Science of Atomism: A Brief History

2

I... a Universe of Atoms, an Atom in the Universe
(Richard P. Feynman)

2.1 Atomism

In natural philosophy, *atomism* is the theory that all the objects in the universe are composed of very small, indestructible elements—*atoms*. The notion of atomism first arose because of philosophic deduction. This idea of atomism is by no means self-evident. Since ancient times, philosophers in many cultures have been speculating on the nature of the fundamental substance or substances of which the universe is composed. These fundamental or basic substances are called *elements* in English, from a Latin word of unknown origin.

In India, during the sixth century BC, Kanada and Pakhuda Katyayana had propounded ideas about the atomic constitution (*Anu and Paramanu*) of the material world (Limouris 2006). Philosophy and science were not originally separate but, were born together as natural philosophy in Greece, at the beginning of the sixth century. In fact, the ancient Greeks were the first to propose that all matter in the universe was created from the following four elements: *water*, *earth*, *fire*, and *air*. They also believed that matter is continuous; there is no *vacuum* (space without any matter). The Greek philosopher Leucippus and his pupil Democritus (460–370 BC) (Fig. 2.1) conceived the idea of an *atom* as the smallest piece of a substance. The word atom comes from the Greek word *atomos* (ατομοσ) meaning "not cuttable" (unbreakable) and advocated that atoms are in continuous motion and are indestructible. The most famous Greek philosophers Plato (427–347 BC) and Aristotle (384–322 BC), however, completely rejected the idea of atomism. Nevertheless, the ideas of Democritus were further developed by the influential Greek Philosopher Epicurus almost a century later. One of the most important followers of the Epicurean philosophy was a Roman poet named Titus Lucretius Carus (96–55 BC), who explained the philosophy of atomism in a long poem entitled, *De rerun Natura* (On Natural Things). One copy of this poem survived the Dark and Middle Ages (it was discovered in 1417) and became a major source of the Greek theory of atomism. The French philosopher Pierre Gassendi (1592–1655) accepted atomism and spread this doctrine throughout Europe.
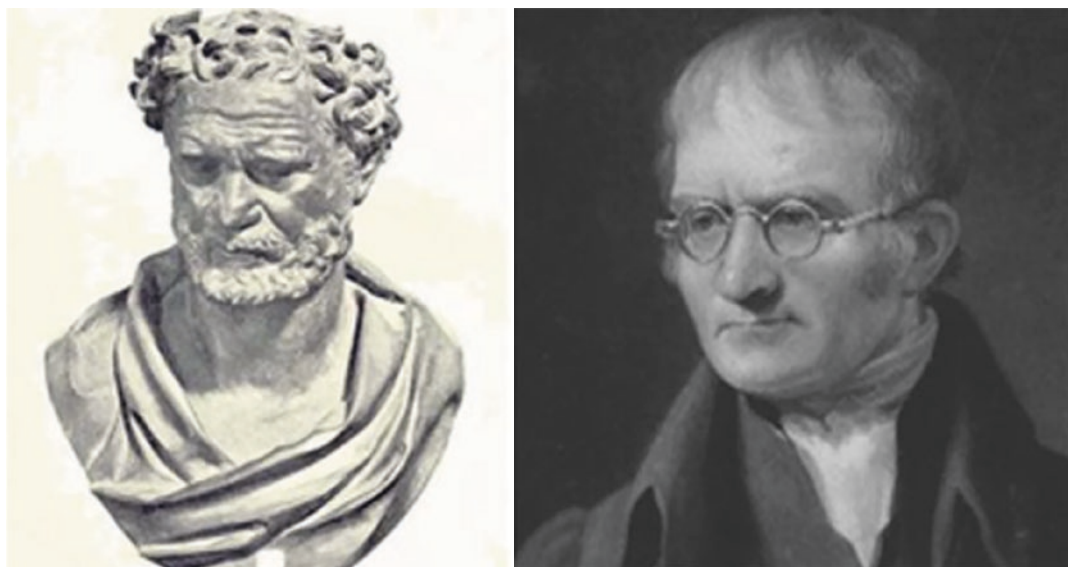
Fig. 2.1 Democritus, the Greek philosopher (on left), and John Dalton, an English chemist, and physicist (on right)

2.2   Chemical Elements

The British scientist Robert Boyle (1627–1691) was strongly influenced by Gassendi's writings and was probably the first person to perform experiments in connection with atomism. Boyle carefully measured and demonstrated an inverse relationship between the pressure and the volume of air (known as *Boyle's Law*), which clearly suggested that both atoms and vacuum are real. He, thus, revived the atomic hypothesis and called it the *Corpuscular Theory of Matter*. Newton also wrote in his *Opticks* that all matter is composed of solid and impenetrable particles—expressing a view similar to Democritus and Boyle.

Boyle was also the first chemist to recognize the significance of a *chemical element*. In his book, the *Skeptical Chemist*, published in 1661, he proposed that a substance was an element if it could not be broken into two or more simpler substances. In early 1700, the quantitative sciences of physics and chemistry were born, and 15 chemical elements came to be known. Following the discovery of important gases, such as carbon dioxide, nitrogen, hydrogen, and oxygen, the French chemist, Antoine Laurent de Lavoisier (1743–1794) in his remarkable book titled, *Traite*

elementaire de chemie, published in 1789, listed 33 substances as chemical elements under four major categories: *gases*, *nonmetals*, *metals*, and *earths*.

2.2.1   Chemical Laws

Lavoisier advocated the importance of accurate measurements in quantitative experiments of chemical reactions and discovered the *law of conservation of mass* which states that: mass is neither created nor destroyed. The principle of the constant composition of compounds, known as the *law of definite proportions*, was discovered by the Frenchman, Joseph Proust who showed that a given compound always contains exactly the same proportion of elements by mass. Proust's discovery stimulated John Dalton (Fig. 2.1) an English school teacher, who noted that a series of compounds can be formed by the combination of two elements in different ratios and, thus, discovered the *law of multiple proportions*. These chemical laws supported the hypothesis that each element consists of a certain type of atom and that compounds are formed from specific combinations of these atoms.

2.2.2 Atomic Theory

In 1808, John Dalton converted the atomic hypothesis into a quantitative theory. In his publication, *A New System of chemical philosophy*, Dalton stated that each element is made up of identical atoms and presented a theory of atoms. He prepared the first table of *atomic weights* for different elements and suggested that atoms of each element had individual weights and that these could be calculated relative to one another. Dalton made the simple assumption that one atom of hydrogen combined with one atom of oxygen makes a molecule of water. Many of the atomic masses proposed by Dalton were later proved to be incorrect but, the construction of a table of atomic weights of different elements was a major step forward.

In 1808, Joseph Louis Gay-Lussac made the remarkable observation that although all elements combine in definite proportions of weight, gases combine in definite proportions by volume. For example, he observed that two volumes of hydrogen combined with one volume of oxygen make one volume of water vapor. The explanation of the *law of combining volumes* was provided in 1811 by Amadeo Avogadro, an Italian physicist, who hypothesized that equal volumes of any gas at a given temperature and pressure always contain an equal number of the particles (atoms or molecules) of gas. Avogadro was the first to realize that certain gaseous elements, like hydrogen (H_2), nitrogen (N_2), and oxygen (O_2), under ordinary conditions contain two atoms each (also known as *diatomic molecule*). Avogadro's hypothesis was a brilliant guess and we now know, based on the *kinetic theory of gases*, that under normal conditions of temperature and pressure (NTP), 22.4 L of any gas contain exactly the same number of atoms or molecules. In chemistry, the concept of *mole* (as a unit of mass) is defined as gram atomic weight or molecular weight and 1 mol of any substance contains Avogadro's number (N_A) of atoms or molecules. Avogadro, however, never knew the exact value of this universal constant. Almost 100 years later the value of N_A was determined to be 6.022×10^{23}.

Based on Avogadro's hypothesis, Jons Jakob Berzelius, a Swedish chemist published more accurate atomic weights of many elements between 1814 and 1826. He also invented a simple set of symbols for elements along with a system for writing the chemical formulas of compounds, in order to replace the awkward symbolic representations of alchemists. By the end of the nineteenth century, not all chemists and physicists believed in the reality of atoms, however, they accepted that atomic weight is a very important property of an element.

In the late 1860s, two chemists, the Russian Dmitri Ivanovich Mendeleev, and the German Julius Lothar Meyer, arranged the elements in the order of increasing atomic weight in a tabular form, called the *periodic system of elements*, since elements with similar chemical properties recurred at regular, periodic, intervals.

The discovery of electricity eventually provided important clues and the experimental evidence necessary to demonstrate the existence of atoms.

2.3 Electricity and Magnetism

The phenomena of magnetism and electricity have been known since ancient times. A certain piece of iron ore or loadstone, first found near the town of Magnesia on the eastern shore of the Aegean Sea, was the basis for scientific investigation. The English physician William Gilbert (1544–1603), a contemporary of Galileo carefully studied the magnetic interactions and published the famous book, *De Magnete*, in which he concluded that the planet earth can be regarded as a giant magnet with geographical north and south poles; the magnetic south always pointing to the geographical north.

Since ancient times, people have also been aware that a piece of *amber*, when rubbed with fur will attract small bits of hair and other materials. Gilbert first introduced the term *electric* (*electrica* in Latin), after the Greek word *electron* for amber, and found that other substances such as glass, sulfur, wax, and gems also exhibit similar attractive property as amber. He also proposed

that electricity is some sort of fluid (an *effluvium*) that is produced or rubbed when bodies are rubbed together. Gilbert also recognized that despite their similarities, electricity, and magnetism are different phenomena, but are deeply related.

The French chemist Charles-Francois de Cisternay Du Fay, eventually, realized that there are two types of electricity (*vitreous and resinous*), which are very different from each other; unlike types of electricity attract each other while like types repel each other. In contrast, the American inventor Benjamin Franklin (1706–1790) concluded that electricity consists of a single type of fluid and that this fluid consists of extremely subtle particles. He referred to the deficiency of electricity as *negative* electricity and to an excess as *positive* electricity. The amount of electricity (positive or negative) in any body is called the electric *charge* of the body. Franklin also observed that electricity is not created or destroyed and, thus, was the first one to introduce the fundamental hypothesis of the conservation of electric charge.

During the second half of the eighteenth century, physicists in many countries were trying to understand the quantitative aspects of both electric and magnetic forces. For example, French physicist Charles Augustine de Coulomb developed the so-called *torsion balance* for measuring very weak forces and published his results on electric and magnetic forces during 1785–1791. More specifically, Coulomb discovered that the forces of electrical attraction and repulsion are directly proportional to the product of two charges and inversely proportional to the square of the distance between them. Subsequently, this law, known as *Coulomb's law*, helped to establish the unit for the electric charge. One *coulomb* of charge is defined as the amount of electric charge that passes a given point in one second in a wire that carries a one *ampere* current. Coulomb also found that the strength of the force of attraction or repulsion between the magnetic poles declines as the square of the distance between the poles increases. In 1687, Newton showed that the gravitational attraction between two bodies also followed the so-called *inverse square law*.

In 1786, the Italian physiologist Luigi Galvani accidentally discovered *electric current* while studying the phenomenon of muscular contraction in frog's legs. His friend, Alessandro Giusuppe Volta (1745–1827), a physicist, soon proved that electric current is purely an inorganic phenomenon (also known as *galvanism*) by demonstrating that electricity could be produced when two different metals were both dipped into a salt solution. Electricity, thus, was produced as a result of a chemical reaction. To produce a large electric current, Volta in 1800 constructed what is known as *Volta pile* using a number of alternating copper and iron or zinc disks, separated by layers of cloth soaked in a salt solution. Volta's invention of an electric battery had a significant impact on both chemistry and physics.

2.3.1 Electrolysis

While repeating Volta's experiments, William Nicholson, and Anthony Carlisle in England, accidentally observed that when terminals of wires from a battery are immersed in a tube of water, hydrogen gas is produced at the wire attached to a negative terminal and oxygen gas at the positive wire. Soon Humphrey Davy (1778–1829), a professor of chemistry at the Royal Institution in London, found that various salts could be decomposed by passing an electric current through molten salt solutions. He soon discovered a series of alkali and alkaline earth elements (Na, K, Ca, Mg, Sr, and Ba) based on the decomposition of molten salts or salt solutions. This was the discovery of chemical decomposition by means of an electric current or an *electrolysis*, as Michael Faraday, who had been Day's assistant and protégé called it in the 1830s.

The passage of an electric current through an electrolyte (salt solution) induces chemical changes and elements can appear at either electrode. If they are gases, they bubble off. Faraday introduced the term *ions* (Greek word meaning wanderer) to describe the chemical species passing through the solution. He also introduced the terms *anion* and *cation* for positive and negative ions and *anode* and *cathode* for positive and neg-

ative electrodes. Faraday carefully measured the mass of an element produced as a function of the amount of electricity and discovered two basic laws.

1. For a given solution, the amount of material deposited or liberated on the electrodes is proportional to the total amount of electricity.
2. The monovalent ions of different substances also carry an equal amount of electricity while multivalent ions carry correspondingly larger charges.

The Faraday laws, for the first time, suggested the existence of a universal unit of electric charge, known at that time only to be attached to the chemical species. He defined that one *Faraday* of electricity represents 96,500 C. A Faraday of electricity can be viewed as containing Avogadro's number of electrical units. This indivisible unit of electricity identified in electrolysis was given the name *electron* (ηλεκτρον), the Greek word for amber, by the Irish physicist and astronomer George Johnstone Stoney (1894). The Swedish chemist Savante August Arrhenius in his *theory of ionic dissociation* presented in 1887 proposed that Faraday's ions were actually atoms carrying positive and negative electric charge.

2.3.2   Electromagnetism

The credit for the discovery of *electromagnetism* belongs to Hans Christian Oersted, a professor of physics at the University of Copenhagen. In 1820, Oersted demonstrated that an electric current deflects a compass needle, thus showing an intimate connection between electricity and magnetism. A current carrying wire exerts a force on a compass needle. If the compass is continuously moved in the direction it is pointed, it will trace out a circle around the wire. Oersted also observed that a magnet will exert a force on a coil of wire (*solenoid*) carrying an electric current—the solenoid would act like a bar magnet, one end acting like the north pole and the other end as the south pole. Thus, the concept of electromagne-

tism as a unified force was realized. In 1820, Andre Marie Ampere, professor of mathematics at the Ecole Polytechnique in Paris, observed that parallel wires attract or repel each other if they carry electric currents flowing in the same or opposite directions, respectively. He concluded that all magnetism is electromagnetism and that the properties of a magnet (or loadstone) are due to tiny electric currents within the particles of the magnet.

In 1831, Faraday also observed that a magnet can induce an electric current in a wire and that the electric current in one coil can induce a current in another coil placed nearby. Before Faraday, the electric and magnetic forces (like gravity) were considered as acting across empty space between the interacting objects. Faraday was the first to propose the idea of a field of forces (or simply *field*) to explain how forces act over large distances. In the 1860s, the field concept of Faraday was developed into a quantitative mathematical formulation by James Clerk Maxwell, a British physicist. Maxwell showed that electric and magnetic fields do not exist independently, but only as a combined electromagnetic field with each of the components at right angles to each other. Using his equations Maxwell was also able to show that the electromagnetic field propagates through space as waves carrying away energy in the form of free electromagnetic radiation with a constant speed of 300,000 km s^{-1} or 3.0×10^{10} cm s^{-1}. In 1665, Newton showed that sunlight is not pure but consists of a band of colored light particles, which he called *spectrum* (from a Latin word meaning "ghost"). In contrast, the Dutch physicist, Huygens (1629–1695) revealed that light is composed of waves with different colors having different *wavelengths*. In 1801, Thomas Young, an English physicist, showed that the different colors of the spectrum have different wavelengths; red has longer wavelength (700 nm) than violet (400 nm). Since electromagnetic radiation travels with the same speed as light, in 1864, Maxwell was able to conclude that light is an electromagnetic radiation with certain wavelengths. His equations also suggested that there are many more varieties of electromagnetic radiations, differing only in their

wavelengths. Maxwell theory predicted that radiations of different wavelengths, which our eyes cannot see, can exist.

In 1800, even before Maxwell, the German–British astronomer, William Herschel discovered *infrared rays* by showing that the temperature of the dark area beyond red end of the spectrum is almost 1° higher than that of visible light. In 1801, the German chemist, John William Ritter discovered *ultraviolet rays* when he observed that a paper soaked in silver nitrate solution darkens more rapidly when exposed to the dark area beyond the violet end of spectrum.

Almost 20 years after Maxwell's prediction of the existence of electromagnetic radiations of different wavelengths, in 1888 the German physicist, Heinrich Rudolph Hertz, while setting up an oscillating electric current in a rectangular wire, accidentally discovered a new kind of radiation. These rays called *radiowaves* lay far beyond the infrared radiation and could have wavelengths of anywhere between a few centimeters to kilometers. Subsequently, electromagnetic radiations, such as *X-rays* and *γ rays*, far beyond the ultraviolet X-rays were discovered with wavelengths exceedingly smaller than that of visible light, thus confirming Maxwells' electromagnetic theory.

2.4   Thermodynamics

The scientific study of heat started with the construction of the first thermometer in an attempt to express the amount of heat in quantitative terms. In 1592, Galileo first invented an instrument known as *thermoscope* to measure the temperature; however, he did not introduce temperature scale. The first thermometer using mercury was built in Italy around 1650 by the *Accademia del Cimento*. In 1714, the German physicist Daniel Gabriel Fahrenheit assumed that the temperature of a mixture of ice and salt is zero degree, while the body temperature is set at 96 degrees. On this *Fahrenheit scale*, water has a freezing point of 32 degrees and a boiling point of 212 degress. In 1743, the Swedish astronomer Anders Celsius introduced a *Celsius*

or *centigrade scale* and showed that the freezing point of water is 0 °C and the boiling point is 100 °C. Both these scales are based on the assumption that the expansion coefficient of mercury is relatively constant.

While working on the mechanical properties and the compressibility of air and other gases, Boyle discovered that the volume of a gas at a constant temperature is inversely proportional to its pressure. Almost a century later, it was discovered that gases expand at higher temperature. In 1791, the expansion coefficient for air at constant pressure was measured by Volta and was found to be 1/273 on the Celsius scale. Around 1800, two French chemists Joseph Gay-Lussac and Jacques Charles observed that this expansion coefficient is the same for all gases regardless of the chemical nature of the gas. Similarly, the pressure of any gas at a constant volume increases at a constant rate, 1/273 of its initial volume at 0 °C for each degree of increase in temperature. Thus, at −273 °C, the pressure and volume of any gas are expected to drop to zero value.

2.4.1   Heat, Energy, and Temperature

Two different doctrines developed in the eighteenth century helped to explain the nature of heat and to establish units for the quantity of heat, separate from that of temperature. According to one theory heat is a substance with or without mass (or weight) while the other theory suggests that heat is a type of motion or vibration. The Scotch physician Joseph Black regarded heat as a substance and called it *calor*. He defined the unit of heat as the amount necessary to raise the temperature of 1 lb of water by 1 °F. In the Metric system, 1 cal is the amount of heat needed to raise 1 g of water by 1 °C. In 1799, Benjamin Thompson (also known as Count Rumford) presented some data which suggested that heat is a type of motion and not a material substance. In 1842, the ideas of Count Rumford were further developed by the German physician Julius Robert Meyer who tried to establish a relationship between heat production and mechanical work,

and in the process discovered the *law of conservation of energy*. In the 1840s, the Englishman James Prescott Joule performed many experiments to clearly measure the mechanical equivalent of heat and by 1875 he was able to show that 1 cal is equal to 4.15 J.

The concept of energy is rather difficult to explain precisely; however, energy can be defined as the capacity to do work or to produce heat. In 1738, Daniel Bernoulli was one of the first scientists to show, mathematically, that the pressure of a gas depends on the mass, the number of molecules in a given volume of gas, and the average velocity of the gas molecules. However, he could not explain the relationship between the velocity of molecules and the temperature of gas. The Charles and Gay-Lussac law clearly demonstrated that the pressure of a gas is dependent on the temperature. Subsequently, based on Joule's work on the mechanical equivalent of heat, Maxwell discovered a statistical law which governs the velocity distribution in a monoatomic gas. More specifically, he found that the number of molecules in a given velocity interval is proportional to the density of gas and depends only on the temperature of the gas, and the absolute mass of the gas molecules. His equations can be used to calculate the average kinetic energy of gas molecules at any temperature. The British scientist, William Thompson (also known as Baron or Lord Kelvin), suggested that the kinetic energy of gas molecules be used to establish a temperature scale. Maxwell's equation predicts that at $-273.16\ °C$, the average kinetic energy of gas molecules will have zero kinetic energy. Therefore, the temperature of $-273.16\ °C$ can be regarded as *absolute zero* based on the *Kelvin scale* of temperature.

2.4.2   Emission of Light

In the beginning of the nineteenth century, the German physicist, Joseph von Fraunhofer (1787–1826) repeated Newton's experiments on the solar spectrum, using prisms of much better quality. He also invented a device, known as *diffraction grating* (a plate of glass or metal on which fine and equally spaced scratches or grooves) which divided light into its component colors, and observed that the spectrum of colors is intersected by a large number of very thin separate black lines. Von Frauenhofer recognized that these lines correspond to emission lines in sparks and flames. The significance of these lines (the signals coming from atoms and molecular species) was discovered in the 1860s by two German scientists Robert Wilhelm von Bunsen and Gustav Robert Kirchhoff.

It is well known that metals, such as iron and tungsten become luminous or give off visible light when heated to sufficiently high temperatures. The color of light varies with the temperature of the metal, going from red to yellow to white as it becomes hotter and hotter, while other frequencies of electromagnetic radiation that are invisible are also emitted. At room temperature, most of the radiation emitted is in the infrared range of the spectrum. Thus, at a high temperature, the emitted radiation has a high frequency and rapidly becomes more intense. In contrast, if we look through a prism at the light emitted by a hot gas, we see a continuous spectrum from red to violet. In a Bunsen burner however, the gas becomes very hot and emits very little of bluish light only. Bunsen discovered that when pure sodium or potassium is introduced into the Bunsen flame, the corresponding spectra contain only yellow or red colors. With the use of a spectroscope, Bunsen and Kirchhoff quickly realized that the dark lines in the solar spectrum correspond to the emission lines of specific hot gaseous elements. The law that all substances absorb the same light frequencies which they can emit was discovered by Kirchhoff, in 1860. The spectral analysis was soon utilized to discover new elements, such as Ce, Rb, Tl, In, and Ga.

2.5   Major Discoveries

2.5.1   Cathode Rays

Faraday's electrolysis experiments demonstrated the existence of ions, charged atoms, and molecules. In order to detect the particles of electricity

that are not associated with atoms or molecules, investigations were initiated to pass an electric current through a good vacuum. In 1838, Faraday was the first to actually force an electric current through a vacuum, however, since the vacuum was not good enough the observations lacked any significance.

In 1858, the German glassblower Johann Heinrich Wilhelm Geissler and the German physicist Julius Plucker developed a glass tube with two electrodes with very good vacuum (known as *Geissler tubes*). When the electrodes were connected to a source of electric current, a greenish luminescence appeared on the glass tube near the cathode. It was soon realized that the position of the glow does not depend on the anode, the nature of the gas molecules in the tube, or the kind of metal used to make the cathode. Instead, something from the cathode appeared to be moving straight and hitting the glass before being collected by the anode. The German physicist Johann Wilhelm Hittorf suggested that objects placed in front of a cathode cast shadows. The German physicist Eugen Goldstein, however, maintained that the glow is associated with the current itself and in 1876 introduced a name for this mysterious phenomenon: *Cathodenstrahlen*, or *cathode rays*. In 1878, the British physicist William Crookes devised vacuum tubes that produced cathode rays which clearly moved in straight lines and which were better than the cathode rays produced in Geissler tubes. The investigations on the nature of cathode rays with the Hittorf and Crookes vacuum tubes ultimately led to the discovery of X-rays and electron.

2.5.2 X-Rays

In 1895, the German physicist Wilhelm Röntgen, while investigating the effects of cathode rays in a discharge tube, accidentally, discovered a new form of penetrating radiation, which he called *X-rays*. He observed that when cathode rays (negatively charged particles) strike the atoms of a glass vacuum tube, they produce penetrating rays that cause salt (barium platinocyanide) to

glow. Soon thereafter, it was realized that X-rays are (1) more penetrating than the cathode rays and (2) not prone to deflection by a magnetic field and physicists started to discuss what these mysterious X-rays might be.

The true nature of X-rays was discovered in 1912 when the German physicist Max von Laue, using crystals as a type of three-dimensional grating, discovered that X-rays do not behave like particles, but instead have the wave-like characteristics of an electromagnetic radiation. An accelerated electric charge will radiate electromagnetic waves. As the fast-moving cathode rays approach the positive charge in the nucleus of glass atoms, electrons are brought to rest (accelerated) and the kinetic energy of the electrons is converted to electromagnetic waves. Radiation produced under these circumstances has been given the name *bremsstrahlung* (breaking radiation). It was also discovered, that when denser more massive atoms in a metal are used to stop the accelerated electrons, X-rays of higher energies can be generated. In 1911, the British physicist Charles Barkla noticed that each metal produced X-rays of a particular wavelength, called characteristic X-rays of a particular metal, and called the more penetrating beam *K* X-rays and, the less penetrating beam *L* X-rays. Subsequently, it was discovered that these characteristic X-rays emitted by metals are due to the deexcitation of electrons in the atomic shells.

2.5.3 Electron

Following the discovery of cathode rays and radiowaves, the Dutch physicist Hendrick Antoon Lorentz refined Maxwell's equations and developed a new theory, called *electron theory*. More specifically, Lorentz proposed that microscopic particles, each of which carry an electric charge, must be contained in all atoms and that these charged particles generate electric, and magnetic fields. He also proposed that oscillations of these charged particles inside the atoms are the source of light.

In 1895, the French physicist Jean Baptiste Perrin demonstrated that cathode rays, emitted from the cathode of a discharge tube, are negatively charged particles. In 1896, Lorentz deduced a value for the charge-to-mass ratio (*e/m*) for charged particles inside the atom. As a result of Lorentz's electron theory, it was presumed that a magnetic field would affect the electron oscillations and thereby the frequencies of the light emitted. In 1896, Pieter Zeeman observed such a broadening of the spectral lines by the magnetic field. Based on the Zeeman effect, Lorentz and Zeeman were, subsequently, able to estimate the *e/m* ratio and predict that the charge of the particles within the atom is negative.

In 1897, the British physicist Joseph John Thompson confirmed Perrin's observations and obtained a precise value for the *e/m* ratio of cathode rays. The ratio turned out to be over a thousand times greater than that of a hydrogen ion. Thompson also demonstrated that the cathode rays could be deflected by both magnetic and electric fields. He also discovered that cathode rays are negatively charged particles, which he initially called *corpuscles*. He later changed the name and called them electrons; the name first suggested by Johnstone G. Stoney in 1894. Thompson's measurement of an electron's mass and charge confirmed that cathode rays (electrons) are the same particles within the atom are also responsible for the emission of light by the atom. In 1911, the American physicist Robert Andrews Milikan succeeded in measuring quite accurately, the minimum electric charge that could be carried by a particle and found that if this charge were carried by an electron, it would have to be only 1/1837 as massive as a hydrogen atom.

In 1899, Philipp Lenard, while investigating the interaction of cathode rays with in metal plates, discovered that electrons are ejected when ultraviolet light strikes metal surfaces. He also discovered that the emission of electrons is dependent on the frequency of light but not on the intensity of light. This phenomenon, known as the photoelectric effect, was later explained by Albert Einstein and is based on the light quantum hypothesis proposed by Max Plank, in 1900.

2.5.4   Radioactivity

Henry Becquerel, professor of physics at the Ecole Polytechnique in Paris, heard about the discovery of X-rays and immediately thought of a possible connection between X-rays and fluorescence. He quickly initiated a series of experiments testing whether fluorescent substances emitted X-rays. In February 1896 he was exploring the possibility that sunlight might cause crystals to emit penetrating rays like the X-rays. As luck would have it, he used uranium–potassium bisulfate (uranium salts were known to be phosphorescent). These crystals were placed next to a photographic plate wrapped in dark paper. If sunlight causes the crystals to emit penetrating rays, then these rays might penetrate the dark paper and darken the plate. Since the weather was cloudy, Becquerel placed the unwrapped plates in the drawer of a cabinet leaving the crystals on the cabinet. Much to his surprise, a couple of days later, when he developed the plates, he found intense darkening of the plate, due to exposure to some intense radiation. Becquerel quickly concluded that invisible rays from uranium had penetrated the cabinet and the dark paper covering the plate and finally exposed the photographic plate. For a few years, these rays were known as "Becquerel rays" or *rayons uranique*. In 1898, Maria Sklodowska Curie and Pierre Curie (Fig. 2.3) discovered that the element thorium also emitted such rays. That year, the Curies coined the name *radioactivity* to describe the phenomenon of penetrating radiation emitted by uranium and thorium.

In the following years, other new radioactive phenomena were discovered. For example, in 1900 the French chemist, Paul Villard discovered an extremely penetrating form of radiation coming from radioactive sources. However, it was Ernest Rutherford (Fig. 2.2) at the Cavendish Laboratory in England who played a major role in the study of radioactivity. Rutherford and his colleagues identified three different components in the radiations from radioactive elements based on their behavior in electric and magnetic fields. He called them, *α-rays*, *β-rays*, and *γ-rays* and these components were eventually identified as being helium nuclei, electrons, and high-energy photons, respectively.

Fig. 2.2 Ernest Rutherford (on left), an English physicist, and the winner of the Nobel prize in chemistry. Niels Henrik David Bohr (on right), a Danish physicist, and the winner of the Nobel prize in physics

In 1903, Rutherford and Soddy sought to explain the cause and nature of radioactivity. They proposed a *disintegration theory*, which defined radioactivity as a change of one chemical element into another with the emission of alpha or beta particles. An unstable element reaches stability spontaneously by undergoing radioactive decay involving transmutation of elements and emission of energy; however, in the 1930s it was discovered that radioactive elements can also emit positively charged electrons or *positrons*.

2.5.5 Light Quantum

The classical theory of matter assumes that matter in general can absorb or emit any quantity of energy. It also predicts that the radiation profile of the emission spectrum has no maximum and goes to infinite intensity, at shorter wavelengths (or higher frequencies). This effect is called *ultraviolet catastrophe*. An ideal material body, known as the *black body*, is one that can absorb all radiations incident. Therefore, since it can absorb all radiations, it should also emit radiations of all frequencies. The experimental evidence, however, indicated that when a piece of metal is heated to incandescence, the profile of radiation emitted shows that the maximum (peak) shifts to shorter wavelengths as the temperature is increased. The question is why does the intensity of radiation drop gradually as the frequency of radiation increases? In 1901, the German physicist Max Planck's postulated that the energy of radiation can be absorbed or emitted by bodies only in specific packets or amounts and called of these small packets of energy a *quantum*. The energy (E) of each quantum is a product of the frequency of radiation (n) and a constant, h (known as Plank's constant). The value of h was determined to be 6.626×10^{-34} J. Hz^{-1}.

2.6   Reality of Atoms

2.6.1   Avogadro's Number

Avogadro's number is the calculated value of the number of atoms (or molecules) in a gram mole of any chemical substance. Although, as early as the seventeenth century, Boyle had attempted to estimate the size of atoms, it was not until 1865 that the first successful attempt was made by the Austrian physicist and schoolteacher Josef Loschmidt. Based on Avogadro's hypothesis, the atomic weights of several gaseous elements were accurately determined in 1860 by the Italian chemist Stanislao Cannizzaro. Subsequently, in 1865, using the new *Kinetic Molecular Theory*, developed by Maxwell and Clausius, Loschmidt found the number of atoms in 1 cm^3 of gaseous substance, under ordinary conditions of temperature and pressure, to be somewhere around 2.6×10^{19} atoms cm^{-3} (this is known as *Loschmidt's Constant*). Since 1 mol of any gas occupies 22.4 L at STP, the number of atoms in 1 mol is approximately equal to 5.8×10^{23} atoms.

2.6.2   Brownian Motion

In 1827, Robert Brown observed the random movement of pollen particles in a liquid. This phenomenon, known as *Brownian motion*, states that microscopic particles in a liquid are never at rest; they are in perpetual movement even under conditions of perfect external equilibrium or constant temperature. The only irrefutable explanation for this phenomenon ascribes the movements of the particles to the shocks produced by the atoms and molecules of the liquid themselves. A mathematical theory of this phenomenon was developed by Einstein, in 1905, and a theoretical estimate of Avogadro's number was given to be 6.2×10^{23} particles. The first experimental proof of this theory was provided by Jean Baptiste Jean Perrin in France around 1908. More specifically, Perrin determined that the number of atoms in 1 mol is approximately 6.8×10^{23}. The work of Einstein and Perrin provided some of the first concrete evidence for the existence of atoms. The current experimental value of $6.022\,140\,76 \times 10^{23}$ atoms per mole is the average for measurements using the best methods (Fig. 2.3).

Fig. 2.3 Antoine Henri Becquerel (on right), Pierre Curie (middle), and Marie Curie nèe Sklodowska (on right) received the Nobel Prize in Physics in 1903 for the discovery of spontaneous radioactivity and radiation phenomena

2.7 Atomic Structure

2.7.1 Nuclear Atom

Since 1890, various discoveries have shown that the atom is not indivisible (as Dalton supposed) but is really composed of parts. The discovery of *radioactivity*, the interaction of electricity with matter, and the discovery of free *electrons* have all contributed to the discovery of the subatomic structure of atoms. In 1910, Rutherford (Fig. 2.2) presented a model of an atomic structure, known as *nuclear atom*. According to this nuclear model, atoms consist of a massive, compact, positively charged core, or *nucleus*, surrounded by a diffuse cloud of relatively light, negatively charged electrons. In 1913, Moseley formulated the property of *atomic number* (*Z*), which is the number of positive charges in the nucleus. Moseley showed that the sequence of elements in the periodic table is, in fact, a sequence of elements that are arranged in order of their atomic numbers and not their atomic weight. In 1914, Rutherford named this positively charged particle in the nucleus, *proton* (from the Greek word "first"). A proton has an electrical charge exactly equal to that of an electron but, positive, and a mass 1836 times that of an electron. Incidentally, the nucleus of a hydrogen atom is known as the proton. In the electrically neutral atom, the number of orbiting electrons is sufficient to exactly balance the number of positive protons. In 1920s, Rutherford speculated that a neutral particle (one that is the same size as a proton) within the nucleus accounts for the total mass of the atom. Such a neutral particle was discovered by James Chadwick, in 1932. Heisenberg soon proposed that nuclei of different elements consist of protons and neutrons which are held together by strong exchange forces, known as nuclear forces. The total number of protons and neutrons within the nucleus is called the *mass number* (*A*), which is very close to the atomic weight of an element. The mass number (*A*) of ^{12}C nuclide is 12 and its atomic mass is considered as 12 atomic mass units (AMU or u). The atomic weight of natural carbon is 12.011 since it is a mixture of ^{12}C (98.89%) and ^{13}C (1.11%) nuclides or isotopes.

2.7.2 Bohr's Model of Atom

The atom consists of an extremely dense, low positively charged nucleus surrounded by a cloud of electrons with small size and mass, with each electron carrying a single negative charge equal but opposite to that of a proton in the nucleus. Because the number of electrons and protons in an atom are the same, the whole atom is electrically neutral. The *atomic volume* (10^{-8} cm diameter) with the cloud of electrons is significantly much larger compared to the volume of the nucleus (10^{-13} cm diameter). Based on Rutherford's discovery of atomic nucleus and Plank's discovery of energy quantum ($E = hn$), Neils Bohr (Fig. 2.2) developed the first quantum model of an atom (Fig. 3.4 in Chap. 3), in 1913. According to this model, an electron in a hydrogen atom rotates around the nucleus at high speeds in closed *circular orbits* associated with a characteristic *quantum number* (*n*). The electron in general exists in a low energy orbit (*ground state*). The gain or loss of a quantum of energy occurs only when an electron moves from one orbital to one of greater or lesser energy. As a result, an atom can absorb or emit energy in discrete units or quanta.

In 1916, Arnold Sommerfeld suggested that the electron orbits can also be elliptical and at different degrees. Subsequently, the orbital *quantum number* (*l*) was introduced, which assumes the circular and elliptical orbits are in a single plane. When atoms are in a magnetic field, however, the orbits may be tipped and can be best represented in a three-dimensional spherical space around the nucleus. To account for this magnetic effect, a *magnetic quantum number* (*m*) was introduced. Subsequently, Wolfgang Pauli introduced the *spin quantum number* (*s*) to represent the direction of the electron spin (clockwise or anti-clockwise). The arrangement of electrons around the nucleus in an atom can be described based on the

four quantum numbers. A more detailed example of electron orbits based on quantum mechanics is provided in Chap. 7.

2.7.3   Isotopes

Dalton assumed that all the atoms of a given element have the same *atomic weight* or *atomic mass*. By 1914, it was realized that atoms of the same element can vary in weight but may have the same chemical properties. The word *isotope* was coined by Frederick Soddy to represent atoms of an element that have different weights but still can be placed in the same place in the periodic table. An isotope can be stable or unstable (radioactive). Some of the elements in nature such as Na, F, Al, and Bi have no isotopes, while 81 of the elements listed in the periodic table have at least one stable isotope. Further, all elements heavier than Bi are unstable; no stable isotope exists for these elements. In 1947, the American chemist Truman Paul Kohman suggested that the word *nuclide* is a more appropriate term to represent both the stable and unstable atoms (or radionuclide), of an element.

For any given element, the percentage of each isotope found in nature is called the isotope's *isotopic abundance*. Natural carbon exists in two stable isotopic forms (^{12}C and ^{13}C); the isotopic abundance of ^{12}C is 98.9% while the abundance of ^{13}C is very small—only 1.1%. Since the atomic mass of an element is expressed as an average of all the naturally occurring isotopes, the average atomic mass of carbon is 12.011. Similarly, the average atomic mass of copper is 63.545, since it has two stable isotopes: ^{63}Cu (69.2%) and ^{65}Cu (30.8%).

In nature, 92 elements (hydrogen to uranium) have been observed. Technetium and promethium, and all elements with atomic numbers greater than 82 have isotopes that are known to decompose through radioactive decay. Stable elements are 82, however, 252 isotopes (nuclides) are stable. In addition, >3000 nuclides are known to be radioactive.

2.7.4   Quantum Atom

At first Bohr's model appeared to be very promising but, by the mid-1920s, it became clear that Bohr's model needed refinement. The wave mechanics or quantum mechanics developed by Werner Heisenberg, Louis deBroglie, and Edwin Schrodinger finally provided a wave or quantum mechanical description of an atom. Quantum theory describes matter (electrons and electromagnetic radiation) as acting both as a particle and as a wave. This characteristic is called wave-particle duality. According to this model, the electron bound to the nucleus is similar to a standing or stationary wave, while the circumference of a particular orbit corresponds to a whole number of wavelengths. Schrodinger's famous wave equation ($Hy = Ey$) describes an electron in an atom, where y called the wave function, is a function of the coordinates (x, y, and z) of the electron's position in three-dimensional space and H represents a set of mathematical instructions called an *operator*. When this equation is analyzed, many solutions are found. Each solution consists of a wave function y that is characterized by a particular value of energy, E. A specific wave function for a given electron is often called an *orbital*. An orbital, however, is not a Bohr's orbit; the orbitals differ from each other in size, angular momentum, and magnetic properties. The wave function corresponding to the lowest energy of a hydrogen atom is called 1 *s* orbital. Quantum mechanics only provides the probability of an electron's position around the nucleus but, not the electron's motion around the nucleus. Also, each electron in an atom has a unique set of quantum numbers. *In a given atom, no two electrons can have the same set of four quantum numbers* (n, l, m_e, m_s). This is called the *Pauli Exclusion Principle*, which can also be stated as follows: *An orbital can hold only two electrons and they must have opposite spins*.

The atom's electron cloud—that is the arrangement of electrons around the nucleus in an atom—determines most of the atom's physical and chemical properties. The electrons in the out-

ermost shell, in particular, determine the chemical properties of an atom. Atoms bond with other atoms by donating or sharing electrons in order to fill their shells. It requires less energy to exist in this bonded state; atoms always seek to exist in the lowest energy state possible.

2.7.5   Discovery of Antimatter

In particle physics, *antimatter* is an extension of the concept of antiparticle to matter, where antimatter is composed of antiparticles (such as antielectron and antiproton) in the same way that normal matter is composed of particles (electrons and protons). In 1928, Paul Adrien Maurice Dirac, a physicist at Cambridge, combined relativity, and quantum mechanics in order to derive an equation that provides a complete description of the electron. Surprisingly, this theory not only described electrons but the particles we call *positrons* or antielectrons, as well. Dirac's theory predicted that when an electron encounters a positron, the two charges cancel each other out, and the pair annihilates, with the combined mass transforming into high-energy radiation of a pair of annihilation photons (511 keV). This conversion of mass into energy is the most dramatic expression of Einstein's celebrated equation $E = mc^2$. The theory also predicted that high-energy photons could rematerialize as matter and antimatter in a process known as the *pair production*. In 1932, positrons were first discovered by Carl D. Anderson, who gave the positron its name. More specifically, the positron was discovered by passing cosmic rays through a cloud chamber. In 1934, Irène Curie and Frédéric Joliot confirmed the existence of the positron by bombarding aluminum with alpha particles. This resulted in the artificial production of radionuclide ^{30}P, which quickly decayed to stable silicon by emitting positrons. Dirac, Anderson, Curie, and Joliot all received Nobel prizes for their pioneering discoveries. Subsequently in 1955, Emilio Segre and Owen Chamberlain discovered the antiproton using high-energy protons (6.5 billion eV) generated in a Bevatron accelerator at the Lawrence Berkeley Radiation Laboratory, in California.

2.8   The Elementary Particles

In particle physics, an elementary particle or a fundamental particle is a subatomic particle that is not composed of other particles. The notion that the atom is the ultimate building block of all matter in the universe is no longer valid. In the 1930s, it seemed that protons (with positive charge), neutrons (with no charge), and electrons (with negative charge) were the smallest objects into which matter could be divided. As a result, these three particles were regarded as the *elementary particles* or fundamental particles.

The Standard Model of particle physics is the theory classifying all known elementary particles, as well describing the three of the four known fundamental forces (electromagnetic, weak, and strong nuclear forces) in the universe. In particle physics, an *elementary particle* is a particle without a substructure; that is, it is not made up of smaller particles. The current accepted "Standard Model" of physics, which describes the interactions of particles and almost all forces in nature, recognizes 17 (seventeen) elementary particles. All elementary particles are either *fermions or bosons*; particles normally associated with matter (such as proton, neutron, and electron) are fermions, while elementary bosons (such as photon) are force carriers that function as the "glue" holding matter together. Among the bosons, only the photon is the most realistic elementary energy particle (Table 2.1).

In 1968, it was discovered that the proton contained much smaller, point-like objects and was, therefore, not an elementary particle. The objects in the proton were identified as up and down quarks. The up quark has a fractional negative positive charge $(+\tfrac{2}{3}e)$, while the down quark has a fractional negative charge $(-\tfrac{1}{3}e)$. Quarks are the fundamental constituents of protons and neutrons. Quarks are thought to have no internal structure, meaning that they exist as zero-dimensional points that take up no space. Individual quarks are never found in nature; however, quarks always bind together to form composite particles—the hadrons. The up quark and the down quark are generally stable, and they are

Table 2.1 Physical properties of elementary particles[a]

Particle	Charge	Mass (MeV/c^2)	Mass (kg)	Charge radius (m)	Spin	Mean lifetime
Photon (γ)	0	0	0	–	1	Stable
Electron (e⁻, β⁻)	−1	0.511	9.109×10^{-31}	–	1/2	Stable
Positron (e⁺, β⁺)	1	0.511	9.109×10^{-31}	–	1/2	Stable
Up Quark (u)	+2/3 e	2.2	–	10^{-18}	1/2	Stable in proton
Down Quark (d)	−1/3 e	4.7	–	10^{-18}	1/2	Stable in proton
Proton or uud (p⁺ or H⁺)	1	938.272	1.672×10^{-27}	$<10^{-15}$	1/2	$>10^{30}$ years
Neutron or ddu (n, n⁰)	0	939.565	1.674×10^{-27}	$<10^{-15}$	1/2	879.6 s

[a] The above values are from Wikipedia
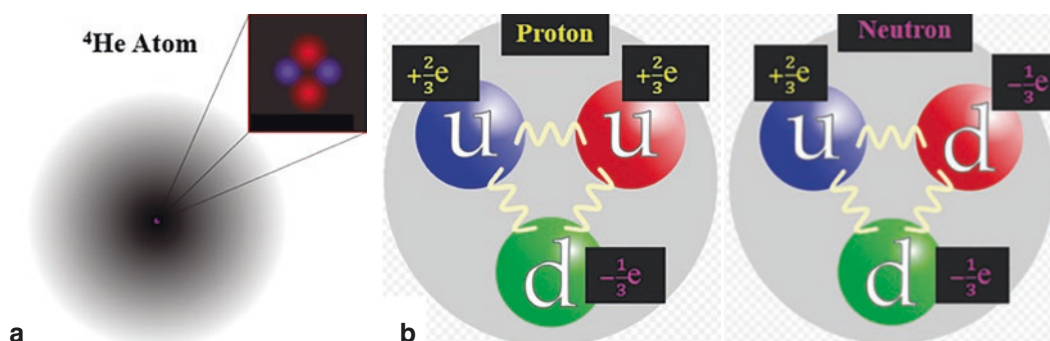

Fig. 2.4 Helium atom (**a**) with nucleus in the center with 2 protons and 2 neutrons. Proton (**b**) consists of 2 up quarks and 1 down quark, while neutron (**c**) consists of 2 down quarks and 1 up quark (b)

found in protons and neutrons. A proton is composed of two up quarks and, one down quark, while a neutron is composed of one up quark and two down quarks (Fig. 2.4). In the radioactive β⁻ process, a neutron "splits" into a proton, an electron, and an antineutrino. This process occurs when one of the down quarks in the neutron (udd) decays into an up quark by emitting a W⁻ boson, transforming the neutron into a proton (uud). The W⁻ boson then decays into an electron (e^-) and an electron antineutrino (ν_e).

Quarks are one of the primary building blocks of matter in the universe. The Nobel laureates Murray Gell-Mann and George Zweig first proposed the quark model, in 1964. It was also discovered that there are six *flavors* of quarks; the three positively charged quarks are called *up-type quarks* (*Up*, *Charm*, and *Top*) and the three negatively charged quarks are called *Down-type quarks* (*Down*, *Strange*, and *Bottom*). The more massive quarks produced in particle accelerators and cosmic rays are unstable and rapidly decay.

Because quarks cannot exist independently, the elementary particles in nature representing fermions are protons, neutrons, and electrons. It is the combination of these three subatomic particles that resulted in the formation of chemical elements, billions of years ago.

Further Reading

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