

RELATIVE ATOMIC MASSES AND EMPIRICAL FORMULAE

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Abstract

Relative Atomic Masses and Empirical Formulae

1 Foundation

We begin by assuming the central postulates of the **Atomic-Molecular Theory**. These are: the elements are comprised of identical atoms; all atoms of a single element have the same characteristic mass; the number and masses of these atoms do not change during a chemical transformation; compounds consist of identical molecules formed of atoms combined in simple whole number ratios. We also assume a knowledge of the observed natural laws on which this theory is based: the **Law of Conservation of Mass**, the **Law of Definite Proportions**, and the **Law of Multiple Proportions**.

2 Goals

We have concluded that atoms combine in simple ratios to form molecules. However, we don't know what those ratios are. In other words, we have not yet determined any molecular formulae. In Table 2 of Concept Development Study 1¹, we found that the mass ratios for nitrogen oxide compounds were consistent with many different molecular formulae. A glance back at the nitrogen oxide data shows that the oxide B could be NO , NO_2 , N_2O , or any other simple ratio.

Each of these formulae correspond to different possible relative atomic weights for nitrogen and oxygen. Since oxide B has oxygen to nitrogen ratio 1.14 : 1, then the relative masses of oxygen to nitrogen could be 1.14:1 or 2.28:1 or 0.57:1 or many other simple possibilities. If we knew the relative masses of oxygen and nitrogen atoms, we could determine the molecular formula of oxide B. On the other hand, if we knew the molecular formula of oxide B, we could determine the relative masses of oxygen and nitrogen atoms. If we solve one problem, we solve both. Our problem then is that we need a simple way to "count" atoms, at least in relative numbers.

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¹ <http://cnx.rice.edu/content/m12432/latest/#table2>

3 Observation 1: Volume Relationships in Chemical Reactions

Although mass is conserved, most chemical and physical properties are not conserved during a reaction. Volume is one of those properties which is not conserved, particularly when the reaction involves gases as reactants or products. For example, hydrogen and oxygen react explosively to form water vapor. If we take 1 liter of oxygen gas and 2 liters of hydrogen gas, by careful analysis we could find that the reaction of these two volumes is complete, with no left over hydrogen and oxygen, and that 2 liters of water vapor are formed. Note that the total volume is not conserved: 3 liters of oxygen and hydrogen become 2 liters of water vapor. (All of the volumes are measured at the same temperature and pressure.)

More notable is the fact that the ratios of the volumes involved are simple whole number ratios: 1 liter of oxygen : 2 liters of hydrogen : 2 liters of water. This result proves to be general for reactions involving gases. For example, 1 liter of nitrogen gas reacts with 3 liters of hydrogen gas to form 2 liters of ammonia gas. 1 liter of hydrogen gas combines with 1 liter of chlorine gas to form 2 liters of hydrogen chloride gas. These observations can be generalized into the **Law of Combining Volumes**.

Law 1: Law of Combining Volumes

When gases combine during a chemical reaction at a fixed pressure and temperature, the ratios of their volumes are simple whole number ratios.

These simple integer ratios are striking, particularly when viewed in the light of our conclusions from the Law of Multiple Proportions. Atoms combine in simple whole number ratios, and evidently, volumes of gases also combine in simple whole number ratios. Why would this be? One simple explanation of this similarity would be that the volume ratio and the ratio of atoms and molecules in the reaction are the same. In the case of the hydrogen and oxygen, this would say that the ratio of volumes (1 liter of oxygen : 2 liters of hydrogen : 2 liters of water) is the same as the ratio of atoms and molecules (1 atom of oxygen: 2 atoms of hydrogen: 2 molecules of water). For this to be true, equal volumes of gas would have to contain equal numbers of gas particles (atoms or molecules), independent of the type of gas. If true, this means that the volume of a gas must be a direct measure of the number of particles (atoms or molecules) in the gas. This would allow us to "count" the number of gas particles and determine molecular formulae.

There seem to be big problems with this conclusion, however. Look back at the data for forming hydrogen chloride: 1 liter of hydrogen plus 1 liter of chlorine yields 2 liters of hydrogen chloride. If our thinking is true, then this is equivalent to saying that 1 hydrogen atom plus 1 chlorine atom makes 2 hydrogen chloride molecules. But how could that be possible? How could we make 2 identical molecules from a single chlorine atom and a single hydrogen atom? This would require us to divide each hydrogen and chlorine atom, violating the postulates of the atomic-molecular theory.

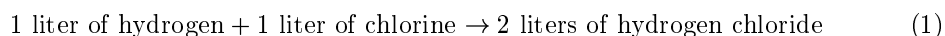
Another problem appears when we weigh the gases: 1 liter of oxygen gas weighs more than 1 liter of water vapor. If we assume that these volumes contain equal numbers of particles, then we must conclude that 1 oxygen particle weighs more than 1 water particle. But how could that be possible? It would seem that a water molecule, which contains at least one oxygen atom, should weigh more than a single oxygen particle.

These are serious objections to the idea that equal volumes of gas contain equal numbers of particles. Our postulate appears to have contradicted common sense and experimental observation. However, the simple ratios of the Law of Combining Volumes are also equally compelling. Why should volumes react in simple whole number ratios if they do not represent equal numbers of particles? Consider the opposite viewpoint: if equal volumes of gas do not contain equal numbers of particles, then equal numbers of particles must be contained in unequal volumes not related by integers. Now when we combine particles in simple whole

number ratios to form molecules, the volumes of gases required would produce decidedly non-whole number ratios. The Law of Combining Volumes should not be contradicted lightly.

There is only one logical way out. We will accept our deduction from the Law of Combining Volumes that *equal volumes of gas contain equal numbers of particles*, a conclusion known as **Avogadro's Hypothesis**. How do we account for the fact that 1 liter of hydrogen plus 1 liter of chlorine yields 2 liters of hydrogen chloride? There is only one way for a single hydrogen particle to produce 2 identical hydrogen chloride molecules: each hydrogen particle must contain more than one atom. In fact, each hydrogen particle (or molecule) must contain an even number of hydrogen atoms. Similarly, a chlorine molecule must contain an even number of chlorine atoms.

More explicitly, we observe that



Assuming that each liter volume contains an equal number of particles, then we can interpret this observation as



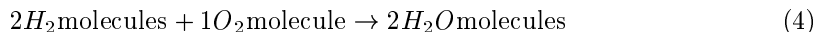
(Alternatively, there could be any fixed even number of atoms in each hydrogen molecule and in each chlorine molecule. We will assume the simplest possibility and see if that produces any contradictions.)

This is a wonderful result, for it correctly accounts for the Law of Combining Volumes and eliminates our concerns about creating new atoms. Most importantly, we now know the molecular formula of hydrogen chloride. We have, in effect, found a way of "counting" the atoms in the reaction by measuring the volume of gases which react.

This method works to tell us the molecular formula of many compounds. For example,



This requires that oxygen particles contain an even number of oxygen atoms. Now we can interpret this equation as saying that



Now that we know the molecular formula of water, we can draw a definite conclusion about the relative masses of the hydrogen and oxygen atoms. Recall² that the mass ratio in water is 8:1 oxygen to hydrogen. Since there are two hydrogen atoms for every oxygen atom in water, then the mass ratio requires that a single oxygen atom weigh 16 times the mass of a hydrogen atom.

To determine a mass scale for atoms, we simply need to choose a standard. For example, for our purposes here, we will say that a hydrogen atom has a mass of 1 on the atomic mass scale. Then an oxygen atom has a mass of 16 on this scale.

Our conclusions account for the apparent problems with the masses of reacting gases, specifically, that oxygen gas weighs more than water vapor. This seemed to be nonsensical: given that water contains oxygen, it would seem that water should weigh more than oxygen. However, this is now simply understood: a water molecule, containing only a single oxygen atom, has a mass of 18, whereas an oxygen molecule, containing two oxygen atoms, has a mass of 32.

²<http://cnx.rice.edu/content/m12432/latest/#table1>

4 Determination of Atomic Weights for Gaseous Elements

Now that we can count atoms and molecules to determine molecular formulae, we need to determine relative atomic weights for all atoms. We can then use these to determine molecular formulae for any compound from the mass ratios of the elements in the compound.

We begin by examining data on reactions involving the Law of Combining Volumes. Going back to the nitrogen oxide data given here³, we recall that there are three compounds formed from nitrogen and oxygen. Now we measure the volumes which combine in forming each. We find that 2 liters of oxide B can be decomposed into 1 liter of nitrogen and 1 liter of oxygen. From the reasoning above, then a nitrogen particle must contain an even number of nitrogen atoms. We assume for now that nitrogen is N_2 . We have already concluded that oxygen is O_2 . Therefore, the molecular formula for oxide B is NO , and we call it nitric oxide. Since we have already determined that the oxygen to nitrogen mass ratio is 1.14 : 1, then, if we assign oxygen a mass of 16, as above, nitrogen has a mass of 14. (That is $\frac{16}{1.14} = 14$.) 2 liters of oxide A is formed from 2 liters of oxygen and 1 liter of nitrogen. Therefore, oxide A is NO_2 , which we call nitrogen dioxide. Note that we predict an oxygen to nitrogen mass ratio of $\frac{32}{14} = 2.28 : 1$, in agreement with the data. Oxide C is N_2O , called nitrous oxide, and predicted to have a mass ratio of $\frac{16}{28} = 0.57 : 1$, again in agreement with the data. We have now resolved the ambiguity in the molecular formulae.

What if nitrogen were actually N_4 ? Then the first oxide would be N_2O , the second would be N_2O_2 , and the third would be N_4O . Furthermore, the mass of a nitrogen atom would be 7. Why don't we assume this? Simply because in doing so, we will always find that the minimum relative mass of nitrogen in any molecule is 14. Although this might be two nitrogen atoms, there is no reason to believe that it is. Therefore, a single nitrogen atom weighs 14, and nitrogen gas particles are N_2 .

5 Determination of Atomic Weights for Non-Gaseous Elements

We can proceed with this type of measurement, deduction, and prediction for any compound which is a gas and which is made up of elements which are gases. But this will not help us with the atomic masses of non-gaseous elements, nor will it permit us to determine the molecular formulae for compounds which contain these elements.

Consider carbon, an important example. There are two oxides of carbon. Oxide A has oxygen to carbon mass ratio 1.33 : 1 and oxide B has mass ratio 2.66 : 1. Measurement of reacting volumes shows that we find that 1 liter of oxide A is produced from 0.5 liters of oxygen. Hence, each molecule of oxide A contains only half as many oxygen atoms as does an oxygen molecule. Oxide A thus contains one oxygen atom. But how many carbon atoms does it contain? We can't determine this yet because the elemental carbon is solid, not gas. This means that we also cannot determine what the mass of a carbon atom is.

But we can try a different approach: we weigh 1 liter of oxide A and 1 liter of oxygen gas. The result we find is that oxide A weighs 0.875 times per liter as much as oxygen gas. Since we have assumed that a fixed volume of gas contains a fixed number of particles, then 1 liter of oxide A contains just as many particles as 1 liter of oxygen gas. Therefore, each *particle* of oxide A weighs 0.875 times as much as a particle of oxygen gas (that is, an O_2 molecule). Since an O_2 molecule weighs 32 on our atomic mass scale, then a particle of oxide A weighs $0.875 \times 32 = 28$. Now we know the molecular weight of oxide A.

Furthermore, we have already determined from the combining volumes that oxide A contains a single oxygen atom, of mass 16. Therefore, the mass of carbon in oxide A is 12. However, at this point, we do not know whether this is one carbon atom of mass 12, two atoms of mass 6, eight atoms of mass 1.5, or one of many other possibilities.

³<http://cnx.rice.edu/content/m12432/latest/#table2>

To make further progress, we make additional measurements on other carbon containing gas compounds. 1 liter of oxide B of carbon is formed from 1 liter of oxygen. Therefore, each oxide B molecule contains two oxygen atoms. 1 liter of oxide B weighs 1.375 times as much as 1 liter of oxygen. Therefore, one oxide B molecule has mass $1.375 \times 32 = 44$. Since there are two oxygen atoms in a molecule of oxide B, the mass of oxygen in oxide B is 32. Therefore, the mass of carbon in oxide B is 12, the same as in oxide A.

We can repeat this process for many such gaseous compounds containing carbon atoms. In each case, we find that the mass of carbon in each molecule is either 12 or a multiple of 12. We never find, for examples, 6 or 18, which would be possible if each carbon atom had mass 6. The simplest conclusion is that a carbon atom has mass 12. Once we know the atomic mass of carbon, we can conclude that the molecular formula of oxide A is CO , and that of oxide B is CO_2 .

Therefore, the atomic masses of non-gaseous elements can be determined by mass and volume measurements on gaseous compounds containing these elements. This procedure is fairly general, and most atomic masses can be determined in this way.

6 Moles, Molecular Formulae and Stoichiometric Calculations

We began with a circular dilemma: we could determine molecular formulae provided that we knew atomic masses, but that we could only determine atomic masses from a knowledge of molecular formulae. Since we now have a method for determining all atomic masses, we have resolved this dilemma and we can determine the molecular formula for any compound for which we have percent composition by mass.

As a simple example, we consider a compound which is found to be 40.0% carbon, 53.3% oxygen, and 6.7% hydrogen by mass. Recall from the Law of Definite Proportions that these mass ratios are independent of the sample, so we can take any convenient sample to do our analysis. Assuming that we have 100.0g of the compound, we must have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. If we could count or otherwise determine the number of atoms of each element represented by these masses, we would have the molecular formula. However, this would not only be extremely difficult to do but also unnecessary.

From our determination of atomic masses, we can note that 1 atom of carbon has a mass which is 12.0 times the mass of a hydrogen atom. Therefore, the mass of N atoms of carbon is also 12.0 times the mass of N atoms of hydrogen atoms, no matter what N is. If we consider this carefully, we discover that 12.0g of carbon contains exactly the same number of atoms as does 1.0g of hydrogen. Similarly, we note that 1 atom of oxygen has a mass which is $\frac{16.0}{12.0}$ times the mass of a carbon atom. Therefore, the mass of N atoms of oxygen is $\frac{16.0}{12.0}$ times the mass of N atoms of carbon. Again, we can conclude that 16.0g of oxygen contains exactly the same number of atoms as 12.0g of carbon, which in turn is the same number of atoms as 1.0g of hydrogen. Without knowing (or necessarily even caring) what the number is, we can say that it is the same number for all three elements.

For convenience, then, we *define* the number of atoms in 12.0g of carbon to be 1 **mole** of atoms. Note that 1 mole is a specific number of particles, just like 1 dozen is a specific number, independent of what objects we are counting. The advantage to defining the mole in this way is that it is easy to determine the number of moles of a substance we have, and knowing the number of moles is equivalent to counting the number of atoms (or molecules) in a sample. For example, 24.0g of carbon contains 2.0 moles of atoms, 30.0g of carbon contains 2.5 moles of atoms, and in general, x grams of carbon contains $\frac{x}{12.0}$ moles of atoms. Also, we recall that 16.0g of oxygen contains exactly as many atoms as does 12.0g of carbon, and therefore 16.0g of oxygen contains exactly 1.0 mole of oxygen atoms. Thus, 32.0g of oxygen contains 2.0 moles of oxygen atoms, 40.0g of oxygen contains 2.5 moles, and x grams of oxygen contains $\frac{x}{16.0}$ moles of oxygen atoms. Even more generally, then, if we have m

grams of an element whose atomic mass is M , the number of moles of atoms, n , is

$$n = \frac{m}{M} \quad (5)$$

Now we can determine the relative numbers of atoms of carbon, oxygen, and hydrogen in our unknown compound above. In a 100.0g sample, we have 40.0g of carbon, 53.3g of oxygen, and 6.7g of hydrogen. The number of moles of atoms in each element is thus

$$\begin{aligned} n_C &= \frac{40.0g}{12.0\frac{g}{\text{mol}}} \\ &= 3.33\text{moles} \end{aligned} \quad (6)$$

$$\begin{aligned} n_O &= \frac{53.3g}{16.0\frac{g}{\text{mol}}} \\ &= 3.33\text{moles} \end{aligned} \quad (7)$$

$$\begin{aligned} n_H &= \frac{6.7g}{1.0\frac{g}{\text{mol}}} \\ &= 6.67\text{moles} \end{aligned} \quad (8)$$

We note that the numbers of moles of atoms of the elements are in the simple ratio $n_C : n_O : n_H = 1 : 1 : 2$. Since the number of particles in 1 mole is the same for all elements, then it must also be true that the number of atoms of the elements are in the simple ratio $1 : 1 : 2$. Therefore, the molecular formula of the compound must be COH_2 .

Or is it? On further reflection, we must realize that the simple ratio $1 : 1 : 2$ need not represent the exact numbers of atoms of each type in a molecule of the compound, since it is indeed only a ratio. Thus the molecular formula could just as easily be $C_2O_2H_4$ or $C_3O_3H_6$. Since the formula COH_2 is based on empirical mass ratio data, we refer to this as the **empirical formula** of the compound. To determine the **molecular formula**, we need to determine the relative mass of a molecule of the compound, i.e. the molecular mass. One way to do so is based on the Law of Combining Volumes, Avogadro's Hypothesis, and the **Ideal Gas Law**. To illustrate, however, if we were to find that the relative mass of one molecule of the compound is 60.0, we could conclude that the molecular formula is $C_2O_2H_4$.

7 Review and Discussion Questions

Exercise 1:

State the Law of Combining Volumes and provide an example of your own construction which demonstrates this law.

Exercise 2:

Explain how the Law of Combining Volumes, combined with the Atomic-Molecular Theory, leads directly to Avogadro's Hypothesis that equal volumes of gas at equal temperatures and pressure contain equal numbers of particles.

Exercise 3:

Use Avogadro's Hypothesis to demonstrate that oxygen gas molecules cannot be monatomic.

Exercise 4:

The density of water vapor at room temperature and atmospheric pressure is $0.737 \frac{g}{L}$. Compound A is 80.0% carbon by mass, and 20.0% hydrogen. Compound B is 83.3% carbon by mass and 16.7% hydrogen. The density of gaseous Compound A is $1.227 \frac{g}{L}$, and the density of Compound B is $2.948 \frac{g}{L}$. Show how these data can be used to determine the molar masses of Compounds A and B, assuming that water has molecular mass 18.

Exercise 5:

From the results above (Exercise 4), determine the mass of carbon in a molecule of Compound A and in a molecule of Compound B. Explain how these results indicate that a carbon atom has atomic mass 12.

Exercise 6:

Explain the utility of calculating the number of moles in a sample of a substance.

Exercise 7:

Explain how we can conclude that 28g of nitrogen gas (N_2) contains exactly as many molecules as 32g of oxygen gas (O_2), even though we cannot possibly count this number.