Early Theories of the Structure of Atom

One of the deeply interesting stories in Science is about how the existence of atoms was first established, and further how its structure was revealed to us, step by step. One of the notable features of this story is how many of the discoveries did not, and indeed could not, involve the direct observation of atoms. In fact, the case for the existence of atoms rested on novel insights into long-known facts about chemical reactions. In this sense, the atom has no physical existence, but is rather a theoretical entity. At the very least, it fulfils the role of a conceptual or theoretical model of the nature of matter. But viewed from another angle, the atom is an actual constituent of matter on the basis of which we can do various calculations and make predictions as well.
So, the atom has played two major roles in Science. One is as a concept which explains a theory about the nature of matter and the other is as an actual constituent of matter. This is not only helpful in understanding chemical reactions, but is also a tool that helps us to control these reactions.

A question that is often asked (at least of me) is - why is it that we believe in the existence of atoms even though we cannot see them. Why do we accept that matter is made up of atoms? Not only this, we are also willing to make statements about the structure of atoms with great confidence. On what basis do we make all these claims?

I shall try to answer these questions in a few articles. In them I will articulate our increasing understanding of the nature of matter and the structure of atoms. I may not be able to take you all the way, some later concepts might have to be taken up by someone else. But let us begin this tale.

The modern theory of atoms was put forward/given by John Dalton. Of course, these ideas are not new. Since ancient times philosophers have maintained that there are tiny constituents of matter, but there were heated debates about this too. However, philosophical thoughts are all very fine, but it is an altogether different issue to think about and give coherent explanations for observations and experimental results. When experiments were carried out and observations made with great accuracy, then we were able to arrive at a deeper understanding of matter. For example, people observed that objects expand on heating. In particular, this expansion is remarkable in gases. This gave rise to the question of why matter, especially the gases, expands when it gets hotter.

Similarly, it was observed that gases mix very easily with each other. Some other substances also mix with each other, but not to this extent, or so indiscriminately. Salt will dissolve in water, but not in kerosene. That is to say, it seems like solids and liquids have their likes and dislikes when it comes to mixing with other substances. There is a limit to how much of a liquid can be taken up by a solid too. But gases are gregarious, they mix with all gases and in any ratios. Why does this happen? Are there empty spaces within a gas? Are gases made of particles with spaces between them?

It was also observed that gases mix and form homogenous solutions regardless of their densities. This means that all the component gases mix independent of each other.

When experiments were done with reactions, especially when they were specifically quantitative experiments, then a lot of things like this became clear. One of them was that even if new products were formed during a reaction, the amount (quantity) taken at the beginning remains unchanged – the sum of the amounts of different products formed was found to be the same as the sum of the reactants. When this was found to be true of all changes, for all reactions, it was stated in the form of a law: The Law of Conservation of Matter. The law states that the amount of matter is conserved during a reaction, matter is neither created nor destroyed in the course of a chemical reaction.

Another thing that happened was that we were able to identify different kinds of matter. We learnt to differentiate between mixtures and pure substances. More refined techniques of separation were continuously being developed, and this resulted in many substances that had been considered pure being found to be mixtures. Slowly, we began to get an inkling of how to recognise whether a given substance is pure or not.

Then, pure substances themselves turned out to be of two types. Some pure substances were such that they could be separated into two or more pure substances by chemical processes. Other pure substances were such that, whatever you tried, you could not break them into simpler substances. The latter substances were termed elements, while former were called compounds.

All these were not the result of arm-chair theorising by any one scientist, nor was it any one person's fanciful dream. All this was the result of a long series of experiments done by various people in different places.

Now, elements were pure substances that could not be broken down into anything simpler. But compounds could be further analysed. Many compounds were analysed to find out what elements each one was made of. One more law was derived from these studies. It was seen that any compound was always made up of the very same elements. For instance, if you were to take water from any source, you would see that it was made up of the same two elements – oxygen and hydrogen. This is from the qualitative analysis of water. When quantitative techniques became available, we got to know one more interesting fact. This was that any compound is always made of a given set of elements and these elements are always combined in the same proportion. This law was seen to apply in every single case and was given the name – The Law of Constant Proportions.

A third law was also put forward. This was a rather convoluted law but it explained the nature of reactions between different elements. This law came about when chemists had studied a great many reactions and is called The Law of Reciprocal Proportions. This law is applicable when a set of three elements react with each other in pairs to form three different compounds. That is, take three elements A, B and C that can react with each other to form compounds. Let us say that A and B react, B and C react and so do A and C to form three different compounds AB, BC and AC respectively. Now, if we look at the proportions in which they react with each other, that is, the ratio between A and B, and the ratio between B and C; then the ratio in which A will react with C can be arrived at. For example, if A and B were to react in the ration 2:1, and B and C were to react in the ratio 1:3, then A and C would react in the ratio 2:3.

When Dalton presented his atomic theory, then all we knew of the nature of interactions between substances were these three laws – The Law of Conservation of Matter, The Law of Constant Proportions and the Law of Reciprocal Proportions. Dalton had not seen what happens inside atoms when substances react with each other. But he tried to figure out what must be happening as each time these three laws were found to hold true. And from this he arrived at the atomic theory.

He stated upfront that matter is made up of atoms. This is the smallest possible particle of matter. What was the basis for this statement? It might to be better to state the answer in Dalton's own words instead of trying to guess what was going on in his head. Read an excerpt from Dalton's book 'A new system of chemical philosophy' in which he presents the logic behind his theory of the nature of matter.

"*There are three distinctions states, namely, elastic fluids, liquids, and solids. A very familiar instance is exhibited to us in water, of a body, which, in certain circumstances, is capable of assuming all the three states...These observations have tacitly led to the conclusion which seems universally adopted, that all bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter...*

It is not my design to call in question this conclusion, which appears completely satisfactory, but to show that we have hitherto made no use of it, and that the consequence of the neglect has been a very obscure view of chemical agency..."

It is not as if Dalton was the first person to talk of matter being made up of atoms. Since ancient times, the atom has played an important role in philosophical discussions. With the onset of modern science, atoms (as the ultimate particles of matter) had been used to explicate phenomena like the pressure of gases, their mixing, etc. What Dalton did, was to put together these different strands in an organised manner to give a coherent picture of the particulate nature of matter.

Various issues arise out of this one concept (about matter being made up of atoms). Since the amount of reactants and products are the same during the course of a chemical reaction, it is obvious that the number of atoms present in the beginning survive till the end of the reaction. That is, atoms are not destroyed (or created) during the course of a reaction.

The second point that Dalton came up with is that atoms move as a whole during a reaction, they do not break. On what did he base this assertion? If atoms were to break during a reaction, then The Law of Constant Proportions would soon be invalidated. Because if atoms were to break, they would be able to form compounds in any ratiowhatsover. If atoms were to break, then it would also be unlikely that every time a compound was prepared, the same proportion of each element would end up in it. So, it was simpler to suppose that when an element is part of a compound, atoms of this element go into the formation of this compound as intact atoms.

Dalton's third postulate was that all atoms of an element are exactly alike, and that they are different from the atoms of any other element. Where do you think he got this idea from? Well, he could not have gotten the atoms to stand in lines and inspected them! He was again trying to bring about an agreement about the nature of atoms and the three laws (of chemical combination). Let us see what he has to say in defence of this idea:

"*The opinions I more particularly allude to, are those of Berthollet on the Laws of Chemical Affinity; such as that chemical agency is proportional to the mass, and that in all chemical unions there exist insensible gradations in the proportions of the constituent principles. The inconsistence of these opinions, both with reason and observation, cannot, I think, fail to strike everyone who takes a proper view of the phenomena.*

Whether the ultimate particles of a body, such as water, are all alike, that is, of the same figure, weight, etc., is a question of some importance. From what is known, we have no reason to apprehend a diversity in these particulars: if it does exist in water, it must equally exist in the elements constituting water, namely, hydrogen and oxygen. Now, it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others — if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observations may be made on other substances; therefore, we may conclude that the ultimate particles of all homogeneous bodies are 'perfectly alike in weighty figure, etc.' In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen."

This is the most important point made by Dalton. He said that all the atoms of an element have the same weight. As a matter of fact, it is this point that differentiates Dalton's atomic theory from all the other preceding theories of the particulate nature of matter – that he gave the atom an attribute that could be measured. He called this attribute the atomic weight.

The next step was a logical consequence of trying to apply this understanding of the nature of matter. Dalton calculated the atomic weights of various elements. Once again, he made use of the available data and some superb reasoning to carry out this work and arrive at his values.

The data available to him at that time were records of how much of one element reacts with a given amount of another element. By the end of the 18^{th} century and the beginning of the 19^{th}, we knew what elements were present in a particular compound and what ratio they were combined in. Like, 9 g of water had 8 g of oxygen and 1 g of hydrogen in it. From this, how could we possibly find out the weight of one atom of hydrogen and oxygen atom's weight?

So, Dalton was satisfied with trying to arrive at the relative atomic weights. But how did he manage to do this? He assumed the relative atomic weight of hydrogen to be 1. This was based on the findings that hydrogen was (and is) the element with the lowest density, and that the analysis of any compound with hydrogen in it, always gives the smallest amount of hydrogen as compared to the other elements in it. How can we proceed any further? After all, one has no way of knowing (for example), how many atoms of hydrogen are there in 1 g of hydrogen and how many atoms of oxygen in 8 g. So, how are they (the weights of hydrogen and oxygen) to be compared? An inspired solution to this problem was to assume that when two elements react to form only one compound, this compound is formed by the addition of one atom of each element. That is, if only one compound is known to be formed by the reaction of two elements, we will assume that the number of atoms of each of these elements is the same in this particular compound. If we accept this assumption, then it means that the number of atoms of hydrogen in 1 g is equal to the number of atoms of oxygen in 8 g. Now, one can easily calculate how much heavier than an atom of hydrogen an atom of oxygen would be.

In trying to reconcile experimental facts with the idea of atoms, we often come across such assumptions. Sometimes, these assumptions have turned out to be correct, while they have been proved wrong in some other cases. This particular assumption made by Dalton (that if only one compound is known to be formed from two elements, then one atom of each element goes to form that compound) was later proved to be erroneous. But we have to admit that by making this simple assumption, Dalton found a way to assign weights to the atoms of different elements. Later on, we were able to amend this assumption and move further still in our search for knowledge. However, here I would like to move beyond this problem of assigning atomic weights and look at another assumption.

According to Dalton's atomic theory, an atom is the ultimate particle of matter and cannot be further divided. This postulate was, as expounded above, derived from the

Laws of Chemical Combination. But if the atom is the ultimate constituent of matter, then it should be able to explain different properties of matter. Whether we talk of electricity, heat or light, the atom should help us to explain all these phenomena. Atoms were of some help, but in trying to understand these phenomena, we had to relinquish the 'uncuttability' of atoms. The next time, we shall break atoms. We will see whether atoms are the ultimate particles or whether they are in turn made up of still more elementary particles.