

UNIT III

The Chemical Revolution

The Chemical Revolution, also known as the First Chemical Revolution, marked a transformative period in chemistry during the 17th and 18th centuries. This revolution led to the development of modern chemistry, characterized by the reformulation of chemical theories, practices, and methods. Several key factors contributed to this transformation:

(i) *Focus on Experimental Methods:*

Pioneers like Robert Boyle emphasized rigorous experimentation. His work, especially in *The Sceptical Chymist*, shifted the focus from speculative theories to empirical observations, paving the way for a more methodical approach to chemistry.

(ii) *Use of Equipment:*

Chemists began using special instruments like thermometers and balances to measure temperature, pressure, and weight accurately. This helped them perform better experiments and make more reliable discoveries. Boyle's air pump was a key instrument that allowed for the experimentation with gases and the study of their properties. Boyle used the air pump to investigate the behavior of gases, leading to the formulation of Boyle's Law, which describes the inverse relationship between the pressure and volume of a gas at constant temperature.

(iii) *Importance of Accurate Measurement:*

Accurate measurement became essential for understanding chemical processes. Antoine Lavoisier, for example, used precise weighing methods to prove the law of conservation of mass, which states that matter is neither created nor destroyed in chemical reactions. This fundamental principle required careful measurement of reactants and products, allowing Lavoisier to refute the phlogiston theory and develop the modern theory of combustion.

Chemists during the Chemical Revolution, especially Robert Boyle, Stephen Hales, Joseph Black, Henry Cavendish, Joseph Priestley and Antoine Laurent Lavoisier laid the foundations for modern chemistry by rejecting mystical explanations, introducing quantitative methods and accurate laboratory techniques with the use of special equipment.

Robert Boyle (1627-1691)

Robert Boyle was a significant figure in the history of chemistry, playing a key role in transforming the field from alchemy to what we now know as modern chemistry. Boyle is best known for his work on the nature of chemical elements and his use of the scientific method, which emphasized observation, experimentation, and careful reasoning.

Boyle challenged the traditional alchemical ideas, such as the theory that all substances were composed of four elements (earth, water, air, and fire) or three principles (mercury, sulfur, and salt). In his

book, *The Sceptical Chymist* (1661), he argued against these theories and proposed a more practical definition of elements. He believed an element should be defined as a substance that could not be broken down into simpler substances by any known chemical method. This approach introduced the idea that substances previously thought to be elements could be further decomposed as scientific knowledge progressed. Boyle's definition was provisional, meaning a substance could be considered an element until it could be broken down into simpler substances. This idea laid the groundwork for the modern understanding of chemical elements.

Boyle was also a proponent of the mechanistic view of chemical reactions. He believed that all matter was made up of small particles, and these particles could form different substances based on their size, shape, and motion. According to Boyle, chemical reactions were the result of rearrangements of these particles. However, Boyle did not propose a specific list of elements, as he felt that there could be far more than the three or four proposed by alchemists. His focus was more on how chemical reactions occurred rather than why, marking a shift from philosophical speculation to scientific inquiry.

Boyle's work with gases was particularly groundbreaking. Working with his assistant, Robert Hooke, he developed an improved version of the air pump, which allowed them to conduct experiments on the properties of gases and vacuums. Boyle and Hooke's experiments led to the formulation of Boyle's Law, which describes the inverse relationship between the volume and pressure of a gas at constant temperature.

Boyle also conducted experiments on combustion using the air pump. He discovered that materials like sulfur would not burn in a vacuum, concluding that air is necessary for combustion. However, he also observed that gunpowder could ignite in a vacuum, leading him to speculate that the nitre (potassium nitrate) in the gunpowder produced "agitated vapours" that behaved like air. This work contributed to a better understanding of gases and laid the groundwork for later studies in pneumatic chemistry.

Boyle's experiments went beyond gases. He was one of the first to understand that metals gain weight when they are heated in air because they react with something in the air. In experiments where he heated metals in sealed containers, Boyle found that when the container was opened, the metal (or calx) had gained weight. He mistakenly believed that "fire particles" contributed to this weight gain. Nonetheless, his work on calcination contributed to later theories about oxidation and the role of oxygen in combustion.

Boyle also produced hydrogen gas by dissolving iron in dilute acids like sulfuric or hydrochloric acid. He collected this gas in an inverted glass vessel and noted its inflammability, marking an early study of gases other than air.

Boyle's insistence on rigorous experimentation and his challenges to existing alchemical theories helped shift chemistry away from mysticism and towards empirical science. While he did not identify new elements himself, his work paved the way for the scientific approach to chemistry that would be fully realized in the Chemical Revolution of the 18th century.

The Phlogiston Theory

The Phlogiston theory was introduced in the late 17th century by Georg Ernst Stahl, who built upon the ideas of Johann Becher. According to this theory, when something burns or a metal is heated, a substance called phlogiston is released. Phlogiston was thought to be an invisible, weightless material present in all combustible materials. Once it escaped during combustion, what remained was the dephlogisticated material, like ash or a metal's calx (what we now know as an oxide).

The theory helped explain several chemical processes. For instance, when charcoal burned and left little ash behind, it was said to be rich in phlogiston. In metalworking, when metals were heated with charcoal, phlogiston from the charcoal was thought to combine with the metal's calx, turning it back into metal. Air was believed to absorb phlogiston, so combustion stopped when the air was saturated, and it was impossible to burn something in a vacuum where there was no air to absorb phlogiston.

Although many chemical reactions could be explained by this theory, there were some significant problems. For example, the increase in weight of metals when they were heated and turned into calx couldn't be explained by phlogiston, as the material was supposed to lose phlogiston. Some supporters argued that phlogiston had negative weight to explain this increase, but it wasn't very convincing.

Most chemists in the 18th century accepted the phlogiston theory because it provided a simple explanation for many observations. However, not everyone agreed. One of the critics was Hermann Boerhaave, a famous teacher and chemist. He didn't accept the idea that metals were compounds of phlogiston and instead focused on experiments rather than speculation.

Stephen Hales (1677-1761)

Stephen Hales was an English chemist who made important contributions to the study of gases in the early 18th century. He developed a simple but effective method to collect gases over water. When a chemical reaction produced gases, Hales used a tube to guide the gas into a jar filled with water, which had been placed upside down in a basin of water. As the gas entered the jar, it displaced the water, allowing Hales to collect it. This technique, though basic, was a significant advancement because it provided a way to trap gases, making further study possible.

While Hales measured the volume of the gas produced, he did not study the properties of these gases in detail. He believed all gases were just atmospheric air with extra particles added, so he did not distinguish between different gases. Though he did not identify individual gases, Hales's method of gas collection was a major contribution to science.

Joseph Black (1728-1799)

Joseph Black was a Scottish chemist who made key contributions to understanding gases. In 1756, Black published his findings in *Experiments on Magnesia Alba, Quick-lime, and Other Alkaline Substances*. He found that when magnesium carbonate (magnesia alba) was heated, it lost a significant amount of weight. This

was not just water evaporating, but a gas escaping, which he called "fixed air" (now known as carbon dioxide). Black demonstrated that this gas was a distinct chemical substance and not just a modification of air.

Black also found that this gas could combine with quicklime (calcium oxide) to form calcium carbonate again. Thus, he showed that gaseous substances were not merely given off by solids and liquids, but could actually combine with them to produce chemical changes. He further discovered that carbon dioxide was a natural part of the atmosphere by observing how limewater left in open air developed a crust of calcium carbonate, but did not do so when kept in sealed bottles. This indicated that carbon dioxide was present in the air. Here was the first clear indication that air was not an element by Boyle's definition. It consisted of a mixture of at least two distinct substances, ordinary air and carbon dioxide.

In studying the effect of heat on calcium carbonate, Black measured the loss of weight involved. He also measured the quantity of calcium carbonate that would neutralize a given quantity of acid. This was a giant step toward the application of quantitative measurement to chemical changes.

Black's work was important for several reasons. He used quantitative measurement in his experiments, paving the way for more precise chemical research. His discovery that gases like carbon dioxide were distinct entities helped develop the field of pneumatic chemistry, which focuses on the study of gases. Black's work also provided important clues to later chemists like Lavoisier in understanding chemical reactions without relying on the phlogiston theory.

Daniel Rutherford (1749-1819)

When Joseph Black was studying the properties of carbon dioxide, he found that a candle would not burn in it. Black turned this problem over to his student Daniel Rutherford in 1772. Rutherford kept a mouse in a space with a confined quantity of air until it died. Then, he burned a candle in the remaining air until it went out. Afterwards, he burned phosphorus in that, until it would not burn. Then the air was passed through a carbon dioxide absorbing solution. The remaining component of the air did not support combustion, and a mouse could not live in it. Rutherford called the gas (which we now know would have consisted primarily of nitrogen) "noxious air" or "phlogisticated air".

Henry Cavendish (1731-1810)

Henry Cavendish was an important scientist who studied gases. In 1766, he carefully investigated a gas produced when acids reacted with metals like zinc, iron, and tin. Although other scientists, such as Robert Boyle, had prepared this gas before, Cavendish was the first to study its properties in detail, which is why he is credited with the discovery of hydrogen gas. He called it "inflammable air from metals," and it was later named hydrogen.

Cavendish found that hydrogen was much lighter than air, with only one-fourteenth of its density. He also observed that hydrogen was highly flammable, which made it different from other gases like carbon dioxide or air.

Joseph Priestley (1733-1804)

Joseph Priestley was a Unitarian minister who had a deep interest in chemistry. In the late 1760s, while working at a church in Leeds, England, he had access to a nearby brewery that produced carbon dioxide during fermentation. He collected this gas and discovered that when it dissolved in water, it gave the water a tart taste, which is now known as “soda water.” This work led Priestley to be considered the father of the modern soft drink industry.

Priestley’s experiments with carbon dioxide showed him that gases could dissolve in water and be lost from experiments. To prevent this, he began collecting gases over mercury, allowing him to study gases like nitrogen oxide, ammonia, hydrogen chloride, and sulfur dioxide.

In 1774, while heating mercuric oxide (then called “calx”) with sunlight, Priestley made his most significant discovery. The substance broke down, releasing a gas that made combustibles burn more brightly than in regular air. He called this gas “dephlogisticated air,” which was later renamed oxygen. Priestley noticed that mice thrived in this gas, and when he breathed it himself, he felt light and energized. This discovery of oxygen was key to understanding the nature of air and combustion.

Antoine Laurent Lavoisier (1743-1794)

Antoine Laurent Lavoisier played a key role in revolutionizing chemistry. He is called the "father of modern chemistry." His contributions laid the groundwork for the Chemical Revolution by emphasizing the importance of precise measurements and logical explanations for chemical processes.

One of Lavoisier's early experiments, conducted in 1764, involved heating gypsum and measuring the water it released. This was his first major work in using measurements to study chemical changes. He believed that accurate measurements could solve the mysteries of chemical transformations and debunk long-held beliefs. For example, he disproved the idea that water could turn into earth, as was widely accepted in the 18th century. By boiling water for 101 days, Lavoisier showed that the sediment that formed was not the result of transmutation but came from the glass container itself. This demonstrated how careful weighing and measurement could lead to clear, factual conclusions, rather than relying on mere observation.

Lavoisier’s work on combustion was groundbreaking. In the 1770s, he began investigating how materials like metals and diamonds burn in closed containers. When he heated a diamond in a closed vessel, he found it disappeared and carbon dioxide formed, proving that diamonds were made of carbon. He also showed that metals, such as tin and lead, when heated, formed a calx (oxide), which gained weight. Lavoisier’s systematic weighing of the vessel and its contents before and after combustion revealed that the total weight remained unchanged, leading him to conclude that the metal had combined with a portion of the air. This was a key insight, as it directly challenged the prevailing "phlogiston theory," which claimed that materials lost an invisible substance called phlogiston when they burned.

In a crucial discovery, Lavoisier explained that air was not a single substance but a mixture of two gases: one-fifth of the air was the gas we now call oxygen, which supports combustion and life, while the remaining four-fifths was what we now call nitrogen, which does not support combustion. He gave the name "oxygen" (meaning "acid producer") to the part of the air responsible for combustion and life. Although he initially believed oxygen was present in all acids, this assumption was later corrected.

His works showed that combustion was not the loss of phlogiston but the chemical combination of a substance with oxygen.

Lavoisier also developed a new explanation for how metals were extracted from ores. He showed that when ores were heated with charcoal, the charcoal combined with the oxygen in the ore, producing carbon dioxide and leaving the metal behind. This idea of gas transfer was revolutionary because it explained the changes in weight during chemical reactions, something the phlogiston theory could not.

One of Lavoisier's greatest contributions was his formulation of the law of conservation of mass. Through his experiments, he demonstrated that in any chemical reaction, the total mass of the substances involved remained constant. This was a fundamental breakthrough that established the principle that mass is neither created nor destroyed, only transformed. This law became the cornerstone of modern chemistry.

Lavoisier also played a leading role in developing the system of chemical nomenclature we still use today. In collaboration with other French chemists, he introduced a logical system for naming chemical compounds based on their elements and proportions. For instance, calcium oxide was named because it contained calcium and oxygen, and carbon dioxide was named to indicate it had more oxygen than carbon monoxide. This system replaced the confusing and inconsistent naming conventions of alchemy, bringing clarity and order to the study of chemistry.

In 1789, Lavoisier published "Elementary Treatise on Chemistry", the first modern chemistry textbook. It presented a unified picture of chemical knowledge based on his new theories and naming system. It also included a list of 33 known elements, most of which remain valid today, although Lavoisier mistakenly included heat and light as elements, reflecting the scientific understanding of the time.

Lavoisier's later work explored the relationship between respiration and combustion. He and Pierre-Simon Laplace conducted experiments showing that the oxygen animals inhaled was used to produce both carbon dioxide and water, linking respiration to the same chemical processes involved in combustion. This demonstrated that life itself was a form of slow combustion, consuming oxygen to sustain itself.

Sadly, Lavoisier's career was cut short by the French Revolution. He was executed in 1794 due to his association with a tax-collecting agency. Despite his tragic death, his work left an indelible mark on science, reshaping the understanding of chemistry and setting the stage for the future. Joseph Lagrange, the famous mathematician, remarked, "It took them only an instant to cut off his head, but France may not produce another such head in a century."

Lavoisier's contributions, particularly his emphasis on measurement, the development of the conservation of mass, and the creation of a systematic chemical nomenclature, solidified his place as one of the greatest chemists in history. His work fundamentally transformed the field of chemistry, moving it from an era of mystical theories to one based on scientific principles and experimentation.

The Atom

Jeremias Benjamin Richter (1762-1807)

In 1792, the German chemist Jeremias Benjamin Richter studied reactions between acids and bases, specifically how acids neutralized bases. He discovered that when acids and bases combined, they did so in specific, fixed amounts. For example, if you took a certain amount of acid, you would need a precise amount of base to completely neutralize it. Richter introduced the idea of "equivalent weight," which means that a fixed weight of one chemical reacts with a fixed weight of another. This concept showed that chemicals combine according to specific ratios, and it wasn't random like adding ingredients in cooking.

Joseph Louis Proust (1754–1826)

Proust's Law (Law of Definite Proportions)

In the late 18th century, French chemist Joseph Louis Proust made a groundbreaking discovery that laid the foundation for one of chemistry's core principles: the law of definite proportions, sometimes referred to as Proust's Law. Proust was conducting meticulous experiments with various chemical compounds, focusing on how elements combined to form compounds. In 1799, after carefully analyzing a compound called copper carbonate, he observed that regardless of how or where the compound was obtained or synthesized, it always contained the same fixed ratio of copper, oxygen, and carbon. Specifically, it was always composed of 5.3 parts copper, 4 parts oxygen, and 1 part carbon by weight.

This observation was significant because it contradicted the prevailing theory held by Claude Louis Berthollet, another prominent chemist at the time. Berthollet believed that the proportions of elements in a compound could vary depending on how the compound was prepared. He proposed that if you prepared a compound with one element in excess, the compound would contain more of that element. For example, if there was an excess of copper, copper carbonate might contain more copper than in other samples. However, Proust's research showed that this was not the case. No matter how copper carbonate was produced, its composition by weight remained constant.

Proust extended his work beyond copper carbonate, showing that other compounds also followed this pattern. He generalized this into a broader principle: every pure chemical compound contains its constituent elements in a fixed and definite proportion by mass. This became known as the Law of Definite Proportions or Proust's Law.

This law was revolutionary because it introduced the idea that the composition of chemical compounds is not arbitrary or subject to variation. Proust's Law implied that elements combine in fixed ratios and that these ratios reflect something fundamental about the nature of matter itself.

Proust's work was initially controversial, especially because Berthollet's view had widespread support, but by the early 19th century, Proust's findings had been confirmed by other chemists, and his law became a cornerstone of modern chemistry. The Law of Definite Proportions led to further inquiries into why elements combined in fixed ratios, setting the stage for the development of atomic theory.

After the idea of equivalent weight and the Law of Definite Proportions was introduced, several important developments in chemistry followed, leading to the birth of modern atomic theory.

At first, it wasn't obvious that these ideas were linked to atoms. Chemists of that time didn't think in terms of atoms and molecules as we do today. In fact, John Dalton, who later proposed the atomic theory, initially studied gases and their physical properties rather than focusing on chemical reactions.

John Dalton (1766–1844)

Dalton's Early Work and Theories on Gaseous Mixtures

John Dalton initially approached the idea of atoms not from a chemical perspective, but from his work on gases, which was more physical in nature. He adopted a model for gases that was similar to Isaac Newton's. Newton had proposed that gases consist of particles in a three-dimensional arrangement, repelling one another. He had calculated that if the force of repulsion between these particles decreases with distance, this could explain Boyle's Law, where the pressure of a gas is inversely proportional to its volume.

However, Dalton knew from contemporary knowledge that air was not made of a single gas but a mixture of gases like nitrogen, oxygen, and varying amounts of water vapor. The prevailing belief at the time was that air might be a loose chemical combination of these gases. In 1801, Dalton rejected this idea and instead suggested that air was a physical mixture. But if air were a physical mixture, the problem arose that the gases should separate into layers based on their densities, with oxygen, being denser, forming a bottom layer. This did not happen in reality.

Dalton proposed a new idea to explain why air remains homogeneous: he suggested that each gas's particles only repelled particles of the same type and did not interact with particles of a different kind. This led to Dalton's law of partial pressures, which states that in a mixture of gases, each gas exerts the same pressure as if it were occupying the container alone. Although this idea was based on an incorrect assumption about how particles interact, it is still valid today as a practical concept.

Refining Dalton's Theory and Atomic Weights

Dalton soon became dissatisfied with his initial model of gas mixtures, as it seemed unlikely that particles could selectively repel only those of their kind. He then introduced the idea that gaseous particles had different sizes and weights. He thought that the repulsive forces between particles were caused by heat,

which he called "caloric." In this view, particles of different gases would not separate because the varying sizes and weights of the particles would prevent any equilibrium from forming. This also led him to conclude that the particles of different gases must have different weights.

Dalton presented his early theory of different-sized and weighted particles in 1803 to the Manchester Literary and Philosophical Society. His research also built on experiments by William Henry, who discovered that the amount of gas a liquid absorbs is proportional to the pressure of the gas. Dalton argued that this process was not chemical but simply mechanical mixing of particles. He admitted that his theory was incomplete and raised an important point: if all gases were made of particles of different sizes and weights, then their behavior in mixtures and in absorption by liquids could be explained.

Dalton's work on gas solubility led him to consider the relative weights of these particles, which he later called atoms. In his experiments, he calculated the first atomic weights. However, he did not reveal how he arrived at these numbers in his early work, leaving it a mystery. Dalton preferred to use the term "ultimate particles" before later adopting the term "atom."

Chemical Atomic Theory: Multiple Proportions and Atomic Weights

The first full description of Dalton's atomic theory appeared in 1807 when Thomas Thomson, a chemist who had visited Dalton in 1804, included it in the third edition of his book *System of Chemistry*. Thomson had been convinced of Dalton's views, and although he was close to developing a similar theory himself, it was Dalton's ideas that shaped the atomic theory.

Dalton published his own version of atomic theory in 1808 in *A New System of Chemical Philosophy*. By this time, Dalton was fully using the term "atom" for the smallest particles of substances. He proposed that elements are composed of simple atoms, while compounds are made up of compound atoms, which were combinations of two or more different atoms. To assign atomic weights, Dalton had to make assumptions about how elements combined to form compounds. He introduced what he called the "Principle of Simplicity," which stated that when two elements form only one compound, it should contain one atom of each element. For example, Dalton assumed that water consisted of one atom of hydrogen and one atom of oxygen.

However, Dalton's atomic weights were not always accurate because the experimental data available in 1808 was not highly precise. For example, he estimated that water contained hydrogen and oxygen in a weight ratio of 1:7, rather than the correct ratio of 1:8. Despite this error, Dalton's atomic theory successfully explained the law of definite proportions.

Dalton's theory also predicted a new law: the law of multiple proportions. This law states that when two elements form more than one compound, the different masses of one element that combine with a fixed mass of the other element will be in simple whole-number ratios. Dalton observed that this rule applied to compounds like the oxides of nitrogen (nitrogen dioxide and nitric oxide), and it provided strong evidence for the atomic theory.

Dalton's Atomic Symbols and Structural Ideas

Dalton invented a system of symbols to represent atoms and compounds, which was an important step in the development of chemical notation. His symbols were circles with distinctive patterns or letters inside them, each representing a specific atom. For example, the symbol for oxygen might have a circle with a dot inside, while hydrogen had a simpler design. These symbols were not just shorthand; they also carried quantitative meaning. When atoms combined to form compounds, their symbols were drawn as touching circles.

Dalton's symbols also conveyed structural ideas about how atoms were arranged in compounds. For instance, he proposed that atoms of the same type would repel each other, which led him to the correct geometric arrangement for some compounds, like carbon dioxide (linear structure) and sulfur trioxide (triangular structure). Although this was not a fully developed structural theory, it was an early attempt to explain the spatial arrangement of atoms.

Support, Controversy and Avogadro's Hypothesis

Thomson supported Dalton's atomic theory by providing evidence for the law of multiple proportions, while Wollaston criticized Dalton's principle of simplicity, advocating for the use of equivalent weights over atomic weights.

Dalton's atomic theory was not universally accepted. Some chemists objected to his method of calculating atomic weights, which they felt was based on arbitrary assumptions about how atoms combined. Wollaston, for instance, preferred using equivalent weights, which were easier to calculate and seemed less speculative.

In 1808, Joseph Louis Gay-Lussac discovered that gases combine in simple volume ratios. For example, hydrogen and oxygen combine in a 2:1 ratio by volume. This discovery seemed to suggest that equal volumes of gases contain equal numbers of particles, but Dalton rejected this idea, as it did not fit neatly with his theory. Gay-Lussac's results also contradicted Dalton's assumption that carbon monoxide (CO) should be denser than oxygen, which it is not.

It was Amadeo Avogadro, in 1811, who proposed a solution to this problem. Avogadro suggested that gases are made of molecules, which could be split into smaller parts during chemical reactions. For instance, two molecules of hydrogen (H_2) could combine with one molecule of oxygen (O_2) to form two molecules of water vapor (H_2O). Avogadro's hypothesis reconciled Dalton's atomic theory with Gay-Lussac's law of combining volumes, but his ideas were not widely accepted at the time. Chemists found Avogadro's terminology confusing, and his suggestion that the particles of gaseous elements might consist of more than one atom was controversial. It was only much later, in 1860, that Avogadro's ideas gained acceptance, after a conference of chemists recognized the importance of his molecular theory.

