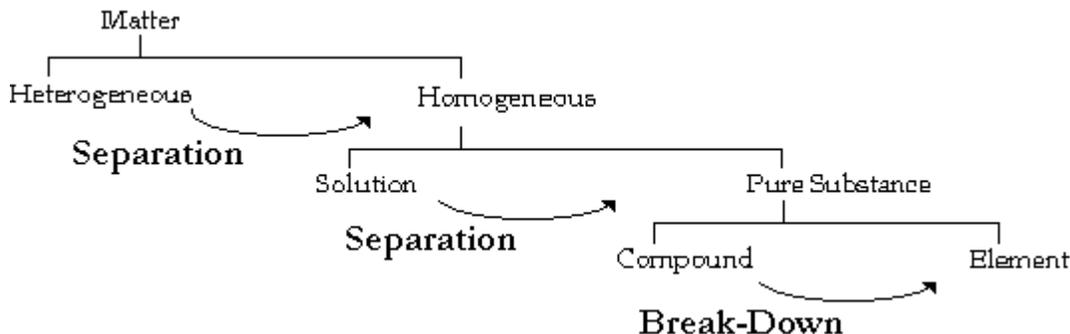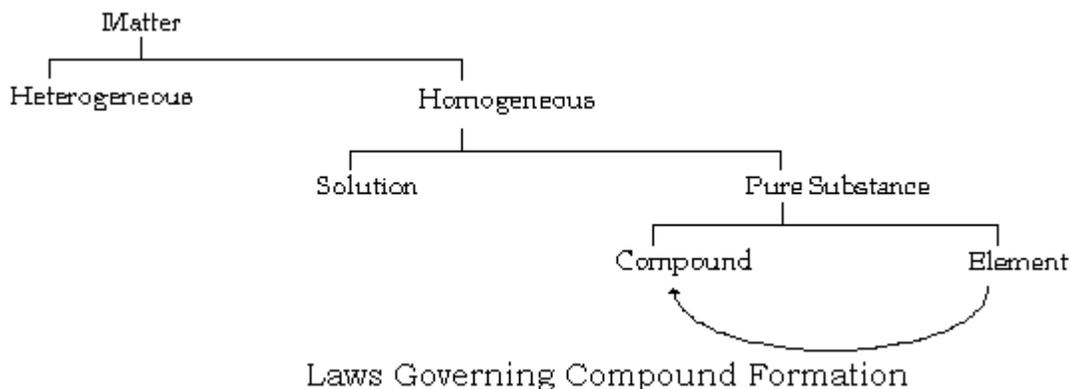# The Fundamental Laws of Chemistry

As we have discussed, matter can be classified into different categories based on directly observable properties, be they physical or chemical.


Heterogeneous systems contain multiple phases and can be separated using fairly standard techniques (e.g., filtration, separatory funnel, etc.) into a series of homogeneous systems. These homogeneous systems can be further classified according to whether they are solutions, containing multiple components, or pure substances. Solutions, themselves, can be further separated into their constituent components, although the techniques to achieve this separation (e.g., distillation, chromatography) are somewhat more complex than those required to separate heterogeneous systems. Pure Substances fall into one of two categories; those which are compounds and those which are elements. Compounds can be broken-down via some standard physical or chemical method, elemental substances cannot. This level of "separation" is significantly more difficult than required of the previous two levels of separation. Lavoisier used strong heating in the presence of Iron to break-down Water, and, thus, demonstrate its compound nature. Water can also be broken-down using electrolysis, where it is decomposed directly into hydrogen and oxygen gases. It has been found there are ~115 chemically elemental substances; each represented in the Periodic Table of the Elements.

At this point, we wish to consider the "rules," or Natural Laws, governing the reconstruction of Compounds from the Elements. These are the Fundamental Laws of Chemistry.

Recall, Laws of Nature are broad statements to which there are no exceptions. The Laws we will discuss are the Fundamental Laws on which the science of chemistry is built.

The central question we wish to answer is, how can such a limited number of elemental substances be combined such as to form the ~15 million known compounds? For concreteness, consider the combination of elemental Carbon and elemental Oxygen by direct chemical reaction. If the reaction is carried out in an excess of oxygen, in other words, in a furnace with adequate ventilation, the compound Carbonic Acid is formed:

$$\text{Carbon} + \text{Oxygen} \xrightarrow{\text{Excess Oxygen}} \text{Carbonic Acid}$$
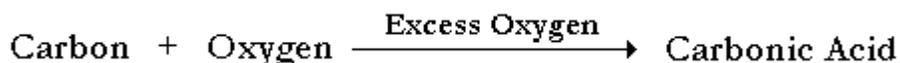
On the other hand, if the oxygen is fed into the furnace in limited amounts, via a Regulator, the compound Carbonic Oxide is formed:

$$\text{Carbon} + \text{Oxygen} \xrightarrow{\text{Limited Oxygen}} \text{Carbonic Oxide}$$
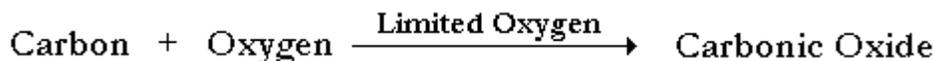
How do we know these gaseous products are indeed different compounds? The intensive physical properties of each gas are distinct:

Carbonic Acid	Carbonic Oxide
Colorless	Colorless
Odorless	Odorless
sublimation pt. = -78$^{\text{o}}$C	melting pt. = -205$^{\text{o}}$C
	boiling pt. = -191$^{\text{o}}$C
Soluble in Water	Insoluble in Water
Non-Combustible	Combustible

Now, back to the question posed above. How can these two elements form two different compounds? The Fundamental Laws of Chemistry will provide an answer to this question. Further, we shall see these Laws led directly to a statement of the Atomic Theory. This Atomic Theory provides the definitive explanation for why two different compounds can be formed from these two elements.
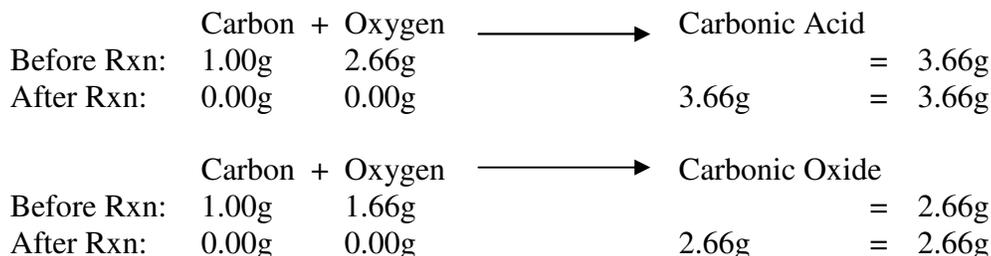
Law of Conservation of Mass

The first of these Fundamental Laws to be discovered was the Law of Conservation of Mass.

> *The total mass of material present after a chemical reaction is the same as before the reaction.*

This Law was discovered by Antoine Lavoisier in about 1789. In a turn about of the Scientific Method, Lavoisier had always assumed this Law was true, and sought out experiments which would verify his assumptions. As a result of numerous combustion experiments conducted on

systems in closed containers, so as to retain any gases present, Lavoisier was able to unambiguously verify his assumptions and formally state the Law of Conservation of Mass.

For an example, consider our combustion reactions of elemental Carbon. If the mass of the gasses are accounted for, it is found:

	Carbon	+ Oxygen	→	Carbonic Acid		
Before Rxn:	1.00g	2.66g			=	3.66g
After Rxn:	0.00g	0.00g		3.66g	=	3.66g

|	Carbon	+ Oxygen	→	Carbonic Oxide		
Before Rxn:	1.00g	1.66g			=	2.66g
After Rxn:	0.00g	0.00g		2.66g	=	2.66g

Of course, these results require that each reactant be present in perfectly balanced amounts, such that the full quantity of each is consumed completely during the reaction. If this is not the case, some of the reagent in excess will remain at the conclusion of the reaction. However, the Law of Conservation of Mass will still apply.

	Hydrogen	+ Oxygen	→	Water		
Before Rxn:	2.00g	10.00g			=	12.00g
After Rxn:	0.74g	0.00g		11.26g	=	12.00g
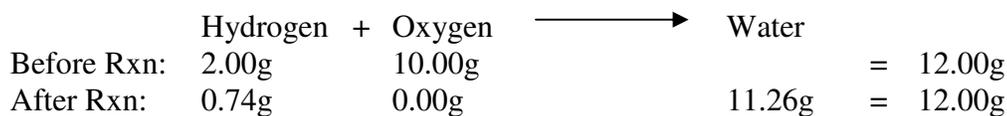
From this example, we see a total of 12.00g of material is present both before and after the chemical reaction occurs, with some of the hydrogen reagent remaining as excess. Further, we can also note that oxygen is the Limiting Reagent in carrying out this reaction; it limits the production of water. If more oxygen were present, a greater amount of water would be produced.

Finally, once this Law is accepted, it can be used to predict the amount of an "unseen" reactant consumed or produced without direct measurement. For instance, when iron burns in the air, its mass is seen to increase:

	Iron	+ Oxygen	→	Iron Oxide
Before Rxn:	5.00g	?g		
After Rxn:	0.00g	0.00g		7.15g
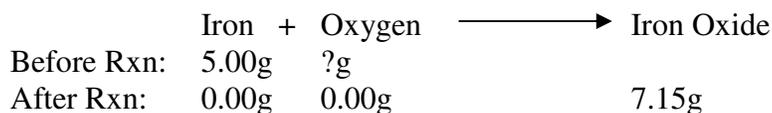
From these results we can calculate the mass of oxygen needed to carry-out the complete combustion of 5.00g of iron:

$$\text{mass Oxygen} = 7.15g - 5.00g = 2.15g$$

Finally, it must be noted the Law of Conservation of Mass, though a Fundamental Law of Chemistry, is not a fundamental law of nature. When an energy difference occurs during a reaction, minute amounts of mass are either gained or lost. Mass is either converted to energy or energy is converted to mass. The energy-mass equivalence was first postulated by Einstein in his

famous formula; $E = mc^2$. While these mass differences are not detectable by the chemist, they are important in nuclear reactions.

Law of Definite Proportions

> *A chemical compound, no matter what its origin or its method of preparation, always has the same composition; i.e., the same proportions by mass of constituent elements.*

This Law, sometimes known as the Law of Definite Composition, was first enunciated by Joseph Proust in 1799. Proust discovered this law while analyzing samples of Cupric Carbonate. He found two samples, one prepared via synthetic methods, and the other mined naturally (Malachite Green), possessed the same composition of elemental Carbon, Oxygen and Copper:

	% Copper	% Oxygen	% Carbon
Synthetic Sample:	51.35%	9.74%	38.91%
Natural Sample:	51.35%	9.74%	38.91%

So, for example, if we decompose water by electrolysis and we recover the elemental gases hydrogen and oxygen (not a difficult task experimentally), and subsequently measure the masses of each gas respectively, we can determine the composition of this compound:

	Water $\longrightarrow$	Hydrogen	+ Oxygen
Before Rxn:	10.00g		
After Rxn:		1.12g	8.88g

This data yields an elemental composition of:

$$\% \text{ Oxygen} = \frac{\text{mass Oxygen}}{\text{mass Compound}} \times 100 = \frac{8.88g}{10.00g} \times 100 = 88.8\%$$

$$\% \text{ Hydrogen} = \frac{\text{mass Hydrogen}}{\text{mass Compound}} \times 100 = \frac{1.12g}{10.00g} \times 100 = 11.2\%$$

In a similar manner, from the data presented above, we can determine the elemental composition of the two Oxides of Carbon:

	Carbonic Acid	Carbonic Oxide
% Carbon	27.29 %	42.88 %
% Oxygen	72.71 %	57.12 %

Thus, we begin to see how these two compounds of carbon and oxygen differ, they differ in their relative proportions of the two constituent elements. Each compound has a definite, well defined composition, but different compounds of the same elements will have different compositions.

The validity of the Law of Definite Proportions was firmly established by a number experiments conducted by Jons Jakob Berzelius. To cite one example, he heated powdered elemental lead with powdered elemental sufur, in different proportions, to form the compound lead sulfide. In each case he found the elemental composition of the lead sulfide remained unchanged.

Expt. #1

	Lead	+	Sulfur		Lead Sulfide	
Before Rxn:	10.00g		1.56g			
After Rxn:	0.00g		0.00g		11.56g	==> % Lead = 86.5 %
						% Sulfur = 13.5 %

Expt. #2

	Lead	+	Sulfur		Lead Sulfide	
Before Rxn:	10.00g		3.00g			
After Rxn:	0.00g		1.44g		11.56g	==> % Lead = 86.5 %
						% Sulfur = 13.5 %

Expt. #3

	Lead	+	Sulfur		Lead Sulfide	
Before Rxn:	18.00g		1.56g			
After Rxn:	8.00g		0.00g		11.56g	==> % Lead = 86.5 %
						% Sulfur = 13.5 %

From the results given above, we see attempts to increase the amount of one elemental substance, without likewise increasing the amount of the other, simply leads to an excess of that substance remaining after the reaction, and not a change in the composition of the compound.

It should be noted that forming a mixture, such as a solution, is a distinctly different process than the process associated with compound formation. Suppose copper and zinc are mixed to form brass. This is a physical process rather than a chemical process. Brass is not a compound because its physical properties (color, density, melting point, etc.) are not distinct; their exact values depend on the proportions in which the copper and zinc are mixed. This is very similar to mixing Table Salt and water to form a Salt-Water solution; the salt and water can be mixed in different proportions. We would not think of Salt-Water as a compound. When we combine, or "mix," hydrogen and oxygen to form water, the result is a compound whose composition is fixed and whose properties are distinct.

Once accepted, this Law can be used to predict the amount of product which can be formed from a given elemental reactant. For example, from the data cited above, we know that Carbonic Acid is 27.29 % carbon and 72.71 % oxygen. So, how much Carbonic Acid can be produced from 5.0g of carbon?

$$\% \text{ Carbon} = \frac{\text{mass Carbon}}{\text{mass Compound}} \times 100$$

or

$$\text{mass Compound} = \frac{\text{mass Carbon}}{\% \text{ Carbon}} \times 100 = \frac{5.00g}{27.29 \%} \times 100 = 18.32g$$

Further, this result can be used to determine how much oxygen would be consumed in the reaction forming this compound:

$$\text{mass Oxygen} = 18.32g - 5.00g = 13.32g$$

Law of Multiple Proportions

The Law of Multiple Proportions was enunciated by John Dalton at about the same time he postulated his Atomic Theory of Matter in ~1803. It was experimental results in the form which suggested the validity of the Law of Multiple Proportions which provided Dalton with the data needed to formulate the Atomic Theory. This Law, therefore, is a central linchpin in the development of modern chemistry.

> *If two elements form more than a single compound, the masses of one element combined with a fixed mass of the second are in the ratio of small whole numbers.*

This Law deals with the relationship between two compounds composed of the same elements. Our Carbonic Acid - Carbonic Oxide example is a case in point. Both are composed of the same two elements; carbon and oxygen. Recall, the above data showed that 1.00g of carbon will combine with 2.66g of oxygen, in the case of Carbonic Acid, and 1.33g of oxygen in the case of Carbonic Oxide. Thus, the amount of carbon, in each case, is fixed at 1.00g. We can, in turn, use this data to illustrate the application of the Law of Multiple Proportions:

$$\cfrac{\dfrac{\text{mass Oxy. in Carb. Acid}}{\text{mass Carbon}}}{\dfrac{\text{mass Oxy. in Carb. Oxide}}{\text{mass Carbon}}} = \dfrac{\dfrac{2.66g}{1.00g}}{\dfrac{1.33g}{1.00g}} = 2$$

fixed masses

As another example, it is found elemental iron combines with elemental chlorine to form two different compounds; ferric chloride and ferrous chloride. The definite composition of these two compounds is:

	Ferrous Chloride	Ferric Chloride
% Iron	44.06 %	34.43 %
% Chlorine	55.94 %	65.57 %

This data can be used to determine the mass of chlorine per 1.00g of iron needed to produce these compounds. The results are:

	Ferrous Chloride	Ferric Chloride
mass Iron	1.00g	1.00g
mass Chlorine	1.27g	1.90g

Applying the Law of Multiple Proportions to these results, we obtain:

$$\left.\begin{array}{c} \dfrac{\text{mass Chlor. in Ferric Chlr.}}{\text{mass Iron}} \\[2mm] \overline{} \\[1mm] \dfrac{\text{mass Chlor. in Ferrous Chlr.}}{\text{mass Iron}} \end{array}\right\} = \dfrac{\dfrac{1.90\,g}{1.00\,g}}{\dfrac{1.27\,g}{1.00\,g}} = 1.5 = \dfrac{3}{2}$$

fixed masses

In the case of the Oxides of Carbon, Dalton would interpret the above results to mean that carbonic acid is composed of 2 Atoms of oxygen for every 1 Atom of carbon, and carbonic oxide contains 1 Atom of oxygen for every 1 Atom of carbon. In the case of the Chlorides of Iron, he would conclude ferric chloride contains 3 Atoms of chlorine for every Atom of iron and ferrous chloride contains 2 Atoms of chlorine for 1 iron Atom.

It must be kept in mind, these results are purely experimental in nature. And yet, they have led directly to an Atomic interpretation for the formation of compounds. The Law of Multiple Proportions, in conjunction with the other Fundamental Laws of chemistry, led directly to the postulates of the Atomic Theory of Matter.

Dalton's Atomic Theory of Matter

The enunciation of the Law of Multiple Proportions and the Atomic Theory of Matter by John Dalton occurred, historically, at the same point in time. The experimental data led to both conclusions simultaneously. Dalton's Atomic Theory consisted of five basic postulates:

Elements are composed of indivisible Atoms.

Atoms are alike for a given element.

Atoms for different elements differ in size and mass and other properties.

Compounds are formed from two or more Atoms of different elements.

Atoms combine in simple numerical ratios to form these compounds. These ratios are different for different compounds.

As has been mentioned, the Oxides of Carbon are found to form from 2 Atoms versus 1 Atom of oxygen to every Atom of carbon in the compound. In Dalton's view, these compounds could be represented as:

Carbonic Acid   Carbonic Oxide

○●○   ●○
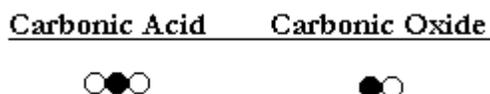
This would clearly explain the results of the Law of Multiple Proportions. Further, since the atoms combine without changing, losing or gaining parts, but instead by merely recombining, this would explain the Law of Conservation of Mass. And, since each "molecule" of Carbonic Acid contains 2 Atoms oxygen to 1 Atom carbon, the proportions of each are always the same; explaining the Law of Definite Proportions. A similar conclusion can be drawn for the case of Carbonic Oxide In modern parlance, we would name the compounds Carbonic Acid and Carbonic Oxide, Carbon Dioxide and Carbon Monoxide, respectively. Finally, we would represent these compounds with the chemical formulas CO_2 and CO, respectively; a convention introduced by Berzelius, and strongly opposed by Dalton.

The compounds Ferric Chloride and Ferrous Chloride are represented by the chemical formulas $FeCl_3$ and $FeCl_2$; where the number of iron atoms is denoted by the symbol Fe (*iron is ferrum in latin*) and the number of chlorine atoms is denoted by the symbol Cl.

Even at this point in the historical development of chemistry, many questions remained. For instance, the application of the Law of Multiple Proportions is not unambiguous. How do we know the order in which to form the ratios? Also, could we interpret the results for the Oxides of Carbon to mean Carbon Dioxide is really 4 Atoms oxygen to 1 Atom carbon and Carbon Monoxide is 2 Atoms oxygen to 1 Atom carbon? This interpretation is in fact consistent with the experimental data and the Law of Multiple Proportions. Thus, the determination of exact chemical formulas for compounds cannot be done on the basis of the Law of Multiple Proportions alone. Much more data is required to perform this task. Further, we are now left with the question of how the atoms bind together to form "molecules?" What accounts for the bonding of these atoms?

Lastly, not all of Dalton's postulates have withstood the test of time. Although his theory is correct in its broad outlines, and is based directly on solid experimental data, several of his postulates have to be modified in order to conform with modern experimental results. We will now turn to an examination of those results.

Questions

1. When a match burns, its mass decreases. Is this a violation of the Law of Conservation of Mass? Explain.

2. An 8.4g sample of sodium bicarbonate is added to a solution of acetic acid weighing 20.0g. The two substances react, releasing carbon dioxide to the atmosphere. After reaction, the contents of the reaction vessel weigh 24.0g. What is the mass of the carbon dioxide given off during the reaction?

3. Is the Law of Conservation of Mass obeyed in the following experiment:
   10.00g of zinc dust is mixed with 2.00g of powdered sulfur and the mixture is heated carefully. The result is 6.08g of white zinc sulfide and 5.92g of unreacted zinc.
   Also, identify the limiting reagent.

4. Is the Law of Conservation of Mass obeyed in the following experiment:
   10.00g of calcium carbonate is dissolved in 100.0 mL of hydrochloric acid solution which has density of 1.148 g/mL. The products are 120.40g of solution and 2.22 L of carbon dioxide gas, which has a density of 1.9769 g/L.

5. When heated directly, Phosphorus reacts completely with Selenium as follows:

   Phosphorus + Selenium ⟶ Compound #1
   (1.00g)   (3.82g)   (4.82g)
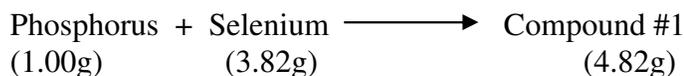
   When heated under carbon dioxide and nitrogen, Phosphorus reacts completely with Selenium as follows:

   Phosphorus + Selenium ⟶ Compound #2
   (1.00g)   (6.37g)   (7.37g)
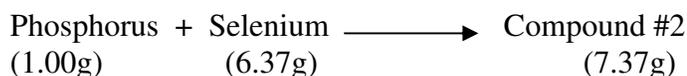
   Determine the elemental composition, percentage by mass, of Compound #1 and Compound #2.

6. For each experiment, determine the elemental composition, percentage by mass, of the compound Sodium Chloride.

   Expt. 1
   1.00g of Sodium metal was allowed to completely react with 10.00g of Chlorine gas. The Sodium was completely consumed and 2.54g of sodium chloride was produced.

   Expt. 2
   In a second experiment, 1.00g of Chlorine was allowed to react with 10.00g of Sodium. The Chlorine was consumed completely and 1.65g of sodium chloride was produced.

Are the results consistent with the Law of Definite Proportions?

7. Elemental Magnesium reacts with elemental Oxygen to form magnesium oxide. Magnesium oxide has a composition of 60.32% Mg and 39.68% O. How many grams of Oxygen are required to react completely with 5.00g of Magnesium?

    Magnesium + Oxygen ⟶ Magnesium oxide

8. Hydrogen forms two different Oxides; water and hydrogen peroxide. The relative amounts of hydrogen and oxygen for these two compounds are:

	Water	Hydrogen Peroxide
mass Hydrogen	1.00g	1.00g
mass Oxygen	7.94g	15.87g

    Form the following ratio:

    (mass O in Hyd. Per. / mass H) / (mass O in Water / mass H)

    Is the result consistent with the Law of Multiple Proportions? (Challenge question: If you know the chemical formula of water is H_2O, what is the chemical formula of Hydrogen Peroxide?)

9. Mercury forms two different Oxides; Mercurous Oxide and Mercuric Oxide. The relative amounts of mercury and oxygen in these compounds are:

	Mercurous Oxide	Mercuric Oxide
mass Mercury	1.00g	1.00g
mass Oxygen	0.0395g	0.0799g

    Form the following ratio:

    (mass O in Mercuric Ox. / mass Hg) / (mass O in Mercurous Ox. / mass Hg)

    Is the result consistent with the Law of Multiple Proportions?

10. Gold forms two different compounds with chlorine:

Aurous chloride	Auric chloride
84.76% Au	64.94% Au
15.24% Cl	35.06% Cl

    a) Calculate the mass of Chlorine required to react with 1.00g of Gold to form each of these compounds.
    b) Form the following ratio:

(mass Cl in Auric Chl. / mass Au) / (mass Cl in Aurous Chl. / mass Au)

Is the result consistent with the Law of Multiple Proportions?

11. Use the data of Problem #5 to form the following ratio:

(mass Se in Cmpd. #2 / mass P) / (mass Se in Cmpd. #1 / mass P)

Is the result consistent with the Law of Multiple Proportions?