

The Fundamental Chemical Laws

This is an addition to the textbook used for CHEM 205.
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Strongly inspired from “Chemistry”, 4th edition, by S. S. Zumdahl, USA, 1997.

Law of Conservation of Mass

- **Author:** Antoine LAVOISIER, France, 18th century;
- Method used: by careful weighing of the reactants and the products of various reactions, particularly the reaction of oxygen with metals;
- **The law:** *In a chemical reaction, mass is neither created nor destroyed, i.e., in a chemical reaction, the sum of the mass of all products is equal to the sum of the mass of all reactants;*
- His work on oxidation of metals lead Lavoisier to discover the role of oxygen (which Lavoisier named) in oxidation reactions and in life processes.

Law of Definite Proportion = Law of Constant Composition

- **Author:** Joseph PROUST, France, 18-19th century;
- **Method used:** Careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds;
- **The law:** *A given compound always contains exactly the same proportion of elements by mass;*
- **Example:** copper(II) carbonate is always made of 5.3 parts of copper and 4 parts of oxygen for 1 part of carbon, by mass

Law of Multiple Proportions

- **Author:** John DALTON, England, 18-19th century;
- Method used: Comparing the relative amounts of two elements that combine to form several compounds;
- **The law:** *When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers;*
- **Example 1:** Carbon and oxygen react together to form two compounds. Let's call the two compounds formed "Compound I" and "Compound II." Let's take carbon to be the first element and oxygen to be the second element.
- Experiments show that:
 - 1.33 g of oxygen combines with 1.00 g of carbon to form compound I;
 - 2.66 g of oxygen combines with 1.00 g of carbon to form compound II;
- The ratio $2.66 \text{ g} / 1.33 \text{ g}$ is equal to $2/1$, which is a ratio of small whole numbers

Law of Multiple Proportions

- **Example 2:** Nitrogen and oxygen form several compounds. Let's call three of these compounds "Compound A", "Compound B" and "Compound C." Let's take oxygen to be the first element and nitrogen to be the second element.
- Experiments show that:
 - 1.750 g of nitrogen combines with 1 g of oxygen to form compound A;
 - 0.8750 g of nitrogen combines with 1 g of oxygen to form compound B;
 - 0.4375 g of nitrogen combines with 1 g of oxygen to form compound C;
- The ratios of nitrogen that combines to 1 g of oxygen to form compounds A, B and C are the following:
 - $A/B = 1.750 \text{ g} / 0.8750 \text{ g}$ is equal to $2/1$, which is a ratio of small whole numbers;
 - $B/C = 0.8750 \text{ g} / 0.4375 \text{ g}$ is equal to $2/1$, which is a ratio of small whole numbers;
 - $A/C = 1.750 \text{ g} / 0.4375 \text{ g}$ is equal to $4/1$, which is a ratio of small whole numbers;

Law of Multiple Proportions

- Possible chemical formulas for nitrogen oxides are:

• Compound A	N_2O	NO	N_4O_2
• Compound B	NO	NO_2	N_2O_2
• Compound C	NO_2	NO_4	N_2O_4

- There are an infinite number of possibilities.
- Dalton could not deduce absolute formulas from the available data on relative masses. It is necessary to know the formula of one of the compounds in a series in order to determine the others. Assuming that nature is as simple as possible, Dalton supposed erroneously that the formula of water was HO.
- Dalton derived the *Atomic theory*. The data on the composition of compounds in term of the relative masses of the elements supported the hypothesis that each element consisted of a certain type of atoms and that compounds were formed from specific combination of atoms.

Law of Multiple Proportions

- **Example of a question about the use of the law of multiple proportions:**
- Sulfur reacts with fluorine to give several compounds. Let's call two of these compounds A and B. Compound A contains 3.5547 g of fluorine for each 1.0000 g of sulfur. Compound B contains 2.3698 g of fluorine for each 1.0000 g of sulfur. In compound A, all the valence electrons of sulfur are used for bonding to fluorine.
- What is the *chemical formula* of compound B?
- 1. S_2F_2
- 2. SF_2
- 3. SF_4
- 4. S_2F_{10}
- 5. SF_6

Law of Multiple Proportions

- Answer: Since sulfur belongs to group 16, it has 6 valence electrons, and since in compound A, all the valence electrons of sulfur are used for bonding to fluorine, compound A is SF₆.
- Let's m_A be the mass of F that combines to 1.0000 g of S in compound A, and m_B be the mass of F that combines to 1.0000 g of S in compound B
- The following ratio of masses must be calculated:
$$m_B/m_A = 2.3698 \text{ g of F in A} / 3.5547 \text{ g of F in B}$$
$$m_B/m_A = 0.66667 = 2/3$$

=> there are 2 F in B for each 3 F in A, for each S
- number of F per S in compound B = (6F in A) * (2 F in B) / (3 F in A)
$$= 4F \text{ in B}$$

=> Compound B is SF₄
=> Answer 3 is correct

The Atomic Theory

- **Author: John DALTON**, England, 18-19th century;
- Method used: Compiling together the results of the above laws;
- **The theory of atoms:**
- *Each element is made up of tiny particles called atoms.*
- *The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.*
- *Chemical compounds are formed when atoms combine with each other. A given compound always has the same relative numbers and types of atoms.*
- *Chemical reactions involve reorganization of the atoms – changes in the way they are bound together. The atoms themselves are not changed in chemical reactions.*

Volume of gases in chemical Reaction

- **Author:** Joseph GAY-LUSSAC, France, 18-19th century;
- **Method used:** Comparing the volume of gases that react together and the volume of gases produced;
- **Observation:** *At the same conditions of temperature and pressure, the ratio of the volume of gases that react together can be reduced to a ratio of whole numbers. In addition, the ratio of the volume of each gas produced to the volume of each reactant can also be reduced to a ratio of whole numbers.*

Volume of gases in chemical Reaction

- **Example 1:** 2 volumes of hydrogen combines with 1 volume of oxygen to form 2 volumes of gaseous water.
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- Let's call V_H , V_O and V_{H_2O} the volumes of hydrogen, of oxygen and of water, respectively. In terms of volumes of gases, the reaction can be summarized by the following chemical equation:
- $V_H (= 2V) + V_O (= V) \rightarrow V_{H_2O} (= 2V)$
- The ratios of gas volumes can be reduced to ratios of whole numbers, as follows:

$$V_H / V_O = 2V / V = 2 / 1$$

$$V_H / V_{H_2O} = 2V / 2V = 2 / 2 = 1 / 1$$

$$V_O / V_{H_2O} = V / 2V = 1 / 2$$

Volume of gases in chemical Reaction

- **Example 2:** 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.
- Let's call V_{H} , V_{Cl} and V_{HCl} the volumes of hydrogen, of chlorine and of hydrogen chloride, respectively. In terms of volumes of gases, the reaction can be summarized by the following chemical equation:
- $V_{\text{H}} (= V) + V_{\text{Cl}} (= V) \rightarrow V_{\text{HCl}} (= 2V)$
- The ratios of gas volumes can be reduced to ratios of whole numbers, as follows:

$$\begin{aligned}V_{\text{H}} / V_{\text{Cl}} &= V / V = 1 / 1 \\V_{\text{H}} / V_{\text{HCl}} &= V / 2V = 1 / 2 \\V_{\text{Cl}} / V_{\text{HCl}} &= V / 2V = 1 / 2\end{aligned}$$

Avogadro's Hypothesis

- **Author:** Amadeo AVOGADRO, Italy, 18-19th century;
- Method used: Interpretation of Gay-Lussac's observation on comparing the volume of gases that react together and the volume of gases produced;
- **Avogadro's hypothesis:** *At the same temperature and pressure, equal volumes of different gases contain the same number of particles.*
- Note: Here, a "particle" of gas is a "molecule" of gas.
- **Limitations:** Avogadro's hypothesis makes sense only if the distance between the particles in a gas is very great compared with the sizes of the particles. This works only at low pressures and high temperatures, and such gases are called "**ideal gases**" and they obey the "**ideal gas law.**" At low temperatures and/or high pressures, deviations from the ideal gas behavior occur and then the gases are called "**real gases**" and they obey the "**Van der Waals equation.**" Note: The behavior of gases will be studied in chapter 12.

Avogadro's Hypothesis

- **Example 1:** “2 volumes of hydrogen combines with 1 volume of oxygen to form 2 volumes of gaseous water” means “2 molecules of hydrogen combines with 1 molecule of oxygen to form 2 molecules of gaseous water.”
- $V_H (= 2V) + V_O (= V) \rightarrow V_{H_2O} (= 2V)$
means $2H_2 + O_2 \rightarrow 2H_2O$
- It should be noted from Gay-Lussac's observation and Avogadro's hypothesis that the atomic ratio H/O = 2 in water and therefore its chemical formula should be H_2O , instead of HO as assumed by Dalton;

Avogadro's Hypothesis

- **Example 2:** “1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride” means “1 molecule of hydrogen combines with 1 molecule of chlorine to form 2 molecules of hydrogen chloride”.

