General Article

Evolution of Chemistry—Part 2: The Birth of Modern Chemistry

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IT HAS BEEN explained in the first part of the article that the roots of modern chemistry can be traced back to the unglamorous, yet ambitious period of Alchemy. The processes and reagents used in the long periods when alchemy ruled, generated a vast body of empirical knowledge, even as its theoretical framework was erroneous. Subsequently, in the 17th century, chemistry was heading for a breakthrough especially due to the efforts of Robert Boyle. He imparted the necessary impetus to the culture of doing quantitative experiments. In the next century, Lavoisier, filtering and systematically compiling the then existing empirical knowledge, laid the foundation for modern chemistry.

Lavoisier gave a precise definition to 'Elements' and identified around thirty of them. Some of these elements were solids and some were gases. Lavoisier and Cavendish experimentally proved that water could be formed by combining hydrogen and oxygen in definite proportions. The idea that air is a mixture of many other gases was also developed later. It was gradually becoming clear that the four basic elements fire, air, water and earth propounded by Aristotle were not so fundamental or unique, but compounds or mixtures. The question: 'What is the nature made up of?' started agitating the minds of scientists.

It was at this stage that a quiet, soft spoken, village teacher from Manchester in England, named John Dalton (1766-1844), stepped into the history of science.

Study of weather was Dalton's primary interest. Without affecting his teaching assignments, he observed atmospheric temperature, humidity, state of the clouds, etc., for years and compiled long records of them. He observed that the composition of atmospheric air was uniform everywhere. Air contains gases like oxygen, hydrogen, nitrogen, carbon dioxide etc. These gases have different densities. But they are not segregated in air according to their densities. There were two viewpoints about the nature of air prevailing at that time. One believed the air to be an unstable chemical compound, while the other considered it a physical mixture of gases. Dalton's observations led him to conclude that air was indeed a physical mixture of gases. Yet the composition was uniform. "Why did the heavier carbon dioxide not settle at the bottom layer with the lighter ones at the top?" he asked.

There was another question stirring his mind. Through meticulously conducted experiments, Lavoisier had already shown that the total mass of all the reactants of a chemical reaction was equal to the total mass of the ensuing products. Generalizing

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this, Lavoisier had established the law of conservation of mass. Dalton thought that this law should be theoretically explained.

Joseph Louis Proust
(26 September 1754 – 5 July 1826)

Atomic theory

Dalton approached both these problems and sought an answer in a more general framework. This search led him to propose the celebrated atomic theory. He founded the theory on some brave and simple postulates. These were

1. Elements are made of extremely small particles called atoms.
2. Atoms of a given element are identical in size, mass, and other properties; atoms of different elements differ in these properties.
3. Atoms cannot be subdivided, created, or destroyed.
4. Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated, or rearranged.

It is remarkable that at the time of these postulates, Dalton did not know any experiment to determine the weight or size of the atom.

Dalton explained the uniform nature of air in a simple way, with his 'atoms'. He postulated that if the existence of atoms were assumed, the above mentioned questions could be answered. He knew the approximate composition of the air to be about four fifths nitrogen and one fifth oxygen. In addition there were hydrogen, carbon dioxide and water vapour. One would definitely ask, with all the different gases of different weights in the air, why was the composition of air so uniform? He answered that all these gases would exist in air as an ensemble of their atoms. The atoms of various constituents of air mixed themselves up by colliding with one another and causing a uniform distribution of the different gases. It seemed to be so simple and naive. But it was truly revolutionary in Dalton's time, when the idea that the air was a mixture of gases was still fairly new.

Changes taking place in chemical reactions could also be explained with Dalton's atomic theory. Atoms of different elements combine in definite proportions to form compounds in chemical reactions. Atoms of the elements in the reactant compounds of a chemical reaction, would separate out and through new combinations form new compounds. Different elements would always combine together in definite ratios of weights to form compounds. This would be the ratio between the atomic weights of the elements. This ratio of weight of atoms in a compound could be determined experimentally. Thus he defined relative atomic weight and proposed a way to determine the same. For instance, it was known then that hydrogen and oxygen would combine in the ratio of one to seven of their weights to form water. Then the ratio of weights of atoms of hydrogen and oxygen would also be the same, that is, oxygen atom is seven times heavier than hydrogen atom. Relative to the weight of hydrogen, the then known lightest element, atomic weights of other elements could be ascertained. Thus everything was made so simple and elegant. Dalton could reveal the beauty of numbers as Pythagoras had believed would be there behind natural phenomena. The concept of relative atomic weight later became one of the main pillars of modern chemistry. Dalton prepared the first table of relative atomic weights consisting of fourteen elements. Many of the values were corrected afterwards based on precise experiments.

We see from history that before Dalton's atomic theory, it was the French scientist Joseph Louis Proust who proposd the law of constant composition, which stated that different elements combine in definite proportions, by weight to form compounds. During that period, most chemists were followers of Claude Louis Berthollet, who believed the composition of a compound would vary according to the amounts of reactants used to produce it. In contrast, Proust proposed that pure reactants always combine in the same proportions to produce exactly the same compound. For about eight years, Proust and Berthollet engaged in a friendly polemic over this issue, but, in the end, Proust was proved to be right. Berthollet, instead of compounds, had used impure reactants and mixtures such as glass and alloys in his experiments, and thus he had analyzed the products inaccurately. Berthollet, when proved wrong, unreservedly accepted the truth in true scientific spirit. Atomic theory thus gave the correct theoretical explanation to the law of constant proportions. It is worth noting in passing that Berthollet, the discoverer of the use of chlorine as a bleaching agent, declined to patent it and gave to the world free.

Claude Louis Berthollet
(9 December 1748 – 6 November 1822)

While continuing the research on atomic weights Dalton noticed another mathematical simplicity, inherent in the structure of chemical compounds. Carbon and oxygen combine in the ratio of 3:4 by weight to form the toxic gas, carbon monoxide, while they combine in the ratio of 3:8 to form carbon dioxide. The weights of oxygen in both compounds, combining with same amount of carbon would be in the simple ratio 4:8 that is 1:2. He observed similar simple ratios in various compounds of nitrogen and oxygen. He was extracting another fundamental principle of chemistry, the law of multiple proportions. Berzelius later stated this law as follows: In a series of compounds made up of the same elements a simple ratio exists between the weights of one and the fixed weight of the other element. He wrote to Dalton to tell him that "this Law of Multiple Proportions was a mystery without the atomic hypothesis."

Dalton, thus, made chemistry amenable to mathematical manipulations and converted it into a modern scientific discipline. Atom, the favourite thought object of philosophers and metaphysicians for the

Sir Humphry Davy
(17 December 1778 – 29 May 1829)

past two and half millennia, now became a physical reality that could be proved in the laboratory. Democritus in ancient Greece and Kanada in India conceived of an 'atom', as the final indivisible particle, one would obtain after successive divisions of material bodies. All such individual atoms were thought to be different from one another. At that time it was a philosophical conjecture. In the seventeenth century Robert Boyle and Isaac Newton believed that matter was created with solid, hard, impenetrable and movable particles. Dalton's concept of atom was qualitatively different from all these. It was a scientific idea capable of explaining physical and chemical changes.

It was not true that Dalton's 'atoms' received universal acceptance. Even though scientists like Thomas Thomson and William Hyde Wollaston confirmed the Law of Multiple Proportions experimentally in the laboratory, England's most celebrated chemist Humphry Davy, was bitterly hostile. He wondered "how any man of sense or science would be taken up with such a tissue of absurdities." Davy even walked out once from Dalton's talk in the Royal Society. Thomson tried hard to convince Davy, but in vain. Many other scientists who were under Davy's prominent influence viewed atomic theory with derision. It may be hard to believe now that even in the beginning of twentieth century, front ranking scientists like Ernst Mach and Wilhelm Ostwald declined to believe the existence of atoms. They were philosophically inclined to positivism which rejected the existence of any entity, not perceptible to sense organs.

Many other scientists were generous enough to accept the atomic theory only as a useful hypothesis. But gradually, as with the case of any realistic theory, experimentation and efforts of verification followed. The results from laboratories could not be dispensed with. As time passed, atomic theory was accepted and treated as a valid theory among scientific community. Later, Davy himself admitted openly the 'absurd' atom and its unassuming proponent unreservedly.

Electricity and chemistry

While Dalton was developing his theory, some other new breakthroughs were happening, which eventually could throw light on the structure of matter. In Italy, Luigi Galvani (1737-1798) had discovered that frog legs that had been preserved in brine and hung on copper hooks would jerk as though alive when the wind blew them against an iron railing. Galvani believed that this might be caused by something happening in the muscles of the dead legs. His countryman, Alessandro Volta (1745-1827), concluded correctly that the phenomenon was caused by an electric current generated by the action of salt water on the two metals, copper and iron. Taking lessons from this discovery, Volta invented the voltaic pile, or the first battery. Volta later used electric current to break down water and showed that hydrogen and oxygen could be generated by the electrolysis of water. Remember Lavoisier's experiment of forming water with hydrogen and oxygen. Volta's analysis was the view of truth from the other side. Meanwhile Davy in England used a huge voltaic pile for the electrolysis of molten salts of potassium and sodium to isolate those metals. Sooner calcium, strontium and barium and later chlorine and iodine joined this list of elements isolated by electrolysis. Davy then concluded that elements in compounds were held together by electrical forces.

However Davy did not extend this view beyond the range of his experiments. But the Swedish scientist, Berzelius working at the same time as Davy, went ahead in this direction. He also used the pile to isolate the elements cerium, selenium and thorium and developed the electrolytic theory of compounds. The theory stated that elements united because different elements had different charges. In electrolysis, the positive and negative electrodes of the pile were placed in molten salts. Metals were attracted to the negative pole, were said to be positive whereas nonmetals like chlorine and iodine, attracted to the positive pole, were said to be negative. Likewise, the electrolysis of water indicated that hydrogen was positive and oxygen was negative. Elements have either positive or negative charge and those with opposite charge attract each other to form compounds. However, the errors in this classification were revealed later.

Berzelius was one of the prominent personalities in the history of chemistry. He was instrumental in fulfilling a colossal task initiated by Lavoisier. Even after Lavoisier's efforts in reforming the nomenclature and the mode of expressing chemical reactions, these were nightmare to prospective chemistry students. Berzelius thoroughly revised the nomenclature of elements as the way we use them now. He introduced a method to designate elements with the first letter of its English or Latin name suffixed by the number of atoms in one molecule.

Jöns Jacob Berzelius
(20 August 1779 – 7 August 1848)

Atoms and molecules

During the same period the French scientist Gay-Lussac observed that hydrogen and oxygen formed by the electrolysis of water were in the ratio 2:1 by volume. It was not a new finding. But, attracted by this simple ratio, he began to explore such ratios in other compounds too. At the end of this enquiry he formulated the famous law of combining volumes. This law stated that when gases react they do so in volumes bearing a simple ratio to one another and to the volumes of their gaseous products, provided that temperature and pressure remain constant. In precise experiments, however, there revealed some inconsistencies with the predictions of Dalton's atomic theory. One volume of nitrogen and one volume of oxygen combine to form two volumes of nitric oxide. It would be one volume only according to Dalton's theory. Similar inconsistency was observed in ammonia also, formed by nitrogen and hydrogen.

Dalton refused to accept the new law as it appeared to contradict his theory of the atom. Since the law of volumes was an experimentally proved one, people started suspecting the atomic theory. The problem arose since the difference between the atom and molecule was not clearly understood at that time. It was to wait until the work of Avogadro in 1811. Amedeo Avogadro proposed a hypothesis which later was known as Avogadro's Law, stated that under equal conditions of temperature and pressure, equal volumes of gases contain an equal number of molecules. He held that the gases in general, were diatomic, that is, they normally existed in pairs of atoms. Instead of simply O or N for oxygen and nitrogen they would be O_2 and N_2. This showed that the atomic weights and molecular weights may be different, removing the inconsistency with the atomic theory. For instance, the chemical equation of hydrogen and chlorine combining to form hydrogen chloride will reveal the fact:

$$H_2 + Cl_2 = 2HCl$$

One volume of hydrogen and one volume of chlorine combine to produce two volumes of hydrogen chloride. The reaction produced twice as many molecules. Hence, there is twice the volume. Before reaction there are one volume each of diatomic H_2 and diatomic Cl_2, but when these react, they create two hydrogen chloride molecules. And with twice as many molecules, volume of the product is doubled. This shows how the reaction produces two volumes of gas from only one volume each of the reactants. The law of volumes is obeyed. Again in terms of number of atoms, it is clear from the equation that one hydrogen atom and one chlorine atom combine together to form one molecule of hydrogen chloride. Dalton's theory is also correct. The fact that hydrogen and chlorine are diatomic molecules solved the issue. Thus the atomic theory was saved.

Joseph Louis Gay-Lussac
(6 December 1778 – 9 May 1850)

This hypothesis was not acknowledged in Avogadro's lifetime, and had to wait until Stanislao Cannizzaro demonstrated its significance to the world in 1860, in a conference held at Karlsruhe, Germany. Thereafter, the law became widely accepted. The number of particles in one mole of a substance was named Avogadro's number in his honour, and is numerically equal to 6.02252×10^{23}. It took exactly fifty years for the world to accept Avogadro's hypothesis after its proposition in 1811, and that too after the the great effort of Cannissaro. The then authorities of chemistry—Dalton, Davy and Berzelius—could not accept this law. The idea of Davy and Berzelius, that chemical affinity was electrical in nature, insisted that only atoms of opposite charges could combine. Avogadro's hypothesis made no sense from this point of view. The authorities at the helm of affairs rejected and the theory went into oblivion.

Lorenzo Romano Amedeo Carlo Avogadro di Quaregna e di Cerreto (9 August 1776 – 9 July 1856)

This is how preconceptions retard or even revert scientific advancement.

Elements and the search for order

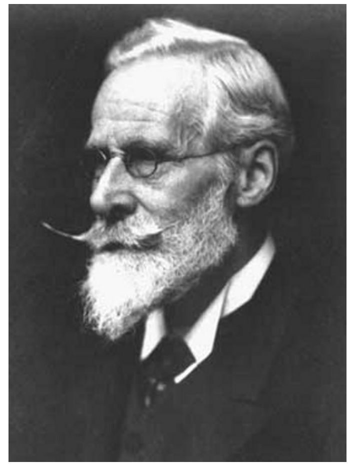
In the early and mid-nineteenth century, newer elements were discovered one after other. Davy in England discovered many of them and reached the summit of his fame. There was a legend that the French Emperor Napoleon once requested his scientists to salvage the nation's pride by discovering at least one element. Be that right or wrong, it was the Frenchman Gay-Lussac who discovered boron thereafter. About fifty elements were discovered altogether during the mid-eighteenth century. It became clear that some substances, which were earlier considered as elements by Lavoisier and Berthollet, were actually compounds. Scientists, particularly Davy, hesitated to believe that the universe is composed of these fifty-plus elements. After all what would be the sanctity of this number fifty? The truth of nature should be simpler, they believed.

William Prout (1785-1850), an English doctor, in line with the thoughts of Greek philosophers, started contemplating about a basic building block of nature. He began from the observations on the atomic weights of elements. Atomic weights were almost whole numbers (atomic weight is the number relative to the weight of hydrogen atom). If so, all these elements would be the multiples of hydrogen atoms. Or, hydrogen atoms combine in different proportions, to form various elements. Otherwise hydrogen atom is the primordial substance of nature. Thus the search for a fundamental particle of nature was, once again posed as a philosophical problem of science.

To comprehend the truth of the elements, which were increasing in numbers, the necessity to place them in order was felt then. Different people in different parts of the world took up the efforts of scientifically classifying the elements. The Englishman, Alexander Reins Newlands (1837-98) noticed an order in the chemical properties of elements when he classified them according to their atomic weights. He noticed a similarity in properties of the elements, to go through repeating groups of seven. This prompted Newlands to propose the "law of octaves" as some analogy between matter and music seemed inevitable. He read some papers in Royal Society along this line. However his papers were derided at rather than ignored. This was due to his wild imaginations without sufficient experimental evidence. Another scientist Julius Lothar Meyer (1830-1895) from Germany also prepared a table of elements, taking into account the atomic weights and volume of elements.

It was the legendary Dmitry Mendeleev who was born in Siberia and later moved to St. Petersburg in Russia, formulated the modern and scientific table of elements. He considered the chemical and physical properties of elements and placed the elements in appropriate columns of the table, after the properties were measured through pre-

Dmitri Ivanovich Mendeleev
(8 February 1834 – 2 February 1907)



William Crookes
(17 June 1832 – 4 April 1919)

cise experiments which ran over a long period. Hence the authenticity of the table was approved easily. He observed a rhythm and order of nature in his table. When he classified elements according to the order in which the physical-chemical properties vary, he had to keep vacant many of the columns of his table. He bravely concluded that those columns were to be filled with elements, to be discovered. A fresh enthusiasm was generated among chemists to unearth those new elements and many of them created history with their successes. Mendeleev's table highlighted the systematic order and continuity with which the properties of elements go hand in hand with their atomic weights. It was revealed that the potential and possibility of an element to form compounds, by combining with other elements, were determined by the position it occupied in the periodic table.

Deep into the atom

Parallel to these developments, other discoveries were also made in that century, which would suggest new ways to test the composition of matter. Michael Faraday further advanced the studies on electricity initiated by Galvani and Volta and introduced the concept of electromagnetic effect. Later James Clarke Maxwell mathematically proved that electricity and magnetism were the expression of the same phenomena electromagnetism. Electro-chemistry emerged as a discipline.

In the latter half of the nineteenth century, William Crookes, with the aid of an induction coil discharged a high voltage electricity through a highly evacuated globe and observed a ghostly fluorescence issuing from the negative plate, or cathode, of the glass tube. He also observed that these cathode rays could be made to bend under the influence of a strong electromagnet brought near the tube. Crookes was surprised by this radiating light, yet unmistakably exhibiting properties of matter. To reconcile the two irreconcilables he tried to explain them as the fourth stage of matter and termed them 'radiant matter'. We would see from history, the more science advanced towards the twentieth century the more it became clear how intertwined energy and matter really were. The outcome! Another energetic wave spread through the scientific centres. John Joseph Thomson

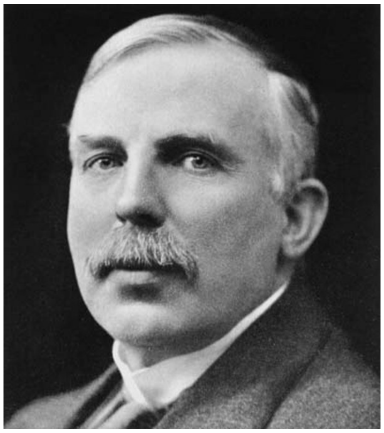
Wilhelm Conrad Röntgen
(27 March 1845 – 10 February 1923)

Marie Sklodowska-Curie
(7 November 1867 – 4 July 1934)

(1856-1940) who, at a young age, was appointed as the head of the Cavendish Laboratory in Cambridge took up the issue. Along with a bunch of young, vibrant scientists, Thomson (affectionately called 'JJ' by his colleagues) continued the experiments on the cathode rays. Two decades of intense and rigorous experimentation ensued. Finally on 30th April 1897 Thomson declared in the Royal Society that the cathode rays of Crookes were actually flow of particles of negative electricity. These particles were given the name 'electrons'. He was in reality questioning the status of atom as the final indivisible particle, by establishing the existence of electrons in the atom.

Earlier in that decade, Wilhelm Konrad Roentgen discovered x-rays in 1895. A year later Henri Becquerel discovered that uranium salt emitted some queer radiations, from observations that it exposed photographic film through a black cloth. It was after this, that an unknown lady, from a backward European colony, gained a frontal position in science history, with sheer determination and intellect, subverting many deep rooted taboos in science and society. Maria Sklodovska, youngest daughter of a poor patriotic teacher from the Russia-occupied Poland, battling poverty and discrimination, reached Sorbonne University in France for higher education. After acquiring two masters degrees in physics and mathematics, she set to research on the rays Becquerel had discovered. Toiling in a laboratory similar to an alchemist's crude workshop, finally, she discovered that these rays were coming from inside the uranium atoms. That was revolutionary because the concept of indivisible atom was prominent then. It was Mary who gave the name radioactivity to the phenomenon. She decided to search for other elements exhibiting the same property. Along with her husband Pierre Curie, she laboured for years. In the end they discovered two radioactive elements polonium and radium.

Thus, the discovery of particles of negative electricity by J. J. Thomson and that of radioactive rays emanating from hitherto considered indivisible atoms attracted the attention of scientists again to the inner details of matter. They were more concerned about the fundamental properties and basic building blocks of nature in those days when the borderline between chemistry and physics was becoming thin.



Ernest Rutherford
(30 August 1871 – 19 October 1937)

Ernest Rutherford, the prolific disciple of J. J. Thomson in his experiments bombarded a thin gold foil with alpha particles. To his astonishment he found that alpha particles were deflected and some even hit back. "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you" Rutherford wrote later. He then understood the existence of a positively charged nucleus at the center of atom where the mass of the atom is concentrated. Rutherford developed a planetary model of atom with electrons revolving around the nucleus. When scientists tried to explain the motion of these atomic particles using the principles of classical mechanics, problems piled up one after another. The necessity for a different and more general mechanics was felt. In this backdrop, quantum mechanics emerged in which scientists like Niels Bohr, Werner Heisenberg, Wolfgang Pauli, Erwin Schrodinger, Louis de Broglie, Paul Dirac played significant role.

An updated model of the atom also came into being. This model depicted a general picture of the atom, with the negatively charged electrons revolving in specified shells around a central nucleus consisting of protons and neutrons. Though not completely correct according to the principles of quantum mechanics, this picture was important as far as chemistry was concerned. The number of electrons in the outer shell would be the deciding factor in the chemical properties of elements. This shell may contain electrons from one to eight. Chemical properties gradually vary with this number. The basis for the systematic order seen in Mendeleev's table could thus be explained. The periodic table was revised too with this new knowledge. The number of oppositely charged electrons and protons would be the same in an atom. This number, the basis for chemical properties, is known as the atomic number. The mass of the atom is contributed in the main by the proton and neutron in the nucleus. The relative weight in comparison with the weight of hydrogen atom is known as the atomic weight. So much of confusions prevailing in the nineteenth century regarding the chemical properties and atomic weights were cleared off. This new atom model also explained the complexities of elements combining to form compounds. The natural tendency of atoms would be to keep the number of electrons in the outer shell eight. This could be achieved by the give-and-take or mutual sharing of electrons in the outer shells of reacting elements. Chemical bond also could be explained, and thus quantum chemistry emerged. The technological and chemical advancements in the twentieth century owe much to the new insight provided by quantum chemistry.

Today, chemistry not only unearths the laws of the microcosm enabling human beings to explain the chemical and physical changes in the universe, but also provides the theory and technological knowhow to manufacture millions of products in medicine, fertilizers, vitamins, cosmetics, etc., and greatly influences modern life. □