



Discovery of Oxygen

Birth of Modern Chemistry

T. V. VENKATESWARAN

Here's an interesting account of the journey from the phlogiston theory to Lavoisier's experiment to establish the composition of air.

IN 1772, the British chemist and dissenting preacher Joseph Priestley (1733-1804), stood in front of the Royal Society and reported on his latest discovery: "This air is of exalted nature...A candle burned in this air with an amazing strength of flame; and a bit of red hot wood crackled and burned with a prodigious rapidity. But to complete the proof of the superior quality of this air, I introduced a mouse into it; and in a quantity in which, had it been common air, it would have died in about a quarter of an hour, it lived a whole hour, and was taken out quite vigorous." Back then

Priestley was not aware what a revolution he was to cause.

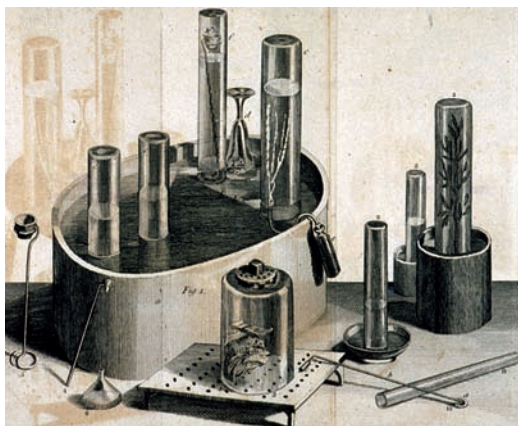
Indeed, Joseph Priestley was interested in revolutions—the French revolution of 1789 and the American Revolution that culminated in the republican constitution in 1787. Influenced by these revolutionary ideals, Priestley wanted to abolish absolute monarchy in England and bring in the republican form of government. He hardly succeeded in his political campaign. Constantly under suspicion and watchful eyes of the authorities, harassed Priestley had to migrate to America in the later part

of his life. Priestley may have been unsuccessful in stirring up the political fervour in his country, but he successfully stirred up a chemical revolution.

Just as the French revolution abolished monarchy and established democracy, alchemy was banished and from its ashes emerged modern chemistry. Just as the American Revolution espoused republicanism and eschewed feudal ideas, modern chemistry banished long held *pancha-bhoota* (five element) theory and phlogiston theories and instead embraced quantitative methods and modern atomic theories. The key foundation was laid by Joseph Priestley but the revolution itself was led by the French chemist Antoine Lavoisier (1743-1794).



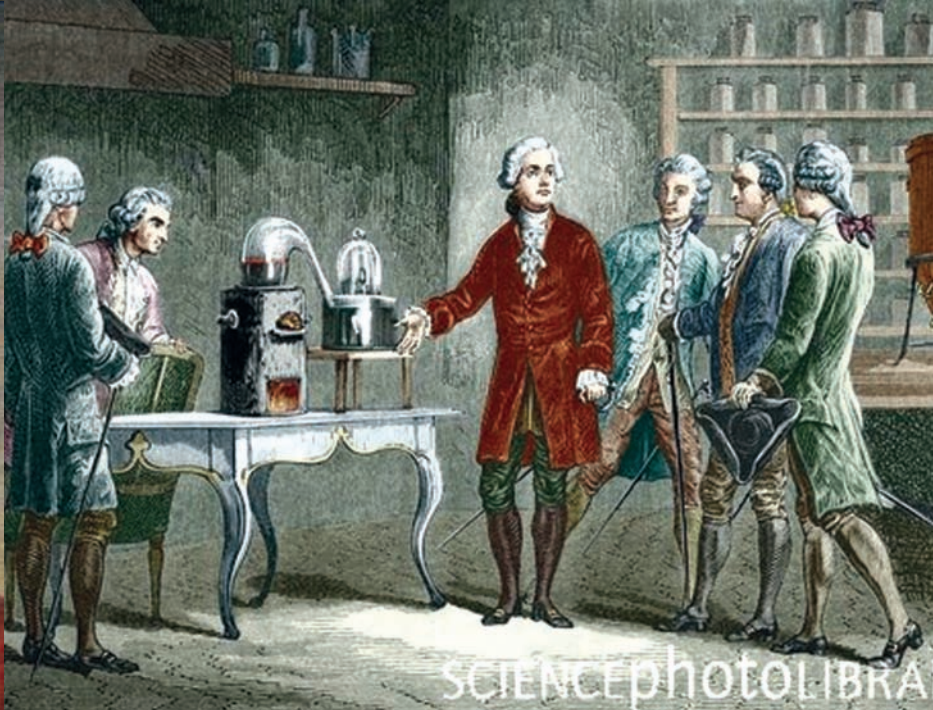
From ancient times, alchemists, forerunners to modern day chemists, investigated various substances (above)



Joseph Priestley and his apparatus (Far left)

Carl Wilhelm Scheele (left)

Actually the gas had been discovered several years earlier by Carl Wilhelm Scheele (1742-1786), a German-Swedish chemist.

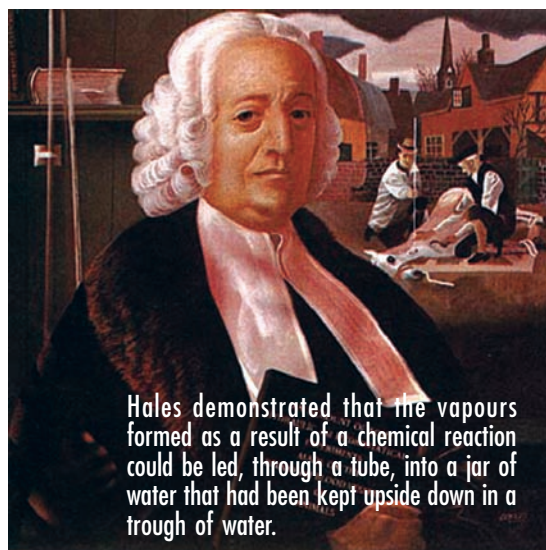


Lavoisier demonstrating his discovery of oxygen (above)

Antoine Lavoisier (left)

Alchemists & 'Phlogiston'

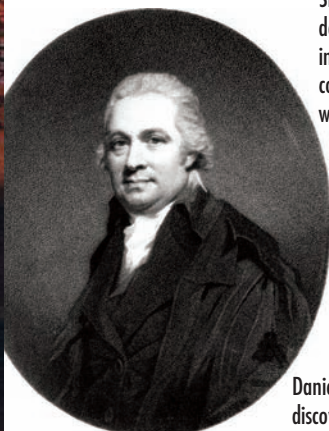
Chemistry is the science of substances and their transformations. From ancient times, alchemists, forerunners to modern day chemists, investigated various substances. Working under the concept that all material things in the world were made out of four (or five) basic elements – Earth, Water, Fire, Air and Space—they observed that some of the chemical changes were spontaneous, proceeding under ambient conditions. Some must be driven with an input of energy, often fire. In those days heat, and its source fire, seemed the only obvious generative principle that was needed to transform wheat into bread, iron ore into steel.



Hales demonstrated that the vapours formed as a result of a chemical reaction could be led, through a tube, into a jar of water that had been kept upside down in a trough of water.

Theorising on all that was known about fire, two alchemists Johann Joachim Becher and Georg Ernst Stahl concluded that the essence of fire was a substance called phlogiston (from a Greek word meaning "to set on fire"). They adopted the ancient view that fire, heat, and light are different manifestations of a common principle that leaves a body during combustion. They called this principle 'phlogiston' and initiated an extensive use of the concept in reasoning about chemical reactions that involved combustion or rusting.

According to this 'phlogiston' theory, when matter burned, it gave off phlogiston. The theory seemed to be rational and explained many phenomena then observed by the alchemists. Burn the wood, phlogiston present in the wood



Stephen Hales devised an ingenious way to collect gases over water (far left)

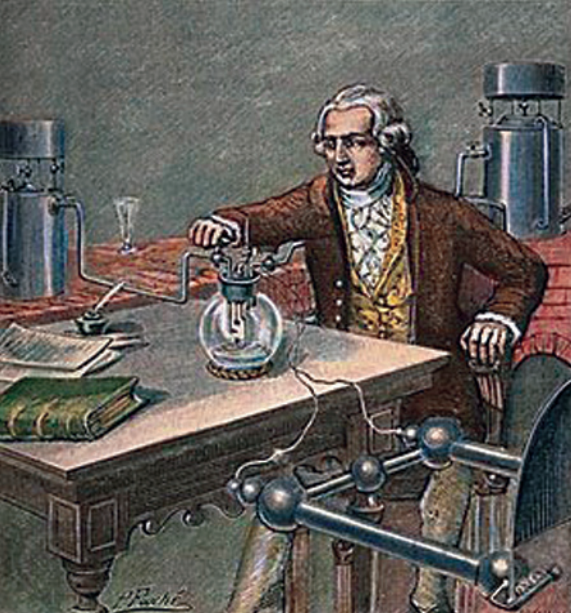
Daniel Rutherford discovered Nitrogen

escapes and ashes remain. Wood was full of phlogiston, therefore heavy, and ashes empty of phlogiston and hence light. Combustible objects, Stahl held, were rich in phlogiston, and the process of burning is in essence loss of phlogiston to the air. What was left behind after combustion was without phlogiston and therefore could no longer burn.

Early alchemists were not able to isolate phlogiston, but the generation of fire during combustion seemed to be a good reason for admitting the production of a substance from the burning body. Later, the existence of phlogiston was supported by a considerable body of evidence as this substance proved useful in explaining many additional reactions.

One of the early successes of the phlogiston theory was its explanation of the smelting of iron from iron ore (calx-of-iron, as it was called then). This was an important insight, and with this percept, a reasonable explanation of the conversion of rocky ores into metals could be advanced. Rocky ore is usually burned with charcoal. The near-pure metal then trickles out in molten state. According to the phlogisticians, this well known process involved the decomposition of charcoal into phlogiston and ash, followed by the combination of phlogiston with calx-of-iron (rocky ore) to form iron. Thus, pure iron was seen to be infused with phlogiston derived from the burning coal. When the same iron was left in open to the vagaries of nature, it rusted. Alchemists explained rusting as the process through which phlogiston slowly and steadily 'evaporates' from iron.

But what about air, is it essential for smelting? Phlogisticians considered that air



Lavoisier in his lab (left)

Lavoisier's experiment on the composition of air (right)

Lavoisier showed that there was no need to postulate a mysterious substance – phlogiston; air is not an element but is composed of at least three types of ‘airs’



itself is indirectly useful for combustion, for it served only as a carrier, holding the phlogiston as it left the wood or metal. If there was no air, then phlogiston could not escape from the charcoal to enter the metal ore.

Nevertheless, one crucial difficulty with the phlogiston theory was that in combustion one saw flame, but in rusting no flame was seen. Stahl explained this apparent difference easily. He reasoned that combustion of substances, such as wood, was when phlogiston left so rapidly that its passage heated its surroundings and became visible as flame. On the other hand, he argued that rusting is a slow process and hence the loss of phlogiston was slower and no flame appeared.

Yet there was a serious flaw in the theory and observation, which neither Stahl nor any phlogisticians could explain. Most combustible objects, such as wood, paper, and fat seemed largely to

disappear upon burning. The remaining soot or ash was much lighter than the original substance, as is to be expected from the phlogiston theory. However, when metals rusted, they also lost phlogiston, according to Stahl's theory, yet the rust was heavier than the original metal.

During the 18th century, alchemists paid careful attention to the solids and liquids in the reaction, but no one paid adequate attention to the vapour or gases that emanate from a chemical reaction. In fact, for long there was no way chemists could study vapours, as vapours could not be captured like liquids or solids in vials.

Is air then a simple element or a compound of gases?

Gases were often obtained in the chemical reactions, but were elusive substances that were hard to study and observe, and easy to ignore. Solids and liquids could be gathered in a container, but the vapour appeared to disappear into thin air. Vapours were seen as mysterious, since usually the generation of gases is accompanied by bubbles, fizz and effervescence.

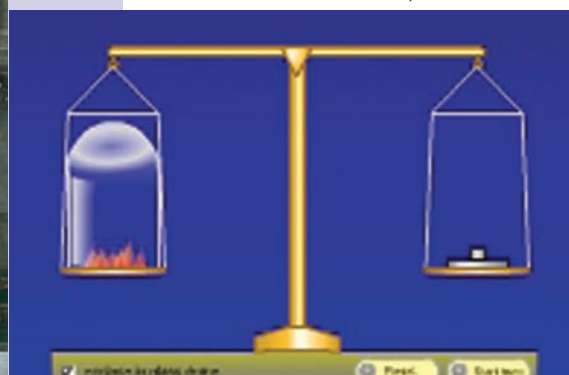
It was not until the English chemist Stephen Hales (1677-1761) devised an ingenious way to collect gases over water, that vapours were investigated by chemists. Hales demonstrated that the vapours formed as a result of a chemical reaction could be led, through a tube, into a jar of water that had been kept upside down in a trough of water. The vapours from the chemical reaction bubbled upward into the jar, displacing the water and forcing it out through the open bottom. In the end, Hales had obtained a jar of the particular gas or gases formed in the reaction. Now these gases could be measured, studied and investigated. In fact, after Hales a new branch of chemistry called 'pneumatic chemistry' emerged to study all sorts of 'airs' and vapours that chemists obtained in their reactions.

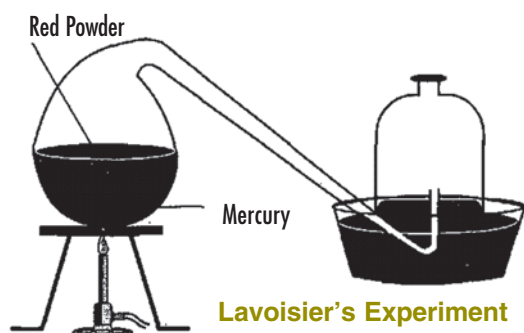
Using the now emergent 'pneumatic chemistry', Scottish chemist Joseph Black (1728-1799) took an important step in chemistry. He heated limestone (calcium carbonate), the limestone decomposed giving off a gas (carbon dioxide) and lime (calcium oxide) remained as residue. Black had collated the gas given off during the reaction using Hales's method. He made the gas to recombine with the lime and was able to obtain his original limestone. Black called this gas "fixed air" because it could be combined ("fixed") in such a way as to form part of a solid substance (today we know that this gas is indeed carbon dioxide). He and other



Lavoisier with wife

Simulation of Lavoisier's experiment showing that mass was conserved





chemists found that the same 'fixed air' could be obtained by burning wood. In both the cases, candle would not burn and a mouse would die in jars filled with 'fixed air'.

His study was significant, for it showed that vapours were not merely given off by solids and liquids, but could combine with them to produce chemical changes. This discovery made gases that much less mysterious and presented them, rather, as a variety of matter to be examined by chemists.

Another perceptive finding by Black that shook the foundations of alchemy was that when calcium oxide was allowed to stand in air, it turned slowly to calcium carbonate. This implied firstly that air has some amount of 'fixed air' (carbon dioxide). This in turn implied that air could not be a basic element but itself is composed of a number of types of 'airs' (or gases). The alchemical idea of four basic elements was now in serious question.

The floodgates were now open. Soon chemists discovered various types of 'airs' (gases) in atmospheric air. Scottish chemist Daniel Rutherford (1749-1819), himself a student of Black, discovered Nitrogen (he called it 'phlogisticated air'). Take a sealed glass container with phosphorus. You can burn the phosphorus with a magnifying glass using sun's rays. Wait until no more phosphorus is left to burn. Now, in the view of chemists of those days, you have saturated the container with phlogiston. Now place an adequate amount of calcium oxide in this phlogiston rich air. Calcium oxide will soak the 'fixed air' (carbon dioxide) and become limestone.

Now what is left in the sealed container is pure phlogisticated air, from which we have removed all the 'fixed air', reasoned Rutherford. He also found that the residual 'air' could not support combustion; a mouse would not live in it

and a candle would not burn. It is phlogisticated air, because it cannot take any more of 'phlogiston' and hence did not allow combustion and burning. But it was different from 'fixed air' (carbon dioxide) for it was not able to combine with lime producing limestone. Today we know that this gas devoid of oxygen (removed by burning phosphorus) and carbon dioxide (scrubbed off by calcium oxide) would be mostly nitrogen.

Oxygen Discovered

Priestley lived next to a brewery, often visiting it. He was intrigued by the 'air' that floated over fermenting grain. He collected these 'airs' and experimented on them. From his first experiment, he was able to show that this 'heavier-than-air' gas was able to extinguish burning wood chips. Priestley devised a new way to produce this 'heavy gas', as he called it, in his home laboratory. He poured acid onto chalk (calcium carbonate), and the heavy gas resulted. Later he understood that his 'heavy gas' and the 'fixed air' of Rutherford were indeed the same.

Today we call this gas carbon dioxide. On dissolving this gas in water he found that it had a pleasant and tangy taste. We now know this as soda water. For this invention of soda water, Priestley was elected to the French Academy of Sciences in 1772, and the following year he received the prestigious Copley Medal from the Royal Society. He also collected and studied such gases as nitrogen oxide, ammonia, hydrogen chloride, and sulfur dioxide.

Priestley wondered, if Rutherford could isolate 'phlogisticated' air (nitrogen) was it possible to isolate pure 'dephlogisticated' air – air totally devoid of phlogiston? He tried a novel experiment to obtain the 'dephlogisticated' air on 1 August 1774. He took Mercury and heated it in air. As the mercury got heated, according to the then extant phlogiston theory, phlogiston from mercury was released into the air turning mercury into mercury calx (what we call today mercury oxide). He placed this mercury calx in to an airtight glass bell jar and removed all the air from it. Now the container was empty, except for mercury calx.

For reversing the reaction, turning mercury calx in to mercury, he had to heat the mercury calx. This he had to do without opening the glass container, so that air from outside would not rush in. He came

up with a creative solution to burn the calx inside a sealed glass container. He used a magnifying glass and focused the rays of the sun onto the calx. The calx burned even while it was inside a sealed jar. Slowly the grey drops of mercury reappeared; along with it a gas of unusual property was released. The gas was now confined to the glass bell jar. As this released vapour was inside the sealed jar, he could study and test the vapour as he wished.

Priestley experimented with this gas. He found that this gas helped the wood to burn more blazingly. Combustibles burned more brilliantly and rapidly in presence of this gas. A mouse placed inside a jar enriched with this gas was particularly active. In comparison to a jar containing common air, a mouse placed inside a jar containing this gas lived four times longer.

Priestley may have been a radical in politics, but in his chemistry he was still a conservative. Indeed Priestley had discovered 'oxygen'; but still being under the influence of the phlogiston theory, he thought that he had isolated dephlogisticated air. He reasoned that calx when heated absorbed phlogiston and became pure mercury, thus taking away from the air phlogiston. Hence the residual air is dephlogisticated air.

Actually the gas had been discovered several years earlier by Carl Wilhelm Scheele (1742-1786), a German-Swedish chemist. Scheele was a pharmacist and a chemist, as was usual in those times. He discovered many acids of hydrogen cyanide, hydrogen fluoride and hydrogen sulfide (all of which he sniffed and tasted, no doubt contributing to his untimely death). He also discovered the elements manganese, oxygen, molybdenum, and chlorine. However, the credit for discovering these elements went elsewhere due to queer circumstances.

Scheele made oxygen by decomposing a variety of salts, including the same mercuric oxide, that too four years before Priestley. Though his discovery was well known in Swedish chemist circles, he published his results too late. He awaited a tardy preface by an authority, the great Swedish chemist of his time, Torbern Bergman, who took his own sweet time and thereafter the publisher inordinately delayed and finally the book appeared in the summer of 1777, two years after Priestley's publication. Incidentally, Scheele, like Priestley, was a staunch advocate of the phlogiston theory and

THE TRAGEDY OF THE HEROES

All the three main heroes credited with the discovery of oxygen suffered. Least among them was Scheele, whose contribution was not recognized for long. As regards Joseph Priestley, his unusual religious views combined with radical political thought cost him dearly.

Joseph Priestley held that Jesus was in nature truly and solely a man, however highly exalted by God and advocated religious tolerance, which did not endear him to Anglican orthodoxy. His stance against slavery, admiration of rights of man and support for the French and American Revolution made him a suspect for the bourgeois. His call for abolition of absolute monarchy and more powers to the House of Commons made him an enemy in the eyes of the Royals.

In 1791, on the second anniversary of the Bastille Day, an alcohol-fuelled mob of royalists burned the New Meeting house, and then Priestley's home. The scientist and his family barely escaped. They fled to London, but eventually it proved no safer. Priestley's sons could not find work and immigrated to Pennsylvania in America. Finally, Priestley and his wife Mary followed them, setting sail for America on 8 April 1794.

Priestley continued his research in America, and his significant achievement was isolating carbon monoxide (which he called "heavy inflammable air") and founding the Unitarian Church in the United States. American president Thomas Jefferson was his close friend and when Priestley died Jefferson said in the funeral speech that Priestley was "one of the few lives precious to mankind."

Lavoisier was one among the twenty-eight French tax collectors and a powerful figure in the deeply unpopular Ferme Générale. No wonder that Lavoisier was branded a traitor during the Reign of Terror by French Revolutionists in 1794 and despised by the anarchists. On trumped up charges, Lavoisier and his father-in-law were beheaded by the Jacobian anarchists. Lagrange, one of the finest mathematicians, on hearing this lamented that "it took them only an instant to cut off his head, but France may not produce another such head in a century".

called his gas 'fire air' as it helped the fire burn vigorously.

Even before Priestley and Scheele, several scientists such as Robert Hooke, Ole Borch, Mikhail Lomonosov, and Pierre Bayen had produced oxygen in various experiments in the 17th and 18th century but none of them recognized it as an element. As pneumatic techniques for collecting vapours were not well developed in those times, it was hard for them to identify the specific properties of this gas.

Antoine Lavoisier

Lavoisier was a wealthy French chemist, tax collector, economist, public servant, and also a debunker of mesmerism. He noticed that while measurement was crucial and indeed the hallmark of modern physics and astronomy, in chemistry it was not valued. He set out to change this. He thought that the only way to clear the confusion in alchemy was to study the reactions systematically.

Alchemists of those days who clung to the old Greek notion of elements held that transmutation was possible because water could be turned to earth on long heating. A glass container heated for a period of many days did develop solid sediments. Lavoisier set out to investigate it by more than eyesight. He made an arrangement wherein the water vapour from the container when heated would

not be lost but would be condensed and returned to the flask. Thus he ensured that no substance was permanently lost in the course of the experiment and each and every aspect could be accounted for. And he, unlike other alchemists, measured. He weighed both water and vessel before and after the long period of boiling.

Indeed, as expected, the sediment did appear, but the water did not change its weight during the boiling. Therefore, Lavoisier reasoned that the sediment could not have been formed out of the water. However, the flask itself, once the sediment had been scraped away, proved to have lost weight, a loss just equal to the weight of the sediment. In other words, the sediment was not water turning to earth; as made out by alchemists, but rather material from the glass, slowly leached by the hot water and precipitated in solid fragments. This was his first salvo against alchemists who held that there were only four (or five) simple elements in the world and one could be transmuted into another.

This incident had a lasting impact on Lavoisier. He was convinced that measuring the weights of the chemicals involved is a necessary aspect of investigating chemical reactions. Indeed with the help of his skilful and educated wife, Marie Anne Pierrette Paulze, he devised several measuring balances

suited to cover a range of weights, each increasing in precision and accuracy. Through a series of careful weighings and experiments that ingeniously isolated the system under study he showed the indestructibility of matter. One by one he undertook the examination of various chemical changes. In each case he found that careful measurement showed that things certainly change, but nothing is lost, and nothing is created in a chemical reaction. Law of conservation of mass was not only a law of physics, now it was extended to chemistry and chemical reactions.

He decided to investigate the process of formation of calx in a systematic manner. He heated metals such as tin and lead in closed sealed containers with limited supply of air. Both metals formed a layer of calx on the surface up to a certain point and then rusted no further. The phlogistonists would say that the air is maximally saturated with phlogiston from the metal that it could hold no further. As was well known, however, the calx weighed more than the metal itself, and yet when Lavoisier weighed the entire vessel (metal, calx, air and all) after the heating, it weighed precisely the same as it had before the heating. Therefore, the air inside the sealed container must be weighing less. Lavoisier was disturbed at this paradox. Calx lost phlogiston yet it weighed more; the air in the container

This air is of exalted nature...A candle burned in this air with an amazing strength of flame;

gained phlogiston yet it weighed less. So, overall the whole system neither lost weight nor gained.

Rejecting the phlogiston theory, Lavoisier argued that if the metal had gained weight on being partially turned to a calx, then something else in the vessel must have lost an equivalent amount of weight. If that were so, then a partial vacuum must exist in the vessel. Sure enough, when Lavoisier opened the vessel, air rushed in. Once that happened, the vessel and its contents proved to have gained in weight. Lavoisier had thus shown that the conversion of a metal into a calx was not the result of a loss of mysterious phlogiston, but was the gain of something very material, a portion of the air by the metal.

But what about the burning of wood? Like calx, wood also burned in the presence of air, but unlike calx it did not gain weight, but lost it. Lavoisier burned a piece of wood in a closed container and showed that ash, plus the vapours formed, plus what was left of the air retained the original weight of wood plus air. In this case he showed that wood released vapours and the weight of the air increased. The pressure inside the sealed container increased, so that once it was opened the air rushed out with a hissing sound.

Oxygen – Recognized

Priestley, who had his sympathies with the French revolutionaries, made a visit to Paris in October of 1774 and Lavoisier invited him over to dinner. Madame Mary Anne Lavoisier, who was fluent in English helped translate their conversation. Priestley told Lavoisier of his experiments in making dephlogisticated air. Within a week, a letter arrived for Lavoisier from Carl Wilhelm Scheele, describing how he had made 'fire air' from mercury calx. Lavoisier was curious.

He repeated the experiments of Priestley and Scheele. He was amazed at the gas produced by them. Since he was obsessed with weighing and measuring, Lavoisier set out to do these experiments in a systematic way, unlike Priestley. He found that the gas discovered by Priestley and Scheele were also involved in acid formation—he named the gas 'oxygen' (meaning acid former).

Lavoisier heated the metals in closed containers with limited supply of oxygen (the new air produced by Priestley). In this way he found that the maximum amount of rust was formed by metals. We know that rust weighs more than metals. But, the metal, rust, air, and flask weighed the same before and after the experiment. So he demonstrated that in a chemical process nothing is 'lost' or 'gained' but only converted from one chemical to another. If the metal, under heating and in presence of oxygen (new air), indeed gained weight something must have lost weight. He guessed that air must have lost it.

To test his hypothesis, he performed this experiment in a tightly sealed container. Once the rust was formed, he opened the container, air from outside rushed in thus establishing that a partial vacuum had been created inside the tight container. Indeed, air had lost something to the metal resulting in rust. He reasoned that oxygen from the atmosphere had been absorbed by the metal leading to the formation of rust (calx).

Lavoisier was not satisfied. Why the formation of rust stopped at some point, why the metal did not absorb all the air? How much air rushed in case of burning of calx? How much did the air gain weight when wood was burned? Did the amount of air that rushed in remain constant every time? Careful observer that Lavoisier was, he set out to design an ingenious experiment to measure them. And this experiment proved to be crucial.

Antoine Lavoisier performed this classic experiment in 1779 answering many questions. First, Lavoisier heated pure mercury in a swan-necked retort over a charcoal furnace for twelve days. As was well known, the mercury would draw oxygen from the air and become slowly mercury oxide, and air in the jar would lose weight. But then how to measure how much of air had been used up?

Cleverly, Lavoisier placed the snout of the swan neck in an inverted bell jar that was placed over a trough of water. Thus, if there were reduction in the air in the swan neck retort, air from the bell jar would rush in. As the air from the bell jar rushes out, it would draw water from the trough. Thus the reduction of the air in the swan neck jar could be measured by measuring the water going into the bell jar.

As the swan neck retort was heated for 12 days, red oxide of mercury was formed on the surface of the mercury in the retort. When no more red powder was formed, Lavoisier noticed that about one-fifth of the air had been used up and that the remaining gas in the retort did not support life or burning.

He did not stop there. He reversed the process. He scrapped out all the mercury oxide formed in this experiment. He placed it in another swan neck retort. The snout of the neck in this case was placed inside a bell jar filled with water kept upended in a trough of water. As the mercury oxide was heated by a magnifying glass using sun's rays, it released oxygen and turned once again into mercury. The additional oxygen produced by the reaction bubbled out through the snout and displaced the water in the bell jar. The water displaced was the same volume of air initially consumed by the mercury for turning into mercury oxide.

Further careful measurements showed that 20% of the volume of air was used up by the metals in forming calx, thus showing that atmospheric air was composed of 20% oxygen. The remaining four-fifths of the air, which could not support combustion or life (Rutherford's phlogisticated air), was a separate gas altogether, argued Lavoisier. He called this gas "ozote" (from Greek words meaning "no life") but later this gas was named nitrogen.

Thus, Lavoisier showed that there was no need to postulate a mysterious substance – phlogiston; air is not an element but is composed of at least three types of 'airs' (oxygen, nitrogen, carbon dioxide). This along with the crucial chemical law—matter is neither created nor destroyed in chemical reactions—paved the way for the emergence of modern chemistry.

Dr T.V. Venkateswaran is a scientist with Vigyan Prasara, Department of Science and Technology, New Delhi. A graduate in mathematics and postgraduate degree in history and a PG Diploma in S&T communication, he was awarded PhD by Tamil University, Thanjavur, Tamil Nadu for his thesis 'Popular perception of science during the late nineteenth century colonial Tamil Nadu'. He has authored more than 20 books on popular science in Tamil and English and regularly contributes to various popular science periodicals. His research interest includes science and media and history of popularization of science in India. Address: A-50, Institutional Area, Sector-62, NOIDA-201307, U.P. Email: tvv@vigyanprasara.gov.in