Recall the **Law of Definite Proportions**. All samples of a compound have the same atomic composition (or) all samples have the same proportions by mass of the elements present.

Recall this question: Given a mass of magnesium in grams, 0.200g, determine the mass of magnesium oxide that would be obtained. The chemical reaction to form magnesium oxide is:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

The quantities in formulas and in chemical reactions can be counted singly or in groups, such as the mole.

C_2H_6O ethanol contains 2 atoms of carbon, 6 atoms of hydrogen, and 1 atom of oxygen. Equivalently, ethanol contains 2 mol C, 6 mol H and 1 mol O. Because of the Law of Definite Proportions, the atom or mole ratio in ethanol can be expressed as a percent by mass: 52.144%C, 13.128%H, 34.728%O. The calculations appear below.

A chemical formula expresses the integer ratio by mole, and this ratio can be converted to and from the percent composition by mass. The steps to go from integer ratio by mol to percent by mass are: (1) calculate the subtotal masses from each component present in a formula using the numbers of elements from the subscripts and molar masses of the elements, (2) add these subtotal masses together to calculate a total that represents the molecular mass or molar mass, and (3) Divide the subtotals in step 1 by the total mass from step 2 and multiply 100% to calculate percentages.

The table below contains the atoms and moles from the chemical formula, molar masses of the elements, and the subtotal masses per step 1 above. For example (see the first line in the table), the subtotal mass for the carbon atoms in C_2H_6O equals 2 mol C x 12.011 g C/mol C = 24.022g. Subscripts not written have a value of 1.

Atom	mol	molar mass(g/mol)	subtotal mass(g)	percent by mass
C	2	12.011	24.022	
H	6	1.008	6.048	
O	1	15.999	15.999	

Step 2 is to add the subtotal masses to get the molar mass for one mole of compound.

Atom	mol	molar mass (g/mol)	subtotal mass (g)	percent by mass
C	2	12.011	24.022	
H	6	1.008	6.048	
O	1	15.999	15.999	
	Molar mass C_2H_6O		46.069	

Step 3. To calculate the percent of each element by mass, divide the subtotal masses by the molar mass and multiply the result by 100%. The calculations are: 24.022/46.069*100%= 52.144% carbon, 6.048/46.069*100%= 13.128% hydrogen, and 15.999/46.069*100%= 34.728% oxygen. As a check of correctness, the percentages by mass should add to 100% to significant digits (52.144%+13.128%+34.728%= 100.000%).

Atom	mol	molar mass (g/mol)	subtotal mass (g)	percent by mass
C	2	12.011	24.022	52.144%
H	6	1.008	6.048	13.128%
O	1	15.999	15.999	34.728%
	Molar mass C_2H_6O		46.069	

The steps can be reversed to obtain the empirical formula by converting the percent by mass to the integer ratio by mole. The steps are (1) convert the percent mass to mass in grams presuming 100g of the formula is present, (2) convert the mass in grams to moles using the molar mass of the component, (3) calculate the mol ratios by dividing the moles by the smallest number of moles, and (4) multiply by a factor, if needed, to obtain integer mol ratios. The integer ratios by mole are the corresponding subscripts of the empirical formula.

It may help to create a table similar to the one shown below. Step 1 is to convert the percent by mass to grams presuming 100g of substance are available. Though it is not necessary to use 100g of substance, the calculations are easier to do mentally using 100g. For carbon, 52.144% C * 100g substance = 52.144g C. The units for this calculation are shown below. If one of the percentage values is missing, it can be calculated by knowing the the percentage values must add to 100%.

$$52.144\%\ \text{C} = \frac{52.144\text{g carbon}}{100\text{g substance}} * 100\text{g substance} = 52.144\text{g carbon}$$

Atom	% mass	grams(g) in 100g	mole	mole ratio	integer ratio by mole
C	52.144%	52.144			
H	13.128%	13.128			
O	34.728%	34.728			

Step 2 is to convert the grams to moles using the molar masses of the components. For carbon, the calculation is

$$52.144\text{g C} * \frac{1\text{ mol C}}{12.011\text{g C}} = 4.34135\text{ mol C}$$

Repeat the calculations for hydrogen and oxygen using the corresponding molar masses of hydrogen and oxygen from the periodic table. Be sure to keep enough significant digits.

Atom	% mass	grams(g) in 100g	mole MM	mole ratio	integer ratio by mole
C	52.144%	52.144	4.34135	2	
H	13.128%	13.128	13.0238	6	
O	34.728%	34.728	2.17064	1	

Step 3 is to divide the each of the moles by by the smallest number of moles to calculate mole ratios. In this example, the smallest number of moles is for oxygen (2.17064). The calculation for carbon is 4.34135/2.17064= 2. Repeat this calculation for the other lines in the table.

		in 100g	MM	Divide by smallest value	
Atom	% mass	grams(g)	mole	mole ratio	integer ratio by mole
C	52.144%	52.144	4.34135	2	
H	13.128%	13.128	13.0238	6	
O	34.728%	34.728	2.17064	1	
	100.000%				

Step 4 is the multiply each line by the same factor to convert the mol ratios to integers. In this example, the mole ratios are already integers, so the factor is 1. The integer ratio by mole is the same as the mole ratio because the factor is 1. For carbon, 2*1= 2.

		in 100g	MM	Divide by smallest value	Multiply by a factor
Atom	% mass	grams(g)	mole	mole ratio	integer ratio by mole
C	52.144%	52.144	4.34135	2	2
H	13.128%	13.128	13.0238	6	6
O	34.728%	34.728	2.17064	1	1
	100.000%				

The formula is written using the integer ratio by mole values as subscripts in the formula C_2H_6O. In this example, we got the same formula because the starting formula (C_2H_6O) was already reduced. The empirical formula is the same as the molecular formula. If the empirical formula was not the same as the molecular formula, the molar mass of the substance would be needed to convert an empirical formula to a molecular formula. As shown last time, the ratio between the molar mass of the substance and the molar mass of the empirical formula gives a factor that would be used to multiply each subscript. In this example, the factor is 1 because the empirical formula and molecular formula are the same.

When calculating the formula of a hydrate from experimental data, for example, it may be helpful to track atoms in groups. The formula of the hydrate is known to consist of X moles of copper sulfate to Y moles of water. Heating the hydrated salt gives the anhydrous (without water) salt. Data are collected by getting the masses of the salt before and after heating to the anhydrous salt. The chemical reaction and the mass data collected are shown below.

	$XCuSO_4.YH_2O(s)$	$\rightarrow$	$XCuSO_4(s)$ +	$YH_2O(g)$
Mass	1.023g		0.654	?

The law of conservation of mass can be used to get the mass of water that escaped as a gas: Mass H_2O = 1.023g - 0.654g = 0.369g. Because the experimental data provided masses, follow the steps to determine the empirical formula in the example above starting in column 3 and tracking the masses of anhydrous copper sulfate to water. The integer ratio by mole will be the X and Y needed for the formula of the hydrate. See the table below and the stepwise calculations that follow. The mass data has 3 significant digits (SD), so the answer has 3SD from applying the multiply/divide rule.

Atom Group	mass	molar mass	mole (convert mass to moles)	mole ratio (divide both moles by 0.004098)	factor (factor is 1 mole ratios are integers to 3SD)	integer ratio
$CuSO_4$	0.654	159.608	0.004098	1	1	1
H_2O	0.369	18.015	0.020483	4.9988	1	5

Step 2

$$\text{mol } CuSO_4\text{: } 0.654\text{g } CuSO_4 * \frac{1\text{mol } CuSO_4}{159.608\text{g } CuSO_4} = 0.004098\text{mol CuSO4.}$$

$$\text{mol } H_2O\text{: } 0.369\text{g } H_2O * \frac{1\text{mol } H_2O}{18.015\text{g } H_2O} = 0.020483\text{mol } H_2O.$$

Step 3

mole ratio($CuSO_4$): 0.004098/0.004098 = 1

mole ratio(H_2O): 0.020483/0.004098 = 5

Step 4

Formula is $CuSO_4.5H_2O$ copper sulfate pentahydrate

Example: A compound of boron and hydrogen (BxHy) is 81.10% boron by mass. Determine the empirical formula from these data. If the molar mass of the molecular formula is 53.324g/mol, what is molecular formula?

Solution: %H is 100% - 81.10%= 18.90%H because percentages must add to 100%.

Atom	%mass	g (Step 1. g in 100g of substance)	MM	mole (Step 2. Convert g to mole)	mole ratio (Step 3. divide by smallest mol)	factor (Step 4. factor is 2 to clear fraction (2.4995 within SD of 0.5=1/2))	integer mol ratio
B	81.10	81.10	10.811	7.5016	1	2	2
H	18.90	18.90	1.008	18.750	2.4995	2	5

The mole ratio of H gets rounded to 4SD or 2.500, which is the decimal for 2½. Multiplying both ratios by 2 clears the ½ fraction to give integers. The empirical formula is B_2H_5. The molar mass of this empirical formula is= 26.662g/mol. The ratio of the molar masses of the molecular formula to the empirical formula are (53.324/26.662) = 2.0000 = 2, so the molecular formula is twice the empirical formula or B_4H_{10}

Example: Calculate the percent by mass of magnesium and oxygen in magnesium oxide (MgO).
Solution: Follow the steps in the first example above to convert integer ratio by mole to percent by mass.

Atom	mol	molar mass	Step 1. subtotal mass	Step 3=step 1/step 2*100% percent by mass
Mg	1	24.305	24.305	60.304%
O	1	15.999	15.999	39.696%
Step 2. Molar mass MgO			40.304	

Magnesium oxide is 60.304% Mg and 39.696% O. Percent by mass can be expressed as mass ratio (factor)

$$60.304\%\ \text{Mg} = \frac{60.304\text{g Mg}}{100\text{g MgO}} \quad \text{and} \quad 39.696\%\ \text{O} = \frac{39.696\text{g O}}{100\text{g MgO}}$$

For simple chemical reactions, such as the one above where each element comes from a single reactant, mass percent offers a straightforward approach to calculate the mass of product obtained.

Example: Given a mass of magnesium in grams, 0.200g, determine the mass of magnesium oxide that would be obtained and the mass of oxygen used. The chemical reaction to form magnesium oxide is:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Solution: Using the mass ratios from the previous example gives

$$0.200\cancel{\text{g Mg}} * \frac{100\text{g MgO}}{60.304\cancel{\text{g Mg}}} = 0.332\text{g MgO}$$

Use the law of conservation of mass to calculate the mass of oxygen used (mass of reactants equals mass of products): 0.332g MgO - 0.200g Mg= 0.132g O. This method gives the same result as the example from the previous set of notes. The mass of oxygen can also be calculated using the two mass percents calculated previously as shown below:

$$0.200\cancel{\text{g Mg}} * \frac{100\cancel{\text{g MgO}}}{60.304\cancel{\text{g Mg}}} * \frac{39.696\text{g O}}{100\cancel{\text{g MgO}}} = 0.132\text{g O}$$

The method of using percent by mass to calculate amounts of products and reactants works well for simple reactions, but this approach gets more mathematically challenging with more complicated reactions. As a result, the stoichiometry model is often used for calculations involving reactants and products of chemical reactions. The stoichiometry model will be shown next time.