

V25.0109: General Chemistry I: Honors

Notes for Lecture 3

The following recounts the key experiments that revealed the structure of the atom.

I. J.J. THOMPSON'S EXPERIMENT AND THE CHARGE-TO-MASS RATIO OF THE ELECTRON

The first is the experiment of Joseph John Thompson, who first demonstrated that atoms are actually composed of aggregates of charged particles. Prior to his work, it was believed that atoms were the fundamental building blocks of matter. The first evidence contrary to this notion came when people began studying the properties of atoms in large electric fields.

If a gas sample is introduced into the region between two charged plates, a current flow can be observed, suggesting that the atoms have been broken down into charged constituents. In 1897, Thompson set out to prove that the cathode produced a stream of negatively charged particles called electrons. (See Figure 1.8 in the textbook for Thompson's experimental setup). From Maxwell's theory, he knew that charged particles could be deflected in a magnetic field. A schematic of the experimental setup is shown below:

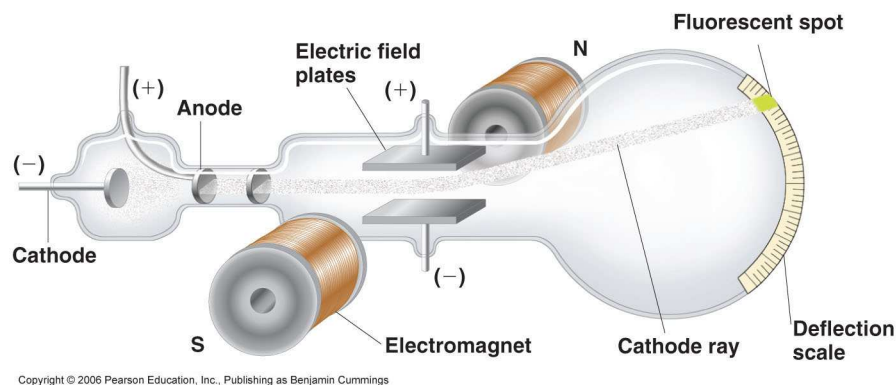


FIG. 1. Schematic of J.J. Thomson's experiment.

We now zero in on the field region and set up a coordinate system as shown in the figure below:

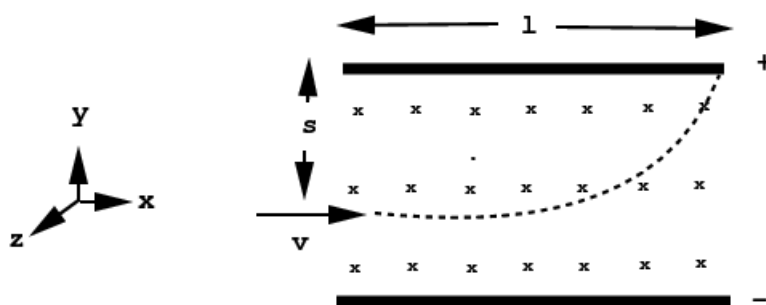


FIG. 2.

In this coordinate system, electrons enter the region between the plates with an (unknown) velocity v in the x -direction. In order to determine this velocity, electric and magnetic fields are both applied, and each gives rise to a force on the electron. These forces are in the y -direction. The electric force $F_E = eE$, where E is the magnitude of the electric field, and the magnetic force is $F_H = -evH$, where H is the magnitude of the magnetic field, and is opposed to the force on the electric field.

If these forces balance, then there will be no deflection of the electron in the y -direction, i.e. all of the electrons' motion will be along the x -direction, which was the initial direction when they entered the field region. If the forces balance, then the total force on the electrons will be zero, that is $F_E + F_H = 0$ or

$$eE - evH = 0$$

from which the unknown velocity can be determined as

$$v = \frac{E}{H}$$

Next, the magnetic field is switched off, so that the total force is due entirely to the electric field. Since the force is non-zero, if the charge carriers can be deflected by the force, this provides evidence for their being fundamental particles. If they *are* fundamental charged particles, then they should have a well defined mass and charge. In this second part of the experiment, the specific trajectory followed by the particle will be used to determine the ratio of the charge to the mass of the particle.

When there is only an electric field, then there is a nonzero force $F_E = eE$ in the y -direction but no force in the x -direction. Thus, this problem is exactly the same as that of a projectile in a gravitational field. As can be done in the projectile problem, the x and y motion of the electrons can be analyzed separately and independently.

In the x -direction, the motion is very simple because there is no force in this direction. The electrons simply move with a constant velocity v , which we already determined has the value E/H . Note that this value is correct even though there is no magnetic in this part of the experiment! It is just the velocity we determined from the previous part of the experiment, and this value has not changed. Thus, as a function of time t , the x -position of the electrons is

$$x(t) = vt = \frac{E}{H}t$$

The force in the y -direction is a constant, hence motion in the y -direction is analogous the gravitational force. The constant force F_E gives rise to an acceleration $a = F_E/m$, and the y -position at time t is then

$$y(t) = \frac{1}{2}at^2 = \frac{1}{2} \frac{F_E}{m} t^2 = \frac{eE}{2m} t^2$$

The electric field is tuned such that the particle traverses the entire plate region in the time required for it to strike the positive plate. Let the total y distance travelled be s , as shown in the figure. The time T required to traverse the plate region ($x(T) = l$) is

$$l = \frac{E}{H}T$$

$$T = \frac{lH}{E}$$

This is also the time required to move a distance s in the y direction:

$$s = \frac{eE}{2m} \left(\frac{lH}{E} \right)^2$$

Solving the above for the ration e/m gives

$$\frac{e}{m} = \frac{2sE}{l^2H^2}$$

Thus, using his experimental apparatus, Thompson was able to determine the charge-to-mass ratio of the electron. Today, the accepted value of e/m is $1.7588196 \times 10^{11} \text{ C}\cdot\text{kg}^{-1}$.

In 1906, Robert Millikan was able to determine the value of the charge on the electron in his “oil drop” experiment. A schematic of his experiment is shown below:

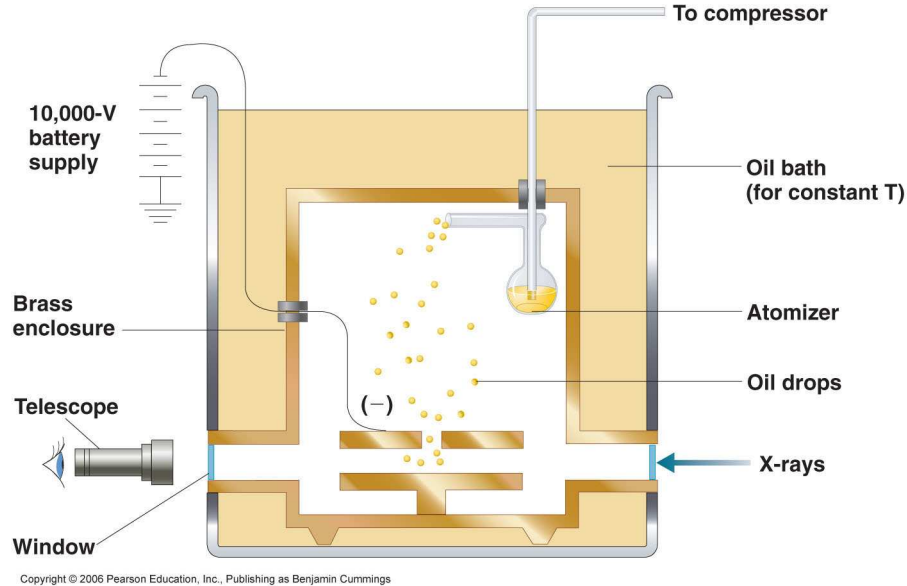


FIG. 3. Schematic of Millikan’s experiment.

Then using Thompson’s value of e/m , he calculated the value of m . In his experiment, Millikan used a fine spray of ionized oil droplets, which he allowed to be acted on by gravity but to which he also applied an electric field in the direction opposite gravity, i.e. up. By tuning the electric field, he balanced the force due to the pull of gravity and the electric field force so that the drops remained suspended in space. Thus, if a drop has a positive charge q and a mass M , the force balance condition becomes

$$Mg = qE$$

where E is the magnitude of the electric field. Solving for the charge-to-mass ratio, we have $q/M = g/E$. In order to determine the mass, the drops are allowed to fall in the gravitational field without the influence of the electric field. In this case, there are still two forces acting on the drops. One is the gravitational force and the other is the frictional force due to air resistance. Since this force is proportional to the velocity, it vanishes when the drop is stationary, which is why it does not need to be taken into account when the electric field is on. However, when the drops are allowed to fall, the total force is $F = Mg - \gamma v$, since friction opposes gravitational force. Here, γ is the coefficient of air resistance. Thus, according to Newton’s law of motion

$$Ma = F$$

$$M \frac{dv}{dt} = Mg - \gamma v$$

Assuming the drop starts initially at rest, the equation can be solved for $v(t)$, yielding

$$v(t) = \frac{Mg}{\gamma} (1 - e^{-\gamma t/M})$$

Since M is very small and γ is relatively large, the exponential factor quickly decays to 0, leaving simply a constant velocity $v = Mg/\gamma$ known as the *terminal velocity*. This velocity can be measured and used to solve for the mass M . Once the mass is known, the charge-to-mass ratio determined above can be used to determine the charge q . The

last remaining technical problem is that it is not known how many electrons are stripped off each drop before the experiment is performed. Thus, each drop will have a different charge q that is a multiple of the fundamental charge unit e . By subtracting successive values of q obtained for different drops, however, it is possible to find a “smallest” value, which can be assumed to be a prediction of e , although the possibility that the result is still a multiple of e cannot be ruled out.

The currently accepted values of e and m are:

$$e = 1.6021773 \times 10^{-19} \text{ C}$$

$$m = 9.109390 \times 10^{-31} \text{ kg}$$

II. RUTHERFORD’S EXPERIMENT AND THE NATURE OF THE ATOMIC NUCLEUS

The nature of the atomic nucleus was first elucidated experimentally by Ernest Rutherford in 1911. He observed the scattering of α -particles (helium nuclei) from a thin gold foil (see schematic below):

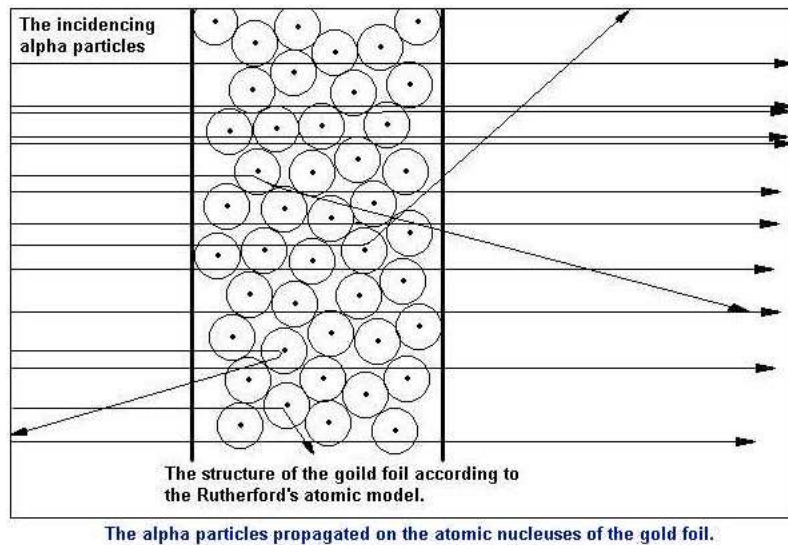


FIG. 4. Schematic of Rutherford’s experiment.

As he had assumed a relatively uniform mass distribution throughout the gold foil, he was surprised to observe that most of the α -particles passed through the foil essentially undeflected, as if through empty space. Occasionally, an α -particle would be scattered strongly, as if it had collided with a dense concentration of mass. He, thus, concluded that most of the mass of the gold atoms was concentrated in a tiny, dense kernel that he called the *nucleus*.

Rutherford estimated the “diameter” of an atom to be approximately 10^{-8} cm and that of the nucleus to be approximately 10^{-13} cm. He proposed a model of the atom as consisting of a small, dense nucleus surrounded by enough electrons to yield an overall charge-neutral aggregate. That is, if the nuclear charge is $+Ze$, then the atom must possess Z electrons. The model later introduced by Bohr, and even the current quantum mechanical picture of the atom (which you will see next semester), were built upon Rutherford’s original model.

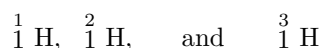
As mentioned in the first lecture, we know today that the atomic nucleus is composed of protons and neutrons. If a nucleus has Z protons and N neutrons, it is said to have a mass number A equal to $Z + N$. Thus, if X represents the chemical symbol of some element, then its nucleus is represented by



Nuclei of the same chemical species having different mass numbers, hence different numbers of neutrons, are called *isotopes* of that species. Thus,



are isotopes of the element X . For example,



are isotopes in the hydrogen family, called “hydrogen,” “deuterium,” and “tritium,” respectively.

III. EXPRESSING THE MASS OF AN ATOM

The mass of a hydrogen atom is 1.6727×10^{-27} kg. To avoid having to work with such small numbers all the time, the tradition of using a relative atomic mass scale was started. Although such a relative scale has undergone several incarnations, in 1961, by international agreement, a scale was settled upon.

A relative scale can be devised by assuming that one of the elements has exactly one mass unit for each of its nucleons. In 1961, it was decided that ${}^{12}\text{C}$ would be the element that defined the scale. Thus, the scale of relative atomic mass of ${}^{12}\text{C}$ is taken to be exactly 12 (and no units are assigned to this number). Then, the masses of *all* other elements are defined with respect to this scale. Thus, knowing the actual mass of a ${}^{12}\text{C}$ atom (1.9927×10^{-26} kg), and the actual mass of a hydrogen atom, we can determine the relative mass of hydrogen on this scale from

$$\frac{\text{mass of an atom of H}}{\text{mass of an atom of } {}^{12}\text{C}} = \frac{\text{relative mass of an atom of H}}{\text{relative mass of an atom of } {}^{12}\text{C}}$$

$$\frac{1.6727 \times 10^{-27} \text{ kg}}{1.9927 \times 10^{-26} \text{ kg}} = \frac{\text{rel. mass of H}}{12}$$

$$\text{re. mass of H} = 1.0073$$

A complete list of relative mass of atoms is given in the table in the inside back cover of the book.

Notice, however, that the number we computed above does not correspond to what is in the table under hydrogen. Since many elements have isotopes, it is customary to express the relative mass of an atom as an average over the different isotopes. Thus, if an element has isotopes ${}^{A_1}\text{X}$, ${}^{A_2}\text{X}$, ${}^{A_3}\text{X}$, ... with relative masses A_1 , A_2 , A_3 , ... then the relative mass A associated with an atom of X is given by

$$A = A_1 p_1 + A_2 p_2 + A_3 p_3 + \cdots = \sum_{i=1}^n A_i p_i$$

where p_i is the *fractional abundances* of the i th isotope.

Example: ${}^{12}\text{C}$ and ${}^{13}\text{C}$ are stable isotopes of carbon with fractional abundances of 98.934% and 1.0664%, respectively. The relative mass of ${}^{13}\text{C}$ is 13.003354. What is the average relative mass of carbon?

$$A = 12.00000 \times 0.98934 + 13.00354 \times 0.010664 = 12.00107$$

In order to establish a link between the mass of macroscopic amounts of matter that we ordinarily deal with and the masses of individual atoms, a connection exists through a number known as Avogadro’s number (N_0), which is defined to be the number of atoms in *exactly* 12 g of carbon. The currently accepted value of N_0 is 6.0221420×10^{23} . Then, the mass of any atom can be determined by dividing its relative mass A by N_0 :

$$m_X = \frac{A}{N_0}$$

For example, the mass of one atom of ${}^{12}\text{C}$ is

$$m_{{}^{12}\text{C}} = \frac{12.000 \text{ g}}{6.022142 \times 10^{23}} = 1.9926465 \times 10^{-23} \text{ g}$$

IV. THE MOLE CONCEPT

In everyday work, we deal with macroscopic amounts of substances. It is, therefore, useful to have a standard definition of macroscopic quantity of something. Avogadro's number is used to provide such a definition. We define 1 *mole* of something to be the amount of that something which contains N_0 individual entities of that thing. Thus, 1 mole of sodium atoms = N_0 sodium atoms. Now, if m_X is the mass of one atom of the element X, then the mass of one mole of X is given by

$$m_X(\text{g/atom}) \times N_0(\text{atoms/mol}) = m_X N_0(\text{g/mol})$$

But $m_X = A/N_0$. Thus, we see that the relative mass A also measures the mass of 1 mole of X (in g/mol, for example). For this reason, the relative mass A is also called the molar mass of X, however to distinguish relative mass A from molar mass, we will use the symbol M for molar mass. Note, therefore, that 12g of ^{12}C is exactly 1 mole of ^{12}C , which explains why Avogadro's number is defined the way it is.

V. STOICHIOMETRY

A. Chemical Formulae

Molecules are aggregates of individual atoms held together by *chemical bonds* (to be discussed in the next chapter). Thus, a symbolic representation of a molecule should be composed of the chemical symbols for the individual atoms that comprise the molecule. There are two types of chemical formulae that are commonly used to represent a molecule:

1. Molecular Formula:

The molecular formula for a molecule expresses the precise number of each type of atom in that molecule.

Examples:

- CO_2 is the formula for a molecule of carbon dioxide.
- H_2O is the formula for a molecule of water.
- $\text{C}_6\text{H}_{12}\text{O}_6$ is the formula for molecule of glucose.

Note that the molecular formula is also the formula for the (bulk) substance, itself. That is, we say H_2O is the molecular formula for water or ice, indicating bulk water or ice. This is true as long as the bulk substance has well defined molecular subunits.

2. Empirical Formula:

The empirical formula is the simplest formula for a molecule that still expresses the correct relative numbers or ratios of numbers of atoms in the molecule.

Example: The numbers of carbon, hydrogen and oxygen atoms in glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) are in the ratio:

$$\begin{aligned} 6 : 12 : 6 \\ 1 : 2 : 1 \end{aligned}$$

Hence, the empirical formula for glucose is



Which contains more information?

Consider the empirical formula



This is a correct empirical formula for the following molecules:

- a. ethylene: C_2H_4
- b. cyclopropane: C_3H_6
- c. cyclobutane: C_4H_8
- d. cyclohexane: C_6H_{12}

or any other molecule for which the number of carbon atoms and the number of hydrogen atoms are in the ratio of 1:2. From this example, it is clear that the *molecular formula* carries more information and is clearly preferable to an empirical formula.

Put another way, an empirical formula specifies a class of molecules, in which the numbers of atoms are in certain basic ratios, while the molecular formula precisely identifies a particular molecule.

Although preferable, a molecular formula is not always possible. For example, in liquids and solids, it may not always be possible to define precise molecular units, in which case an empirical formula is the only possible choice.

Sometimes, enough information about a substance is given to determine the empirical formula only. Consider the following **example**:

A 10.0 g sample of a sand-like substance is known to contain 46.01% iron (Fe) and 53.99% silicon (Si) by mass. What is the formula for the substance?

Solution: The mass of Fe and Si in the sample can be determined from the given percentages:

$$\begin{aligned}\text{mass of Fe} &= 10.0\text{g} \times 0.4601 = 4.601\text{g} \\ \text{mass of Si} &= 10.0\text{g} \times 0.5399 = 5.399\text{g}\end{aligned}$$

We convert masses to moles, since we want to know how many of each type of atom there is in the substance (expressed in moles), and hence how many of each type of atom in a molecule. This is done using the molar masses of each atom type.

$$\begin{aligned}\text{moles of Fe} &= \frac{4.601\text{g}}{55.847\text{g/mol}} = 0.08237\text{mol} \\ \text{moles of Si} &= \frac{5.399\text{g}}{28.086\text{g/mol}} = 0.19223\text{mol}\end{aligned}$$

The ratio is:

$$\begin{aligned}0.08237 : 0.192234 \\ 1 : \frac{7}{3} \\ 3 : 7\end{aligned}$$

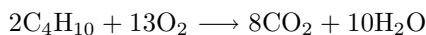
So the formula, which is an empirical formula, is



The reason it is only an empirical formula is that if the true formula were $\text{Fe}_6\text{Si}_{14}$, the same percentages by mass would still hold.

B. Conservation of mass

Consider the balanced reaction from the previous lecture:



In this example, suppose 2 mol of C_4H_{10} are combined with 13 moles of O_2 . What are the masses of the reactants and products?

Quantities in moles are converted to masses via the molar mass of each molecular species. The molar mass of a molecule is obtained by simply adding the molar masses of each of its atomic constituents. Thus, letting M be the symbol for molar mass,

$$M_{\text{C}_4\text{H}_{10}} = 4M_{\text{C}} + 10M_{\text{H}} = 4 \times 12.011 + 10 \times 1.0079 = 58.123 \text{ g/mol}$$

$$M_{\text{O}_2} = 2M_{\text{O}} = 2.0 \times 15.998 = 31.996 \text{ g/mol}$$

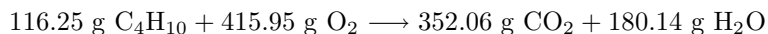
$$M_{\text{CO}_2} = M_{\text{C}} + 2M_{\text{O}} = 12.011 + 2.0 \times 15.998 = 44.007 \text{ g/mol}$$

$$M_{\text{H}_2\text{O}} = 2M_{\text{H}} + M_{\text{O}} = 2.0 \times 1.0079 + 15.998 = 18.014 \text{ g/mol}$$

Then, 2 mol of C_4H_{10} is equivalent to

$$2 \text{ mol } \text{C}_4\text{H}_{10} = (2 \text{ mol } \text{C}_4\text{H}_{10}) \times 58.123 \text{ g/mol} = 116.25 \text{ g } \text{C}_4\text{H}_{10}$$

etc. Thus, the chemical equation can be written as a statement about masses of reactants and products:



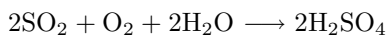
The total mass on the left side is $116.25 \text{ g} + 415.95 \text{ g} = 532.2 \text{ g}$, and the total mass on the right is $352.0 \text{ g} + 180.14 \text{ g} = 532.2 \text{ g}$. Thus, mass conservation is satisfied. The study of such mass relations in chemical reactions is called *stoichiometry*.

C. Limiting reagent

Chemical equations specify precise amounts of reactants that will combine to give products. In a real chemical reaction, arbitrary amounts of reactants are mixed together and allowed to form products, which means generally that one of the reactants will be used up completely, while excess amounts of other reactants will remain after the reaction has run to completion. The species that is fully consumed is called the *limiting reagent*. The limiting reagent will then determine what the yield of product will be.

When the quantities of reactants that are allowed to combine are specified, identifying the limiting reagent amounts to determining which of the reacting species yields the *smallest amount of product*.

Consider the following example. Sulfuric acid is produced in the reaction:



Suppose 400 g of SO_2 , 175 g of O_2 and 125 g of H_2O are mixed and allowed to react. Which reactant is the limiting reagent?

Solution: First convert the given masses to moles:

$$\text{moles of } \text{SO}_2 = \frac{400 \text{ g}}{64.06 \text{ g/mol}} = 6.24 \text{ mol } \text{SO}_2$$

$$\text{moles of } \text{O}_2 = \frac{175 \text{ g}}{31.996 \text{ g/mol}} = 5.47 \text{ mol } \text{O}_2$$

$$\text{moles of } \text{H}_2\text{O} = \frac{125 \text{ g}}{18.02 \text{ g/mol}} = 6.94 \text{ mol } \text{H}_2\text{O}$$

From the reaction equation, we see that

2 moles of SO₂ yields 2 moles of H₂SO₄

or

1 mole of SO₂ yields 1 mole of H₂SO₄

or

6.24 moles of SO₂ yields 6.24 moles of H₂SO₄

Similarly,

1 mole of O₂ yields 2 moles of H₂SO₄

or

5.47 mole of O₂ yields 10.94 moles of H₂SO₄

and

2 moles of H₂O yields 2 moles of H₂SO₄

or

1 mole of H₂O yields 1 mole of H₂SO₄

or

6.94 moles of H₂O yields 6.94 moles of H₂SO₄

Since SO₂ yields the smallest quantity of product, it is the limiting reagent.

D. Percentage yield

A balanced chemical equation tells what the *theoretical* or *ideal* yield of the reaction should be, assuming perfect completion of the reaction. In reality, the *actual* yield may be less than the theoretical yield. Reasons for this include:

1. There may be competing reactions which hinder the process under consideration.
2. External conditions may not be perfectly maintained.
3. Reactants may not be pure.

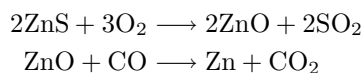
The ratio of the actual yield to the theoretical yield is a quantity known as the fractional yield:

$$\text{fractional yield} = \frac{\text{actual yield}}{\text{theoretical yield}}$$

and the percentage yield is obtained from the fractional yield according to

$$\text{percentage yield} = 100\% \times (\text{fractional yield})$$

Example: Pure zinc can be produced in the following two-step process:



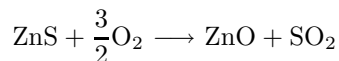
Suppose 5.32 kg of ZnS yield 3.30 kg of pure zinc. What is the percentage yield?

Solution: Convert the mass of ZnS to moles:

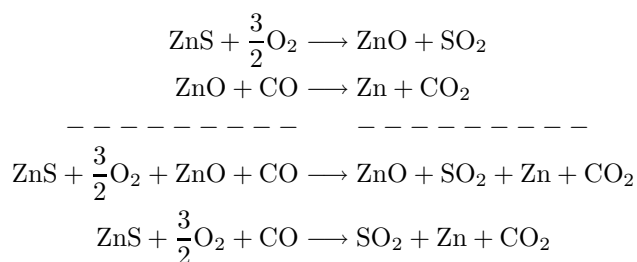
$$\text{moles ZnS} = \frac{5320 \text{ g}}{97.46 \text{ g/mol}} = 54.6 \text{ moles ZnS}$$

How do we figure out how many moles of Zn are produced in the two-step reaction? We need to obtain the *overall* reaction, which is just a “sum” of the individual steps. We can obtain the equation of the overall reaction by adding

the equations for the individual steps. However, this addition must be carried out in a particular way. Specifically, note that the species ZnO is produced in the first step and consumed in the second step. Thus, it does not appear among the final products of the process, and for this reason, it is called an *intermediate*. The equations for the individual steps must be added in such a way that all intermediates cancel out. Since adding reaction equations works like the adding of algebraic equations, this means that the coefficients of intermediates must be the same in the individual steps. In the above process the coefficients of ZnO are different in each step. But, if the first step is divided by 2, so that the reaction equation reads:



then ZnO has the same coefficient in the first step as it does in the second and the equations can now be added:



where ZnO has been “cancelled” algebraically on both sides. From the overall reaction, we see that

1 mole of ZnS yields 1 mole of Zn

or

54.6 moles of ZnS yields 54.6 moles of Zn

Thus, the mass of Zn produced is

$$\text{mass of Zn} = (54.6 \text{ mol}) \times (65.39 \text{ g/mol}) = 3570 \text{ g} = 3.57 \text{ kg}$$

This is the theoretical yield predicted by the reaction equations. The actual yield is only 3.30 kg, so that the fractional yield is

$$\text{fractional yield} = \frac{3.3 \text{ kg}}{3.57 \text{ kg}} = 0.924 = 92.4\%$$

In multi-step processes, it is important that each step have as high a percentage yield as possible. The reason for this is that the overall percentage yield will be a product of the percentage yields of each step. As an example, suppose there is a 10-step process with a 50% yield for each step:

Step 1	percentage yield = 50%
Step 2	percentage yield = 50%
...	
Step 10	percentage yield = 50%

The overall percentage yield would be the product of the individual percentages, or

$$(0.5)^{10} = 0.001 = 0.1\%$$

Even if the percentage yield of each step were 90%, the overall yield would be $(0.9)^{10} = 35\%$, which is better, but still somewhat low. If the percentage yield of each step were 95%, then the overall yield would be $(0.95)^{10} = 60\%$, which might make the process feasible.