ATOMIC STRUCTURE

1. The Atomic Theory

In the fifth century B.C. the Greek philosopher Democritus expressed the belief that all matter consists of very small, indivisible particles, which he named *atomos* (meaning uncuttable or indivisible). Although Democritus' idea was not accepted by many of his contemporaries (notably Plato and Aristotle), somehow it endured. Experimental evidence from early scientific investigations provided support for the notion of "atomism" and gradually gave rise to the modern definitions of elements and compounds. In 1808 an English scientist and school teacher, John Dalton formulated a precise definition of the indivisible building blocks of matter that we call atoms. This, we come to know today as the Dalton's Atomic Theory, marked the beginning of the modern era of chemistry.

Dalton's Atomic Theory

The hypotheses about the nature of matter on which Dalton's atomic theory is based can be summarized as follows:

1. Elements are composed of extremely small particles called atoms.
2. All atoms of a given element are identical, having the same size, mass, and chemical properties. The atoms of one element are different from the atoms of all other elements.
3. Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.
4. A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in their creation or destruction.

Illustrations of the Dalton's Atomic Theory: Dalton's concept of an atom was far more detailed and specific than Democritus'. Dalton imagined an atom that was both extremely small and indivisible.

Theory 1. Elements are composed of extremely small particles called atoms. This means that an ***atom*** is *the basic unit of an element that can enter into chemical combination*.

Theory 2. All atoms of a given element are identical, having the same size, mass, and chemical properties. The atoms of one element are different from the atoms of all other elements. See figure 2.1.

Theory 3. Compounds are composed of atoms of more than one element. In any compound, the ratio of the numbers of atoms of any two of the elements present is either an integer or a simple fraction.

This hypothesis suggests that, to form a certain compound, we need not only atoms of the right kinds of elements, but specific numbers of these atoms as well. This idea is an extension of a law published in 1799 by Joseph Proust, a French chemist. Proust's ***law of definite proportions*** states that *different samples of the same compound always contain its constituent elements in the same proportion by mass.* Therefore, if we were to analyze samples of carbon dioxide gas obtained from different sources, we would find in each sample the same ratio by mass of carbon to oxygen. It stands to reason, then, that if the ratio of the masses of different elements in a given compound is fixed, the ratio of the atoms of these elements in the compound also must be constant.

Dalton's third hypothesis supports another important law, the ***law of multiple proportions.*** According to the law, *if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element are in ratios of small whole numbers.* Dalton's theory explains the law of multiple proportions quite simply: Different compounds made up of the same elements differ in the number of atoms of each kind that combine. For example, carbon forms two stable compounds with oxygen, namely, carbon monoxide and carbon dioxide. Modern measurement techniques indicate that one atom of carbon combines with one atom of oxygen in carbon monoxide and with two atoms of oxygen in carbon dioxide. Thus, the ratio of oxygen in carbon monoxide to oxygen in carbon dioxide is 1:2. This result is consistent with the law of multiple proportions

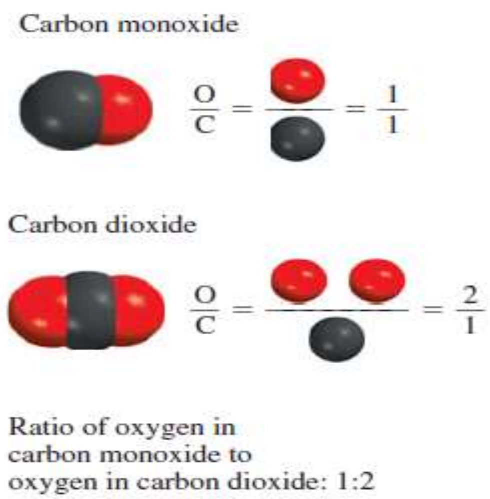


Figure 2.2 *An illustration of the law of multiple proportions.*

Theory 4. A chemical reaction involves only the separation, combination, or rearrangement of atoms; it does not result in their creation or destruction

Dalton's fourth hypothesis is another way of stating the ***law of conservation of mass,*** which is that *matter can be neither created nor destroyed.* Because matter is made of atoms that are unchanged in a chemical reaction, it follows that mass must be conserved as well. Dalton's brilliant insight into the nature of matter was the main stimulus for the rapid progress of chemistry during the nineteenth century.

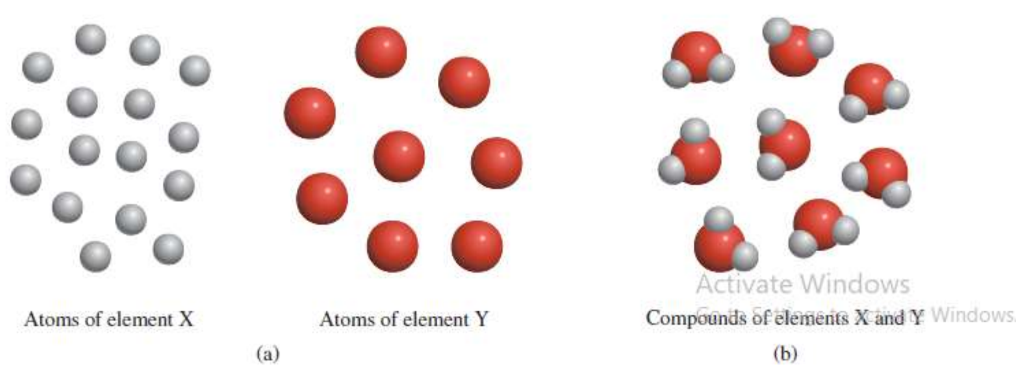


Figure 2.1 *(a) According to Dalton's atomic theory, atoms of the same element are identical, but atoms of one element are different from atoms of other elements. (b) Compound formed from atoms of elements X and Y. In this case, the ratio of the atoms of element X to the atoms of element Y is 2:1. Note that a chemical reaction results only in the rearrangement of atoms, not in their destruction or creation.*

Shortfalls of the Dalton's Atomic Theory: Although the Dalton's atomic theory was widely accepted for decades, discoveries of sub particles and radioactivity have totally countered these theories. Notwithstanding, Dalton's atomic theory remains the basic foundation of modern chemistry.

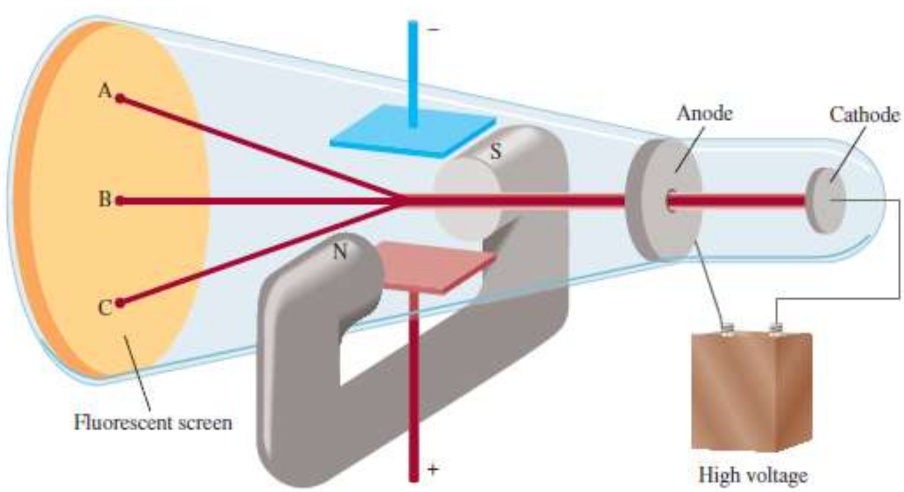
2. **Discovery of Subatomic Particles**

On the basis of Dalton's atomic theory, we can define an ***atom*** as *the basic unit of an element that can enter into chemical combination.* Dalton imagined an atom that was both extremely small and indivisible. However, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure; that is, they are made up of even smaller particles, which are called *subatomic particles.* This research led to the discovery of three such particles—electrons, protons, and neutrons.

i. **The Electron**

In the 1890s, many scientists became caught up in the study of ***radiation***, *the emission and transmission of energy through space in the form of waves.* Information gained from this research contributed greatly to our understanding of atomic structure. One device used to investigate this phenomenon was a cathode ray tube, the forerunner of the television tube. It is a glass tube from which most of the air has been evacuated. When the two metal plates are connected to a high-voltage source, the negatively charged plate, called the *cathode,* emits an invisible ray. The cathode ray is drawn to the positively charged plate, called the *anode,* where it passes through a hole and continues traveling to the other end of the tube. When the ray strikes the specially coated surface, it produces a strong fluorescence, or bright light.

Figure 2.3 *A cathode ray tube with an electric field perpendicular to the direction of the cathode rays and an external magnetic field. The symbols N and S denote the north and south poles of the magnet. The cathode rays will strike the end of the tube at A in the presence of a magnetic field, at C in the presence of an electric field, and at B when there are no external fields present or when the effects of the electric field and magnetic field cancel each other.*



J. J. Thomson's Cathode Rays Experiment: An English physicist, J. J. Thomson (Joseph John Thomson (1856–1940). British physicist who received the Nobel Prize in Physics in 1906 for discovering the electron), used a cathode ray tube and his knowledge of electromagnetic theory to determine the following about the electrons from the cathode rays Experiment:

i. Electrons are negatively charged
ii. The mass of the electron is infinitesimally small, and difficult to determine
iii. the ratio of electric charge to the mass of an individual electron is -1.76×10^{8} C/g, where C stands for *coulomb,* which is the unit of electric charge.

R. A. Millikan's Oil Drop Experiment: in a series of experiments carried out between 1908 and 1917, R. A. Millikan (Robert Andrews Millikan (1868–1953). American physicist who was awarded the Nobel Prize in Physics in 1923 for determining the charge of the electron) succeeded in measuring the charge of the electron with great precision. His work proved that the charge on each electron was exactly the same. In his experiment, Millikan examined the motion of single tiny drops of oil that picked up static charge from ions in the air. He suspended the charged drops in air by applying an electric field and followed their motions through a microscope.

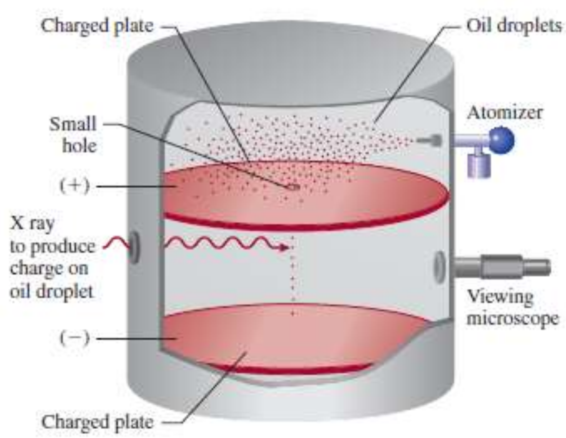


Figure 2.5 *Schematic diagram of Millikan's oil drop experiment.*

Using his knowledge of electrostatics, Millikan found the charge of an electron to be -1.6022×10^{-19}. From these data he calculated the mass of an electron:

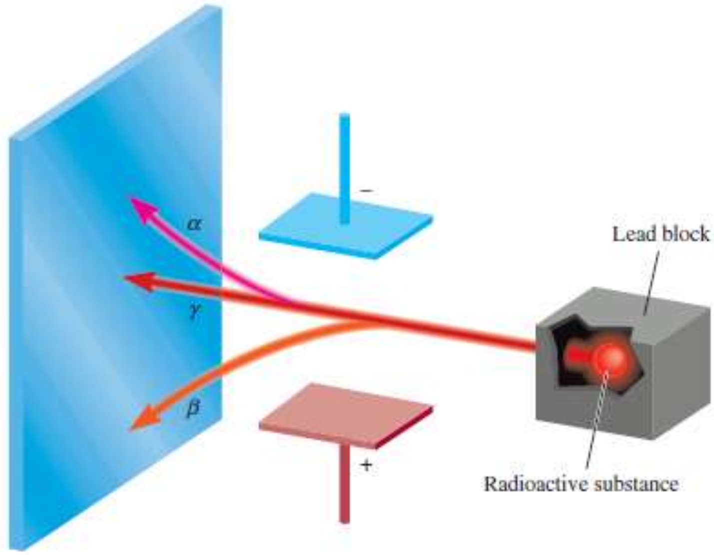
$$\begin{aligned} \text{mass of an electron} &= \frac{\text{charge}}{\text{charge/mass}} \\ &= \frac{-1.6022 \times 10^{-19}\,\text{C}}{-1.76 \times 10^{8}\,\text{C/g}} \\ &= 9.10 \times 10^{-28}\,\text{g} \end{aligned}$$

This is an exceedingly small mass.

W. K. Röntgen's x-rays Experiment: In 1895, the German physicist Wilhelm Röntgen (Wilhelm Konrad Röntgen (1845–1923), a German physicist who received the Nobel Prize in Physics in 1901 for the discovery of X rays) noticed that cathode rays caused glass and metals to emit very unusual rays. This highly energetic radiation penetrated matter, darkened covered photographic plates, and caused a variety of substances to fluoresce. Because these rays could not be deflected by a magnet, they could not contain charged particles as cathode rays do. Röntgen called them X rays because their nature was not known.

Radioactivity: Not long after Röntgen's discovery, Antoine Becquerel (Antoine Henri Becquerel (1852–1908). French physicist who was awarded the Nobel Prize in Physics in 1903 for discovering radioactivity in uranium.}, a professor of physics in Paris, began to study the fluorescent properties of substances. Purely by accident, he found that exposing thickly wrapped photographic plates to a certain uranium compound caused them to darken, even without the stimulation of cathode rays. Like X rays, the rays from the uranium compound were highly energetic and could not be deflected by a magnet, but they differed from X rays because they arose spontaneously. One of Becquerel's students, Marie Curie (Marie (Marya Sklodowska) Curie (1867–1934). Polish-born chemist and physicist. In 1903 she and her French husband, Pierre Curie, were awarded the Nobel Prize in Physics for their work on radioactivity. In 19t11, she again received the Nobel prize, this time in chemistry, for her work on the radioactive elements radium and polonium. She is one of only three people to have received two Nobel prizes in science. Despite her great contribution to science, her nomination to the French Academy of Sciences in 1911 was rejected by one vote because she was a woman! Her daughter Irene, and son-in-law Frederic Joliot-Curie, shared the Nobel Prize in Chemistry in 1935.), suggested the name ***radioactivity*** to describe this *spontaneous emission of particles and/or radiation.* Since then, any element that spontaneously emits radiation is said to be *radioactive.* Three types of rays are produced by the *decay,* or breakdown, of radioactive substances such as uranium. Two of the three are deflected by oppositely charged metal plates.

Figure 2.6 *Three types of rays emitted by radioactive elements. β rays consist of negatively charged particles (electrons) and are therefore attracted by the positively charged plate. The opposite holds true for α rays—they are positively charged and are drawn to the negatively charged plate. Because γ rays have no charges, their path is unaffected by an external electric field.*



Alpha (α) rays consist of *positively charged particles,* called α ***particles,*** and therefore are deflected by the positively charged plate. ***Beta (β) rays,*** or β ***particles,*** are *electrons* and are deflected by the negatively charged plate. The third type of radioactive radiation consists of high-energy rays called ***gamma (γ) rays*.** Like X rays, γ rays have no charge and are not affected by an external field.

Quiz: ***The following subatomic particles can be found in an atom: electrons, x-rays and β-particles, Protons and Neutrons. What do they have in common? What are their differences?***

ii. The Proton and the Nucleus

JJ Thompson's Model of an Atom: By the early 1900s, two features of atoms had become clear: they contain electrons, and they are electrically neutral. To maintain electric neutrality, an atom must contain an equal number of positive and negative charges. Therefore, Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded like raisins in a cake. This so-called "plum-pudding" model was the accepted theory for a number of years.

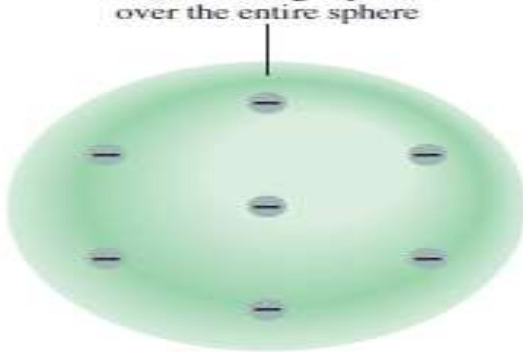


Figure 2.7 *Thomson's model of the atom, sometimes described as the "plum-pudding" model, after a traditional English dessert containing raisins. The electrons are embedded in a uniform, positively charged sphere.*

Rutherford's Model of the Atom (Rutherford's Alpha Scattering Experiment): In 1910 the New Zealand physicist Ernest Rutherford (Ernest Rutherford (1871–1937). New Zealand physicist. Rutherford did most of his work in England (Manchester and Cambridge Universities). He received the Nobel Prize in Chemistry in 1908 for his investigations into the structure of the atomic nucleus. His often-quoted comment to his students was that "all science is either physics or stamp-collecting.") who had studied with Thomson at Cambridge University, decided to use α particles to probe the structure of atoms. Together with his associate Hans Geiger (Johannes Hans Wilhelm Geiger (1882–1945). German physicist. Geiger's work focused on the structure of the atomic nucleus and on radioactivity. He invented a device for measuring radiation that is now commonly called the Geiger counter.) and an undergraduate named Ernest Marsden (Ernest Marsden (1889–1970). English physicist. It is gratifying to know that at times an undergraduate can assist in winning a Nobel Prize. Marsden went on to contribute significantly to the development of science in New Zealand.), Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for α particles from a radioactive source (see figure below).

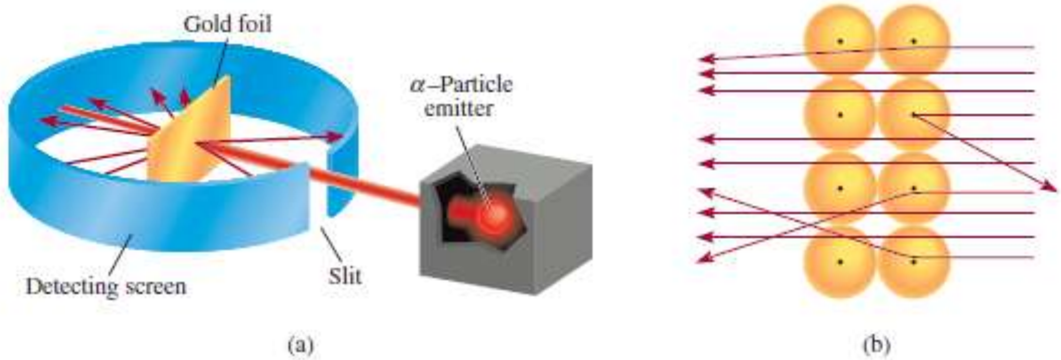


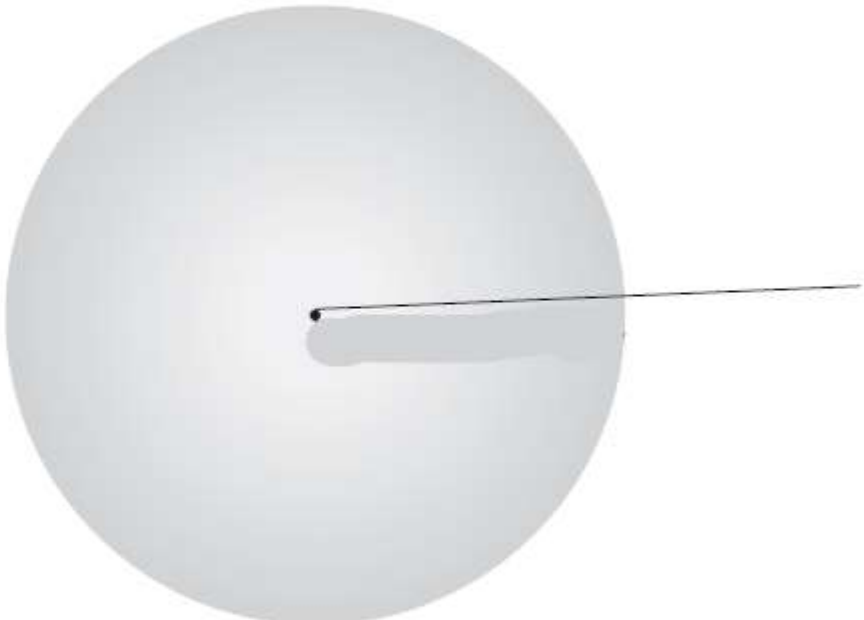
Figure 4.8. (a) Rutherford's experimental design for measuring the scattering of a *particles by a piece of gold foil. Most of the α particles passed through the gold foil with little or no deflection. A few were deflected at wide angles. Occasionally an* α *particle was turned back. (b) Magnified view of* a *particles passing through and being deflected by nuclei.*

The most surprising of Rutherford's findings was that in addition to the deflection of α particles to all direction, an α particle actually bounced back in the direction from which it had come! Thomson's model however proposed that the positive charge of the atom was so diffuse that the positive α particles should have passed through the foil with very little deflection.

Rutherford was later able to explain the results of the alpha-scattering experiment in terms of a new model for the atom. According to Rutherford,

i. most of the atom must be empty space. This explains why the majority of a particles passed through the gold foil with little or no deflection.
ii. The atom's positive charges are all concentrated in the ***nucleus,*** which is *a dense central core within the atom.*
iii. Whenever an α particle came close to a nucleus in the scattering experiment, it experienced a large repulsive force and therefore a large deflection.
iv. Moreover, an α particle traveling directly toward a nucleus would be completely repelled and its direction would be reversed.
v. *The positively charged particles in the nucleus* are called ***protons***

Rutherford's model of atom views an atom as a having a dense nucleus consisting of a positively charged nucleus, surrounded by electrons as a seen below:



In separate experiments, it was found that each proton carries the same *quantity* of charge as an electron and has a mass of 1.67262×10^{-24} g-about 1840 times the mass of the oppositely charged electron. At this stage of investigation, scientists perceived the atom as follows:

i. The mass of a nucleus constitutes most of the mass of the entire atom,

ii. The nucleus occupies only about $1/10^{13}$ of the volume of the atom.

iii. We express atomic (and molecular) dimensions in terms of the SI unit called the *picometer* (*pm*), where

$$1\text{pm} = 1 \times 10^{-12} \text{ m}.$$

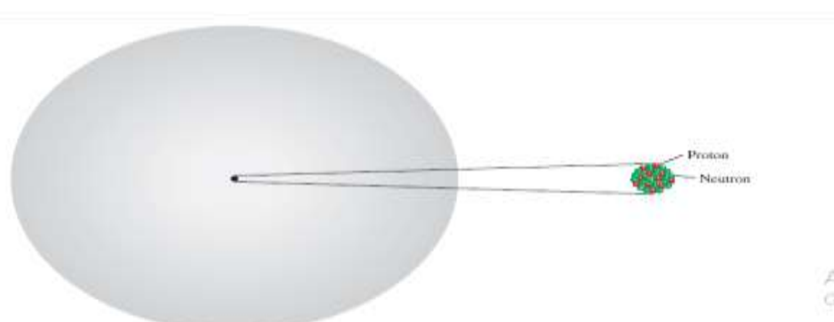
iv. A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is only about 5×10^{-3} pm.

Although the protons are confined to the nucleus of the atom, the electrons are conceived of as being spread out about the nucleus at some distance from it. The concept of atomic radius is useful experimentally, but we should not infer that atoms have well-defined boundaries or surfaces.

iii. The Neutron

Rutherford's model of atomic structure left one major problem unsolved. It was known that hydrogen, the simplest atom, contains only one proton and that the helium atom contains two protons. Therefore, the ratio of the mass of a helium atom to that of a hydrogen atom should be 2:1. (Because electrons are much lighter than protons, their contribution to atomic mass can be ignored.) In reality, however, the ratio is 4:1. Rutherford and others postulated that there must be another type of subatomic particle in the atomic nucleus; the proof was provided by another English physicist, James Chadwick (James Chadwick (1891–1972). British physicist. In 1935 he received the Nobel Prize in Physics for proving the existence of neutrons.), in 1932. When Chadwick bombarded a thin sheet of beryllium with α particles, a very high-energy radiation similar to γ rays was emitted by the metal. Later experiments showed that the rays actually consisted of a third type of subatomic particles, which Chadwick named ***neutrons,*** because they proved to be *electrically neutral particles having a mass slightly greater than that of protons.* The mystery of the mass ratio could now be explained. In the helium nucleus there are two protons and two neutrons, but in the hydrogen nucleus there is only one proton and no neutrons; therefore, the ratio is 4:1. Figure 4.9 shows the location of the elementary particles (protons, neutrons, and electrons) in an atom. There are other subatomic particles, but the electron, the proton, and the neutron are the three fundamental components of the atom that are important in chemistry.

Figure 4.9 *The protons and neutrons of an atom are packed in an extremely small nucleus. Electrons are shown as "clouds" around the nucleus.*



Atomic Number, Mass Number, and Isotopes

All atoms can be identified by the number of protons and neutrons they contain. The ***atomic number (Z)*** is *the number of protons in the nucleus of each atom of an element.* In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its atomic number. For example, the atomic number of fluorine is 9. This means that each fluorine atom has 9 protons and 9 electrons. Or, viewed another way, every atom in the universe that contains 9 protons is correctly named "fluorine."

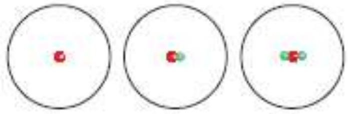
The ***mass number (A)*** is *the total number of neutrons and protons present in the nucleus of an atom of an element.* Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons. In general, the mass number is given by

$$\begin{aligned}\textbf{mass number} &= \textbf{number of protons + number of neutrons}\\ &= \textbf{atomic number + number of neutrons}\end{aligned}$$

The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or (A - Z). For example, if the mass number of a particular boron atom is 12 and the atomic number is 5 (indicating 5 protons in the nucleus), then the number of neutrons is 12 - 5 = 7. Note that all three quantities (atomic number, number of neutrons, and mass number) must be positive integers, or whole numbers. Note also that *Protons and neutrons are collectively called* ***nucleons.***

Atoms of a given element do not all have the same mass. Most elements have two or more ***isotopes,*** *atoms that have the same atomic number but different mass numbers.* For example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The *deuterium* isotope contains one proton and one neutron, and *tritium* has one proton and two neutrons. The accepted way to denote the atomic number and mass number of an atom of an element (X) is as follows:

$$\begin{array}{r}\text{mass number} \searrow\\ \text{atomic number} \nearrow\end{array} {}^{A}_{Z}\mathrm{X}$$



$^{1}_{1}H$ $^{2}_{1}H$ $^{3}_{1}H$

Thus, for the isotopes of hydrogen, we write

$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$
hydrogen	deuterium	tritium

As another example, consider two common isotopes of uranium with mass numbers of 235 and 238, respectively:

$$^{235}_{92}U \qquad ^{238}_{92}U$$

The first isotope is used in nuclear reactors and atomic bombs, whereas the second isotope lacks the properties necessary for these applications. With the exception of hydrogen, which has different names for each of its isotopes, isotopes of elements are identified by their mass numbers. Thus, the preceding two isotopes are called uranium-235 (pronounced “uranium two thirty-five”) and uranium-238 (pronounced “uranium two thirty-eight”).

The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.

Exercises

1. Define the following terms: (a) a particle, (b) b particle, (c) γ ray, (d) X ray.

2. Name the types of radiation known to be emitted by radioactive elements.

3. Compare the properties of the following: alpha particles, cathode rays, protons, neutrons, electrons.

4. What is meant by the term “fundamental particle”?

5. Describe the contributions of the following scientists to our knowledge of atomic structure: J. J. Thomson, R. A. Millikan, Ernest Rutherford, James Chadwick.

6. Describe the experimental basis for believing that the nucleus occupies a very small fraction of the volume of the atom.

7. The diameter of a helium atom is about $1x10^{2}$ pm. Suppose that we could line up helium atoms side by side in contact with one another. Approximately how many atoms would it take to make the distance from end to end 1 cm?

8. Roughly speaking, the radius of an atom is about 10,000 times greater than that of its nucleus. If an atom were magnified so that the radius of its nucleus became 2.0 cm, about the size of a marble, what would be the radius of the atom in miles? (1 mi =1609 m.)

9. Use the helium-4 isotope to define atomic number and mass number. Why does a knowledge of atomic number enable us to deduce the number of electrons present in an atom?

10. Why do all atoms of an element have the same atomic number, although they may have different mass numbers?

11. What do we call atoms of the same elements with different mass numbers?

12. Explain the meaning of each term in the symbol ${}_{Z}^{A}X$.

13. What is the mass number of an iron atom that has 28 neutrons?

14. Calculate the number of neutrons of ${}^{239}Pu$.

15. For each of the following species, determine the number of protons and the number of neutrons in the nucleus:

${}_{2}^{3}He$, ${}_{2}^{4}He$, ${}_{12}^{24}Mg$, ${}^{25}_{12}Mg$, ${}^{48}_{22}Ti$, ${}^{79}_{35}Br$, ${}^{195}_{78}Pt$

16. Indicate the number of protons, neutrons, and electrons in each of the following species:

${}^{15}_{7}N$, ${}^{33}_{16}S$, ${}^{63}_{29}Cu$, ${}^{84}_{38}Sr$, ${}^{130}_{56}Ba$, ${}^{186}_{74}W$, ${}^{202}_{80}Hg$

17. Write the appropriate symbol for each of the following isotopes: (a) $Z = 11$, $A = 23$; (b) $Z = 28$, $A = 64$.

18. Write the appropriate symbol for each of the following isotopes: (a) $Z = 74$, $A = 186$; (b) $Z = 80$; $A = 201$.

19. (a) Name the only element having an isotope that contains no neutrons. (b) Explain why a helium nucleus containing no neutrons is likely to be unstable.