

Section 3: Observation 1: Volume Relationships in Chemical Reactions (In Progress)

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 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

1 liter of hydrogen + 1 liter of chlorine → 2 liters of hydrogen chloride

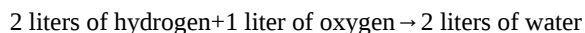
Assuming that each liter volume contains an equal number of particles, then we can interpret this observation as



(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. Recall from the Table 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.

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