2.1 Early History of Chemistry

- Chemistry has ancient roots. Dating back before 1000 B.C.E. are:
  - Smelting of ores for metal.
  - Use of embalming fluid.
  - Fermentation to make beverages.

- Earliest known theories come from Ancient Greece
  - Four elements (earth, air, fire, water)
  - Matter is continuous (Plato)
  - Matter is discrete, i.e., made of atoms (Demokritos)
  - The Greeks had no way to test these contradictory theories.

- Alchemy was the closest thing resembling chemistry until the end of the Medieval Period (i.e., through the 15th century.)
  - Mostly a boondoggle, financed by rich people wanting the secret for making gold from lead or other cheap metals.
  - Produced some real advances: several new elements and processes for making mineral acids.

- Beginnings of modern chemistry:
  - Systematics of Metallurgy (Georg Bauer, 1494-1555)
  - Medical use of minerals (Paracelsus, 1493-1541)
  - Experiments to characterize the relationship of Pressure vs. Volume of air (Robert Boyle, 1627-1691). **Boyle’s Law:** the product of pressure and volume of air at a constant temperature is constant.)
Boyle also conceived the first modern notion of what constitutes an element. He said that an element is an element unless it can be broken down into two or more simpler substances.


### 2.2 Fundamental Laws of Chemistry

- **Law of Conservation of Mass** (Lavoisier): Mass is neither created nor destroyed in a chemical process. Law based on systematic and careful weighing of reactants and products involved in many different chemical reactions. Lavoisier’s two pan balance design was state-of-the-art in chemistry until the 1960’s.

- **Law of Definite Proportions** (Proust): A given (pure) chemical compound always contains exactly the same proportions of elements by mass. Dalton’s atomic theory, that elements consist of tiny, individual particles, provides an explanation of this law. (More on this in Section 2.3)

- **Law of Multiple Proportions** (Dalton): When two elements form a series of different chemical compounds, the ratios of masses of the second element that combine with the first element can always be reduced to small whole numbers. For example: the compositions by mass of two different compounds of carbon and oxygen.

**Another Example:** Three different compounds, all consisting of nitrogen and oxygen, contain these masses of nitrogen for each gram of oxygen. Show how these data illustrate the Law of Multiple Proportions.
Step 1: Compute the ratios of nitrogen in A vs. B, A vs. C, & B vs. C:

\[
\begin{align*}
\frac{A}{B} &= \frac{1.750}{0.875} = 2 \\
\frac{B}{C} &= \frac{0.875}{0.4375} = 2 \\
\frac{A}{C} &= \frac{1.750}{0.4375} = 4
\end{align*}
\]

Step 2: These calculations demonstrate that Compound A contains twice as much nitrogen as Compound B and four times as much as Compound C and also that Compound B contains twice as much nitrogen as Compound C.

If we assume these compounds are composed of molecules containing nitrogen and oxygen atoms, we can hypothesize the following set of compositions (1):

- Or this set (2):

- Or this set (3):

Note that sets (1) and (3) have the same ratios of N vs. O, but that each molecule in (3) has twice the number of atoms. Note also that we could swap (say) molecule (3C) for (1C) and that this would give us two more sets.

Discussion questions: How does set (2) differ from sets (1) and (3)? Is there any limit to the number of different ABC sets we could construct to fit the experimental data?

2.3 Dalton’s Atomic Theory

• The theory
o Each element is composed of tiny particles called atoms.

o Atoms of a given element are identical; the atoms of different elements differ in some fundamental way(s).

o Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.

o Chemical reactions involve reorganization of the atoms – changes in the way they are bound together. Atoms are not changed in a chemical reaction.

• Dalton’s theory did not resolve, for example, whether water had a 1:1 ratio of hydrogen to oxygen, or a 1:2 ratio, or even some other ratio.

• Dalton knew that water contained 8 grams of oxygen for each gram of hydrogen, and he arbitrarily assumed the simplest possible formula, HO. This gave him the relative atomic masses of 8 for oxygen and 1 for hydrogen, as opposed to our modern picture where the formula is H2O, and the relative atomic masses are 16 for oxygen and 1 for hydrogen.

• **Combining Volumes of Gases** (Gay-Lussac): *The volumes of gases that react with each other, and the volumes of the gaseous products of these reactions are in small whole number ratios, if all measurements are made at the same temperature and pressure.* Gay-Lussac measured the volumes of reactant gases and their gaseous reaction products under the same conditions of pressure and temperature. Figure 2.4 shows two of his results.
• **Avogadro’s Hypothesis:** *At the same temperature and pressure, equal volumes of different gases contain the same numbers of particles.*

• If we add Avogadro’s Hypothesis to Dalton’s Atomic Theory, we can interpret Gay-Lussac’s results on an atomic level, as shown in Figure 2.5:

2.4 Early Experiments to Characterize the Atom

• Is there structure to the atom? Can it be cut or broken apart?
Toward the end of the 19th century, developments in the science of Physics, especially in the areas of Electricity and Magnetism provided experimental means to explore this question.

- **Cathode Rays**: Produced as electrical discharges in partially evacuated tubes (J. J. Thompson, c. 1900). Since the rays were emitted from the negative electrode (Figure 2.7) ...

... and since these rays were repelled by the negative pole of an applied electrical field (Figure 2.8), ...

... Thompson concluded that the ray was a stream of negatively charged particles, now called electrons. He also measured the charge-to-mass ratio by measuring the beam’s deflection in a magnetic field.

\[
\frac{e}{m} = -1.76 \times 10^8 \text{ C/g (Coulombs per gram)}
\]
• Thompson used many different metals as electrodes but the cathode rays did not differ. Thus, he concluded, all metals contained electrons, and these electrons did not differ from one metal to another.

• Since metals contain electrons, but are electrically neutral, Thompson reasoned that they must also contain some positive charge, and he postulated the “plum pudding” model, shown in Figure 2.9:

• **Oil Drop Experiment** (Millikan, 1909): Millikan generated small drops of oil in an apparatus where he could neutralize the force of gravity on the drops by applying an opposing electric field. From the strength of the field and the masses of the drops, he could determine the absolute charge on a given oil drop, and he could determine the smallest such charge. Since the next smallest charges were double, then triple, etc., he attributed this smallest charge as being the charge on a single electron. Then using Thompson’s charge-to-mass ratio, he could calculate that the mass of an electron was $9.11 \times 10^{-31}$ kg.

• **Radioactivity**: Certain elements, such as uranium (Becquerel, 1896), were found to emit high energy radiation.

• The three principal types of radiation:
  o gamma ($\gamma$) rays: high-energy light
  o beta ($\beta$) particles: high-speed electrons
  o alpha ($\alpha$) particles: particles with a charge of +2 (vs. -1 for an electron)

• **The Nuclear Atom** (Rutherford, 1911):
  o The plum pudding model of the atom pictures the positive charge as being diffused throughout the atom and pictures the electrons as point charges scattered evenly among the positive charge.
If this is so, alpha (α) particles should pass through a thin foil of metal with little or no deflection of any of their trajectories.

Rutherford constructed his experiment so he could shoot a beam of alpha (α) particles through a piece of gold foil and detect any scattering. The experiment is pictured in Figure 2.12:

The results were unexpected: Most of the alpha (α) particles passed through the foil with little or no deflection, but some were deflected at large angles, and some were even reflected back toward the source.

The only realistic explanation was that the positive charge and most of the mass in a given atom were concentrated in a small volume within the atom. The alpha (α) particles that were reflected back toward the source were those that had made direct hits upon the centers of positive charge, and those that were deflected at large angles were those that had had near misses.

Thus Rutherford disproved the plum pudding model of the atom (Figure 2.13a), and replaced it with the model of a Nuclear Atom (Figure 2.13b) with electrons moving around the nucleus (the center of positive charge) at relatively large distances compared to the size of the nucleus.
FIGURE 2.13
(a) The expected results of the metal foil experiment if Thomson’s model were correct. (b) Actual results.