Electricity, Gases, and the Atom Breaks

Dalton's atomic theory is a major milestone in the history of chemistry and we were able to understand chemical reactions on the basis of this theory. We became adept at predicting how much of any substance would be used up in a given chemical reaction. We arrived at the formulae of compounds on this basis and the periodic classification of elements also became possible. That is, we were able to understand that various properties of elements were a consequence of their atomic nature and we were also able to predict what properties we could expect to see in different substances. New elements (that is, as yet undiscovered elements) were predicted on the basis of the Periodic Law and these predictions were proved to be right. So, the validity of the atomic theory seemed to be getting strengthened.

But there were also parallel developments which seemed to question the atomic theory. Some of the postulates seemed to require rethinking. The atomic theory seemed to need a makeover on the basis of the latest findings. Every time the procedure was similar - new observations called for the reformulation of some assumptions and the model was seen to have limitations in some fields.

For example, let us take the question of why elements react with each other. Some elements react under some specific conditions, while others don't. Or, what decides in what ratio the given elements are going to react with each other? In other words, what decides the valency of each element? Why is the valency of hydrogen 1 while that of carbon is 4? Even long after Dalton, the concept of valency was not there, just the combining weight ratios were known.

The understanding of all this is based on many strands. One of these, a very important strand, was based on the study of electricity. Human beings have been aware of electricity since time immemorial because of lightning, but questions about the nature of electricity came up much later.

When electricity and light were studied in detail, the very atom was shaken and shocked. Let us see how.

It came to be known that some substances were conductors of electricity while some did not conduct electricity. We learnt to produce electricity. And Volta made his cell.

The atom was broken because of the study of electricity. If we forget about lightning for the moment, even then electricity was known since ancient times since people had observed that on being rubbed with cloth or some wool, a rod of amber attracted many things towards itself. Amber is called electricus in Greek, hence the term electricity. It was believed that electricity was a fluid which had the property of attracting things towards itself.

Some experiments done towards the beginning of the 18th century revealed that this attractive force produced by friction is of two kinds. This led some people to believe that there were thus two fluids which caused electricity. Roughly a decade later, Benjamin Franklin suggested that there was in fact only one kind of electricity, and that the different effects seen were because its pressure or amount varied. But Benjamin Franklin was not able to explain whether a certain attraction was due to an excess of electricity or due to its deficiency.

The most interesting experiment in this connection was that dealing with electrolysis. Volta had made his electric cell sometime around 1800. Conductors and non-conductors among solid materials had long been recognised. But the experiments related to the conduction of electricity in liquids (or solutions) were carried out only in the 19th century.

Water is usually a non-conductor of electricity, but if something is dissolved in it, then it sometimes conducts electricity. Experiments like this led to a better understanding of the nature of conduction in liquids. The most exacting experiments were done by Michael Faraday. His experiments and their conclusions have important implications for our understanding of the atomic structure of elements.

So, Volta had made his voltaic cell in 1800. With this, we got our hands on a constant source of electricity. Using the voltaic cell, Humphry Davy was the first person to pass electricity through water and he saw that on doing this, water was broken down into its constituent elements – hydrogen and oxygen. Bubbles of hydrogen gas were collected at the negative electrode (cathode) while those of oxygen were formed at the positive electrode (anode). This process is called electrolysis. Humphry Davy had subjected many substances to electrolysis. When he passed electricity through hydrochloric acid (which was known as muriatic acid at that time), hydrogen was liberated at the cathode and a gas that was unknown at that time, was collected at the anode. This new gas was named chlorine. He used this same process of electrolysis and discovered the elements sodium and potassium.

However, detailed quantitative electrolytic experiments were conducted by Michael Faraday in 1833. For instance, he measured the amount of hydrogen and that of oxygen formed by the electrolysis of water. Then he tried to find the relation between these two amounts and the amount of electricity passed through the water. He found that on passing one unit of electricity through water, two units of hydrogen and one unit of oxygen by volume were produced. If the amount of electricity is doubled, the amounts of these two gases produced are also doubled.

Similarly, he also found that the amount of copper produced at the cathode by the electrolysis of copper sulphate was directly proportional to the amount of electricity passed through the solution.

In the case of the hydrolysis of water, it was also clear that the amount of hydrogen (by volume) produced was always double the amount of oxygen (by volume) formed.

If we look at their weights, if one unit of electricity were to produce 1.008 g of hydrogen, then the amount of oxygen produced would equal 8 g. These weights are related to the atomic weights of these elements. Whereas the amount of hydrogen produced is equivalent to its atomic weight that of oxygen is only equivalent to half its atomic weight.

When Faraday conducted the electrolysis of molten sodium chloride, he found that sodium was collected at the cathode while chlorine gas was formed at the anode. When one coulomb of charge was passed through molten sodium chloride, 2.38 X 10^{-4} g of sodium and 3.68 X 10^{-4} g of chlorine were obtained. This means that we would need to pass 96,500 coulomb of electric charge to get one gram atomic weight of sodium (23 g). Similarly, to get one gram atomic weight of chlorine (35.5 g), we would need to pass 96,500 coulomb of electric charge through molten sodium chloride.

If we were to pass 96,500 coulomb of electricity through water, we would obtain 1.0008 g of hydrogen (one gram atomic weight of hydrogen) and 8 g oxygen (half a gram atomic weight of oxygen). Gram atomic weight refers to the atomic weight of an element being expressed in grams.

The result of all these careful measurements by Faraday were two laws. The first law was that the amount of any substance produced during the process of electrolysis was directly proportional to the amount of electricity passed through the initial substances. And the second law was that this amount of the substance (or element) produced was also directly proportional to its gram atomic weight divided by its valency.

How were these laws to be interpreted? According to the atomic theory, matter was made up of atoms. So, the fact that the amount of an element produced during electrolysis was proportional to its atomic weight reinforced the theory about the existence of atoms.

But what is the connection between the amount of electricity and the amounts of substances produced? Why do we see this proportionality? Even more importantly, a definite amount of electricity produces each element in an amount which is proportional to its atomic weight divided by its valency. From this, we can arrive at the conclusion that electricity also exists in the form of some ultimate particles which act as atoms of electricity. Faraday's laws were used to calculate this minimum amount of electricity and it was found to be equal to the charge of a univalent ion.

Experiments involving electrolysis were first conducted by Humphry Davy and he obtained sodium and chlorine by the electrolysis of molten sodium chloride (common salt). Passing electricity through liquids resulted in their breakdown and the constituents would be liberated at the two electrodes.

Electrolysis takes place because the passage of electric charge causes the molecules to break up. Molecules break into two and each is called an ion – one positive and one negative. Because these are formed in proportion to their atomic weights, it looks like they carry a definite charge. That is, the charge present on an ion is like a unit of charge.

We have seen that the electrolysis of water produces one gram atomic weight of hydrogen, but only half gram atomic weight of oxygen. The valency of sodium, chlorine and hydrogen is one while the valency of oxygen is 2. That means that the passage of 96,500 coulomb of electricity causes the liberation of one gram atomic weight of univalent elements while only half a gram atomic weight of divalent elements is produced.

Faraday had pondered the consequences of his findings, but he was not convinced of the existence of atoms. So, he did not give much importance to this implication of his data.

Arrhenius had proposed his theory of ions by this time. If we were to accept that charges are carried by ions during electrolysis, then it is obvious that there must be a minimum unit of charge which could be associated with an ion. So, it follows logically that like atoms of matter, electricity also must have a fixed minimum unit. Richard Lemming suggested in 1838 that the explanation of the chemical properties of atoms requires the existence of an ultimate unit of electricity too. Lemming even suggested with a leap of imagination that the atom must be having a central portion (core) around which some sub-atomic particles were present; and that these sub-atomic particles were the carriers of electric charge. Another physicist, George Johnstone Stoney devoted considerable time to study the implications of Faraday's laws of electrolysis and suggested that electricity was also made up of ultimate particles with a charge equal to the charge on a univalent ion. He was also successful in calculating the value of this unit charge. In fact, it was Stony who first used the term 'electron' in 1891. According to him - “After estimating this minimum amount of electricity, I have named it ‘electron’.”

However, this idea (of the particulate nature of electricity) did not gain much currency till the end of the 19th century.

After the study of the electrical conductivity of liquids, came the turn of the electrical conductivity of gases. In order to study the conductivity of gases, the gas was taken in a tube. One end of the tube was fitted with a cathode while the other end had the anode. Then, a very high voltage was applied across these electrodes and the effects were observed. These observations were facilitated by the gas in the tube being under very low pressure.

The first studies of the conductivity of gases were carried out by the German physicist Johann Wilhelm Hittorf. In 1869, he observed that when electricity was passed through a gas kept at very low pressure, then the cathode could be seen to produce a glow. He was also able to observe that if the pressure is reduced still further, then this glow increased.

When further experiments were conducted on the rays which caused this glow, it was seen that any object placed in their path cast a shadow. A German physicist named Eugen Goldstein named these rays as cathode rays.

Now the interest of many scientists had been kindled and they began to study these rays. William Crookes managed to produce a cathode ray tube which could maintain very high vacuum. Using this tube, he was able to successfully demonstrate that these rays go from the cathode to the anode and that they carry energy. Most importantly, he was able to show that if the rays were passed through a magnetic field, then they could be deflected from their original path. On the basis of the direction of this deflection, he could prove that these rays are negatively charged.

In order to explain all the above properties of cathode rays, he assumed that cathode rays were a new state of matter – radiating/radioactive matter. According to him, these rays were made up of negatively charged ions which were issued from the cathode at very high speeds.

Crookes had studied the effect of a magnetic field on cathode rays. Another scientist Arthur Schuster applied voltage across two metals plates placed in such a way that the cathode rays passed between them. These cathode rays were then seen to get deflected towards the positively charged plate. This confirmed that the cathode rays were negatively charged. But Schuster went one step farther. On the basis of the extent of deflection, he was able to calculate the ratio between the charge on the cathode rays and their mass. But the value his calculations gave him was so much greater than what was expected that his methods themselves were questioned.

But at least this led to the establishment of the fact that these rays had a mass. That is, they were particles. Finally, J. J. Thomson, John Townsend and H. A. Wilson together in 1896 conducted those historical experiments which led to the discovery of the electron.

Thomson used some extremely elegant experiments and logical reasoning to calculate the charge and mass of these particles. One more fact had been clarified by Faraday's electrolysis experiments. The lightest charged particle had been found to be that of a hydrogen ion. When Thomson calculated the mass of the cathode ray particles (which he called corpuscles), he found that they were approximately 2000 times lighter than this smallest charged particle (hydrogen ion). First let us take a look at his results and the conclusions based on these results.

He had used various materials to make the cathode in the cathode ray tube (which was now being called Crookes' tube). The result seen was that the ratio between the charge and mass of the cathode corpuscles was the same regardless of the material that went into making the cathode. That is, the cathode corpuscles were independent of the material of the cathode. It was also seen that whatever might be the gas filled in the cathode ray tube, the charge by mass ratio of the cathode corpuscles remained unchanged. On the basis of these results, Thomson was able to conclude that these corpuscles were constituents of all atoms.

Thomson was also able to show that the negatively charged particles produced by radioactive substances, or by substances when they were heated, or when light fell on them were all the same. These particles were named as electrons.

So, these various experiments made it clear that the atom was not 'uncuttable', but that particles called electrons were found in the atom and that these particles could be separated from the atom under some circumstances. These particles were negatively charged and they were about 2000 times lighter than the lightest ion (hydrogen ion).

That is, Thomson's experiments had managed to break the atom which had been considered the ultimate particle of matter for about 200 years. And it seemed like the atom itself was made up of some particles and that these particles were common to the atoms of all elements. That is, now we had entered the sub-atomic world of the atoms.

The problem was that the atom as a whole was known to be neutral while the particles coming out of it were negatively charged. This meant that there had to be some positive charge to balance these negative charges.

After the discovery of the electron in 1897, Thomson resorted to some guesswork. No particle (sub-atomic particle) with a positive charge had been found. So, the model of the atom presented by Thomson included all these findings to make a cogent picture. He said that the positive charge is present in the atom as a kind of cloud. And the negative charge was embedded randomly in this cloud. This can be called the watermelon model of the atom. Generally, textbooks call this the 'plum pudding' model of the atom. In the model, the red portion of the watermelon is the spread-out positive charge while the black seeds in it represent the electrons.

So, on the one hand we have the discovery of the electron, and on the other hand, Eugen Goldstein had discovered yet another kind of ray. In 1886, Goldstein discovered canal rays which are also called anode rays. These canal rays were also made up of charged particles, and were formed by the ionization of gases. It was, however, seen that the anode ray particles produced by different gases had differing charge by mass ratios. That is, they could not be considered to be formed of one kind of particle as the cathode rays were.

If there were no positively charged particles, then this (Thomson's model of the atom) was the only way to explain the neutral nature of atoms which contained the negatively charged electrons. But the positively charged particles were to be discovered very soon. The discovery of these positively charged particles were the next step in our understanding of the structure of the atom.