{COO})_2$, and water.

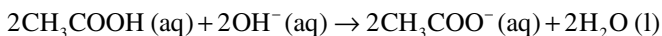
The balanced molecular equation is



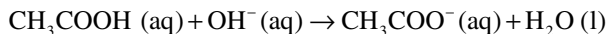
The complete ionic equation shows the dissociation of the strong base, barium hydroxide, whereas the weak acid does not dissociate:



The net ionic equation is



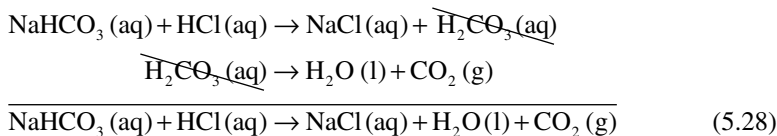
Dividing all stoichiometric coefficients by 2 gives



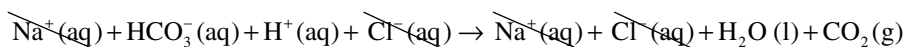
This equation is balanced with respect to the atoms and charges.

GAS-FORMING EXCHANGE REACTIONS. The last type of exchange reaction involves the formation of a gas. Common gas-forming reactions involve the reaction between an acid and a metal carbonate. The common products are a salt and carbonic acid, H_2CO_3 , which decomposes into $\text{CO}_2(\text{g})$ and water $\text{H}_2\text{O}(\text{l})$. Gas-forming reactions can also occur with sulfates, in which case SO_2 is produced.

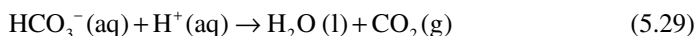
As an example, let's consider the reaction that occurs when you ingest a tablet of Alka-Seltzer made of sodium carbonate, NaHCO_3 , to relieve excess hydrochloric acid in your stomach.



The complete ionic equation for this reaction is



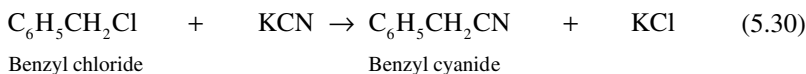
Canceling the sodium and chloride spectator ions gives the following net ionic equation:



See Highlights 5.8 and 5.9.

5.3.5.2 Examples with Organic Compounds

Substitution reactions in organic chemistry involve the replacement of a functional group from one reagent with another functional group from the second reagent. In this case a leaving group will be produced. A typical example is the conversion of benzyl chloride to benzyl cyanide as follows:



In this case the K^+ from the second reagent is exchanged with the Cl^- from benzyl chloride.

Highlight 5.8 Prediction of Products for Exchange Reactions

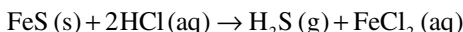
For the following reactions, predict the products and write the molecular, complete ionic, and net ionic equations:

- Iron(II) sulfide reacts with hydrochloric acid.
- Lithium carbonate reacts with sulfuric acid.

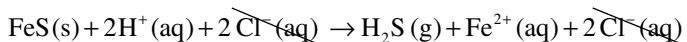
Solutions:

(a) Iron(II) sulfide, FeS, reacts with hydrochloric acid, HCl. This is an exchange reaction, which leads to the production of the naturally occurring toxic gas H₂S, which usually has a very unpleasant “rotten egg” odor, and the salt FeCl₂.

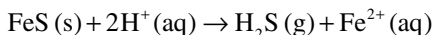
The balanced molecular equation can be written as



The strong ionic species HCl and FeCl₂ completely dissociate, so the complete ionic equation is

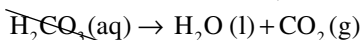
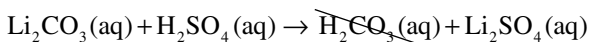


Canceling the spectator ion Cl⁻ provides the net ionic equation:

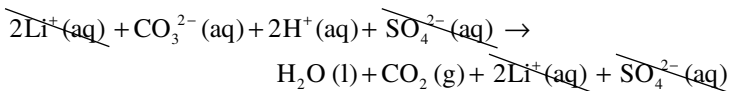


(b) Lithium carbonate, Li₂CO₃, reacts with sulfuric acid, H₂SO₄. When a metal carbonate reacts with an acid, the products of this exchange reaction are a salt (in this case, Li₂SO₄) and carbonic acid, H₂CO₃.

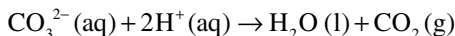
The molecular equation is



The complete ionic equation is



The net ionic equation is then



This equation is balanced with respect to the charges and atoms.

Highlight 5.9 Identification of Chemical Reactions and Prediction of Products

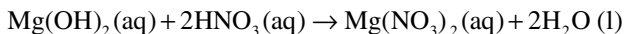
Identify each of these exchange reactions as a precipitation reaction, an acid–base reaction, or a gas-forming reaction. Predict the products of each reaction and write the molecular, complete ionic, and net ionic equations.

- Magnesium hydroxide reacts with nitric acid.
- Potassium phosphate reacts with magnesium nitrate.
- Nitric acid reacts with strontium carbonate.

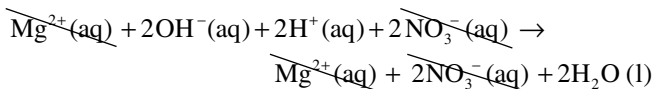
Solutions:

(a) Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is a strong base whereas nitric acid, HNO_3 , is a strong acid. This exchange reaction is an acid–base neutralization reaction.

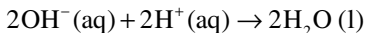
The products are a salt, $\text{Mg}(\text{NO}_3)_2$, and water. The balanced molecular equation is



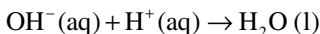
The complete ionic equation is



Eliminating the spectator ions leaves us with the net ionic equation:

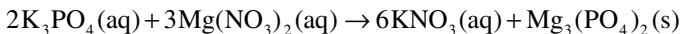


Dividing all coefficients by 2 simplifies the equation:

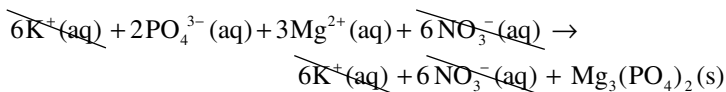


(b) Potassium phosphate, K_3PO_4 , reacts with magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, in an exchange manner to give two products: potassium nitrate, KNO_3 , and magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$. *Remember:* It is crucial to have the correct ionic formulas before writing the molecular equation. All nitrates are soluble so potassium nitrate is in aqueous solution and all phosphates are insoluble (Mg is not an exception), so this is a precipitation reaction.

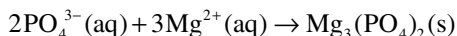
The balanced molecular equation is



The complete ionic equation shows the dissociation of all aqueous species into their respective ions:



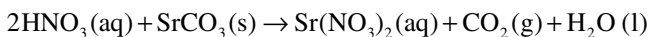
Eliminating the spectator ions gives the net ionic equation:



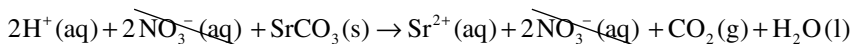
This equation is balanced with respect to the charges and the atoms.

(c) Nitric acid, HNO_3 , reacts with strontium carbonate, SrCO_3 . When an acid reacts with a metal carbonate, an exchange reaction forming a gas occurs. In this case, the two products are a salt, strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, and carbonic acid, which decomposes readily into water and carbon dioxide. Strontium carbonate is insoluble (Sr is not an exception).

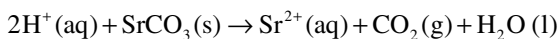
The balanced molecular equation is



The complete ionic equation gives



Eliminating the spectator ions leads to



This equation is balanced with respect to the charges and atoms.

The efficiency and usefulness of substitution reactions in organic reactions really depends on the nature of the leaving group generated.

When evaluating the previously detailed chemical transformations in terms of intrinsic atom economy, we can conclude that:

- Combination, synthesis, or (also called) addition reactions incorporate all reactant atoms into the product(s); therefore, they are 100% atom economical.
- Decomposition reactions are atom economical in theory but the amount of heat or current needed for the reaction to occur prevents the reaction from being “green.”
- Displacement reactions (in particular, redox reactions) are usually not atom economical. There is always the presence of an unwanted by-product. Furthermore, many of the strong oxidizing agents are highly environmentally harmful. However, Terry Collins and his research group at Carnegie Mellon University have developed a new catalyst known as TAML (short for tetra-amido macrocyclic ligand) that catalyzes the decomposition of hydrogen peroxide, creating a green oxidizing agent.

- Exchange or substitution reactions are not atom economical because the substituting group displaces a leaving group, which becomes a wasted by-product.

5.4 EFFECTIVENESS AND EFFICIENCY OF CHEMICAL REACTIONS: YIELD VERSUS ATOM ECONOMY

There are many ways to define the efficiency of a chemical reaction: the most common one being percent yield and selectivity. However, these metrics do not include how much waste is produced in a process (i.e, do not include formation of side products, unwanted isomers, etc.)

From an environmental and economic point of view, it would be useful to know how many atoms present in the reactants end up in the desired products and how many end up as waste. This concept was developed by Barry Trost from Stanford University and published in *Science* in 1991. The concept of atom economy or atom utilization allowed Barry Trost to begin “to change the way in which chemists measure the efficiency of the reactions they design” (award ceremony by Paul Anderson 1997 ACS President). Professor Trost received the Presidential Green Chemistry Challenge Award in 1998.

Atom economy answers the following: “How much of what you put into your pot ends up in your product?” Atom economy can be defined as:

- The mass of desired product divided by the total mass of all reagents, times 100.

Percent atom economy = (mass of desired product / total mass of all reagents) × 100

Or

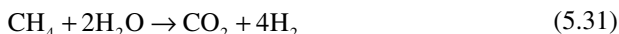
- The mass of desired product divided by the total mass of all products and by-products produced, times 100.

$$\text{Percent atom economy} = \frac{\text{mass of desired product}}{\text{total mass of all products and by-products produced}} \times 100$$

Or

- A measure of the efficiency of a reaction.

The use of atom economy requires conversion of a molecular equation into the mass quantities of all species. An example could be steam reforming of methane to produce hydrogen, an important step in the processing of natural gas and other fossil resources. The reaction is carried out at elevated temperature in the gas phase, and the reaction equation is written as



The mass of the starting materials can be obtained as

$$\text{Mass of CH}_4 = \text{mass of C} + 4 \times \text{mass of H} = 12.01 + 4(1.008) = 16.04 \text{ g}$$

$$\text{Mass of water} = 2 \times \text{mass of H} + \text{mass of O} = 2(1.008) + 15.9994 = 18.02 \text{ g}$$

Thus, the total mass of reactants can be obtained as

$$\text{Mass of CH}_4 + 2 \times \text{mass of water} = 16.04 \text{ g} + 2(18.02 \text{ g}) = 52.08 \text{ g}$$

Hydrogen is the desired product, so we need to calculate the mass of hydrogen:

$$\text{Mass of H}_2 = 2 \times \text{mass of H} = 2.016 \text{ g}$$

And then the total mass of the desired product is

$$4 \times \text{mass of H}_2 = 8.06 \text{ g}$$

Finally, the atom efficiency is the mass of the desired product relative to the total mass of the reactants, which is simply

$$\text{Atom efficiency} = (8.06 \text{ g} / 52.08 \text{ g}) \times 100\% = 15.5\%$$

This is a very low atom efficiency, reflecting the large mass of undesired product that is formed, and the strong desire for carbon capture as an opportunity to minimize air pollution. In addition, the atom economy concept does not take into account the use of energy, auxiliaries, or catalysts and the toxicity of the waste, and in this case, the reaction is impacted by the high temperature required.

While atom economy measures efficiency of the reaction, percent yield answers: “What is the maximum possible quantity of product formed by this reaction?” If the answer is 100%, then the theoretical yield (calculated) and the actual yield (determined through experiment) are identical.

$$\text{Percent yield} = (\text{actual yield} / \text{theoretical yield}) \times 100$$

The actual yield is defined as the quantity of product actually obtained from a synthesis in a laboratory or industrial chemical plant; the theoretical yield is the maximum possible amount of product that can be formed when the limiting reactant is completely used.

Highlight 5.10 Calculations with Reactants Being Completely Consumed

How many grams of oxygen are required to react *completely* with 0.12 mol of propane?

- Write a balanced chemical equation: $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$.
- Using the stoichiometry of the balanced chemical equation determine the number of moles of O_2 needed to react completely with propane and using the molar mass of O_2 as a conversion factor, find the mass of O_2 .

Solutions:

$$0.12 \text{ mol C}_3\text{H}_8 \times 5 \text{ mol O}_2 / 1 \text{ mol C}_3\text{H}_8 \times 32.0 \text{ g O}_2 / 1 \text{ mol O}_2 = 19.2 \text{ g O}_2$$

Thus, 19 g (with 2 significant figures) of O_2 is needed to react completely with propane.

When calculating percent yield, two types of reactions can be discussed.

REACTIONS WITH REACTANTS COMPLETELY CONSUMED. See Highlight 5.10.

REACTIONS WITH ONE REACTANT IN LIMITED SUPPLY. In the previous chemical reactions we assumed that the reactants were completely consumed. No reactant was left when the reaction was over. However, that is usually not the case when chemists carry out an actual synthesis in a laboratory or in industry.

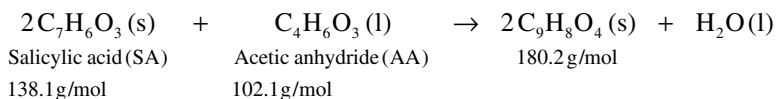
A limiting reactant is the reactant that is completely converted to products during a reaction. Once the limiting reactant has been used up, no more products can form and the reaction will stop. The *limiting* reactant *limits* the amount of product(s) that can be formed.

The moles of product formed are always determined by the starting number of moles of the limiting reactant.

To give you a comparison, when you make sandwiches with bread, lettuce, tomatoes, ham, and cheese, if you run out of bread you cannot make any more sandwiches. In this case the bread is your limiting reactant and the number of sandwiches made is based on how much bread you have. In some exercises the data will state that one reactant was used in excess. Therefore, no calculation is necessary to determine which reactant is the limiting one (the opposite of the reagent in excess). However, in reality we often have to determine which reactant is the limiting one by calculating how much product will be formed (Highlight 5.11).

Highlight 5.11 Calculations with a Reactant in Limited Supply

The synthesis of aspirin by the reaction of salicylic acid, $C_7H_6O_3$, with acetic anhydride, $C_4H_6O_3$, is represented by the following reaction:



If we use 10.0 g of salicylic acid and 5.4 g of acetic anhydride, what is the limiting reactant and what is the maximum amount of aspirin produced?

Solutions:

There are many methods to get to the answer. The following method is called the mass method.

Calculate the number of moles of each reactant available and compare their mole ratio with the mole ratio from the stoichiometric coefficients.

$$10.0\text{ g SA} \times 1\text{ mol SA} / 138.1\text{ g SA} = 0.0724\text{ mol SA}$$

$$5.4\text{ g AA} \times 1\text{ mol AA} / 102.1\text{ g AA} = 0.0529\text{ mol AA}$$

The limiting reagent is the one that produces the least amount of aspirin, which is not necessarily the reactant with the smallest mass.

The number of moles of aspirin produced from 0.0724 mol SA is

$$0.0724\text{ mol SA} \times 2\text{ mol aspirin} / 2\text{ mol SA} = 0.0724\text{ mol aspirin}$$

The number of moles of aspirin produced from 0.0529 mol AA is

$$0.0529\text{ mol AA} \times 2\text{ mol aspirin} / 1\text{ mol AA} = 0.1058\text{ mol aspirin}$$

\Rightarrow AA is in excess; SA is the limiting reagent!

The mass of aspirin produced from 0.0724 mol of SA is

$$0.0724\text{ mol aspirin} \times 180.2\text{ g aspirin} / 1\text{ mol aspirin} = 13.0\text{ g aspirin}$$

REFERENCE

1. Moore, J.; Staniski, C.; Jurs, P. *Chemistry: The Molecular Science*, 4th edition, Brooks Cole Cengage Learning, Belmont, CA, 2011.