Contents

Atoms and the Atomic Theory 2
Law of Conservation of Mass 2
Law of Constant Composition 2
Dalton’s Atomic Theory 3
Electrons and Other Discoveries in Atomic Physics 3
Electric Charge 4
The Discovery of Electrons 4
Michael Faraday 4
J. J. Thomson 5
Robert Millikan 5
The plum-pudding atomic model 6
X-Rays and Radioactivity 7
X-ray 7
Antoine Henri Becquerel 7
Ernest Rutherford 7
Paul Villard 8
The Nuclear Atom 8
Rutherford’s Atom Model 9
Discovery of Protons and Neutrons 10
Properties of Protons, Neutrons, and Electrons 10
Atomic number 10
Mass number 10
Neutron number 11
The atomic mass unit 11
Chemical Elements 11
Isotopes 12
Ions 12
Atomic Mass 13

Atoms and the Atomic Theory

We begin this chapter with a brief survey of early chemical discoveries, culminating in Dalton’s atomic theory. This is followed by a description of the physical evidence leading to the modern picture of the *nuclear atom*, in which protons and neutrons are combined into a nucleus with electrons in space surrounding the nucleus.

We will also introduce the periodic table as the primary means of organizing elements into groups with similar properties. Finally, we will introduce the concept of the mole and the Avogadro constant, which are the principal tools for counting atoms and molecules and measuring amounts of substances.

Law of Conservation of Mass

➘ The total mass of substances present after a chemical reaction is the same as the total mass of substances before the reaction.

In 1774, Antoine Lavoisier (1743 1794) performed an experiment in which he heated a sealed glass vessel containing a sample of tin (Sn) and some air. He found that the mass before heating (glass vessel + tin + air) and after heating (glass vessel + “tin calx” + remaining air) were the same. Through further experiments, he showed that the product of the reaction, tin calx (tin oxide), consisted of the original tin together with a portion of the air.

Experiments like this proved to Lavoisier that oxygen from air is essential to combustion, and also led him to formulate the **law of conservation of mass.**

Law of Constant Composition

➘ All samples of a compound have the same composition the same proportions by mass of the constituent elements.

In 1799, Joseph Proust (1754 1826) reported, One hundred pounds of copper, dissolved in sulfuric or nitric acids and precipitated by the carbonates of soda or potash, invariably gives 180 pounds of green carbonate. This and similar observations became the basis of the law of constant composition, or the law of definite proportions:

Sample A and Its Composition		**Sample B and Its Composition**	
10.000 g		27.000 g	
1.119 g H	% H = 11.19	3.021 g H	% H = 11.19
8.881 g O	% O = 88.81	23.979 g O	% O = 88.81

Dalton's Atomic Theory

From 1803 to 1808, John Dalton, an English schoolteacher, used the two fundamental laws of chemical combination just described as the basis of an atomic theory. His theory involved three assumptions:

1. Each chemical element is composed of minute, indivisible particles called atoms. Atoms can be neither created nor destroyed during a chemical change.
2. All atoms of an element are alike in mass (weight) and other properties, but the atoms of one element are different from those of all other elements.
3. In each of their compounds, different elements combine in a simple numerical ratio, for example, one atom of A to one of B (AB), or one atom of A to two of (AB_2).

➘ If atoms of an element are indestructible (assumption 1), then the same atoms must be present after a chemical reaction as before. The total mass remains unchanged. Dalton's theory explains the ***law of conservation of mass*.**

➘ If all atoms of an element are alike in mass (assumption 2) and if atoms unite in fixed numerical ratios (assumption 3), the percent composition of a compound must have a unique value, regardless of the origin of the sample analyzed. Dalton's theory also explains the ***law of constant composition***.

Law of multiple proportions: If two elements form more than a single compound, the masses of one element combined with a fixed mass of the second are in the ratio of small whole numbers.

▷ **Example:** Consider two oxides of carbon (an oxide is a combination of an element with oxygen).

Oxide 1:1.000 g C	+	1.333 g O	CO
Oxide 2:1.000 g C	+	2.667 g O	CO_2

We see that the second oxide is richer in oxygen;

$Ratio\ of\ oxygens = \frac{2.667}{1.333} = 2.0$

Electrons and Other Discoveries in Atomic Physics

To understand the atomic structure, we do need a few key ideas about the interrelated phenomena of *electricity* and *magnetism*, which we briefly discuss here. Electricity and magnetism were used in the experiments that led to the current theory of atomic structure.

Electric Charge

Certain objects display a property called electric charge, which can be either positive (+) or negative (–) Positive and negative charges attract each other, while two positive or two negative charges repel each other (Fig. 1).

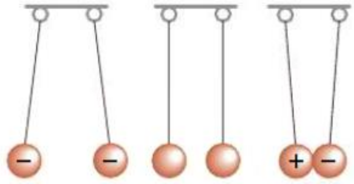

Figure 1. Both objects on the left carry a negative electric charge. Objects with like charge repel each other. The objects in the center lack any electric charge and exert no forces on each other. The objects on the right carry opposite charges one positive and one negative and attract each other.

➘ An object having equal numbers of positively and negatively charged particles carries no net charge and is electrically neutral.

Figure 2 shows how charged particles behave when they move through the field of a magnet. They are deflected from their straight-line path into a curved path in a plane perpendicular to the field. Think of the field or region of influence of the magnet as represented by a series of invisible lines of force running from the north pole to the south pole of the magnet.

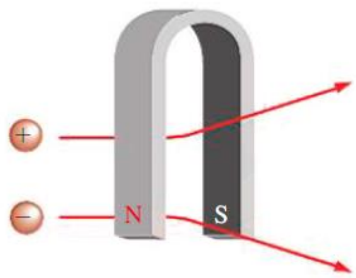

Figure 2. Effect of a magnetic field on charged particles.

The Discovery of Electrons

Michael Faraday

The first cathode-ray tube (CRT) was made by Michael Faraday (1791-1867) about 150 years ago. When he passed electricity through glass tubes from which most of the air had been evacuated, Faraday discovered **cathode rays**, a type of radiation emitted by the negative terminal, or *cathode*.

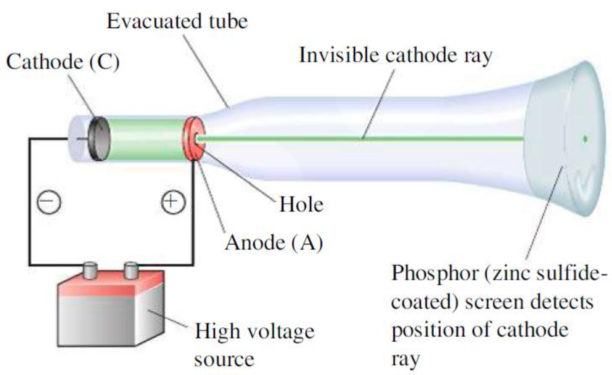

Figure 3. **A cathode-ray tube:** The high-voltage source of electricity creates a negative charge on the electrode at the left (cathode) and a positive charge on the electrode at the right (anode). Cathode rays pass from the cathode (C) to the anode (A), which is perforated to allow the passage of a narrow beam of cathode rays. The rays are visible only through the green fluorescence that they produce on the zinc sulfide coated screen at the end of the tube. They are invisible in other parts of the tube.

The radiation crossed the evacuated tube to the positive terminal, or *anode* (Fig.3).

➘ Later scientists found that cathode rays travel in straight lines and have properties that are independent of the cathode material (that is, whether it is iron, platinum, and so on).

➘ The cathode rays produced in the CRT are invisible, and they can be detected only by the light emitted (fluorescence) by materials that they strike (Fig. 3).

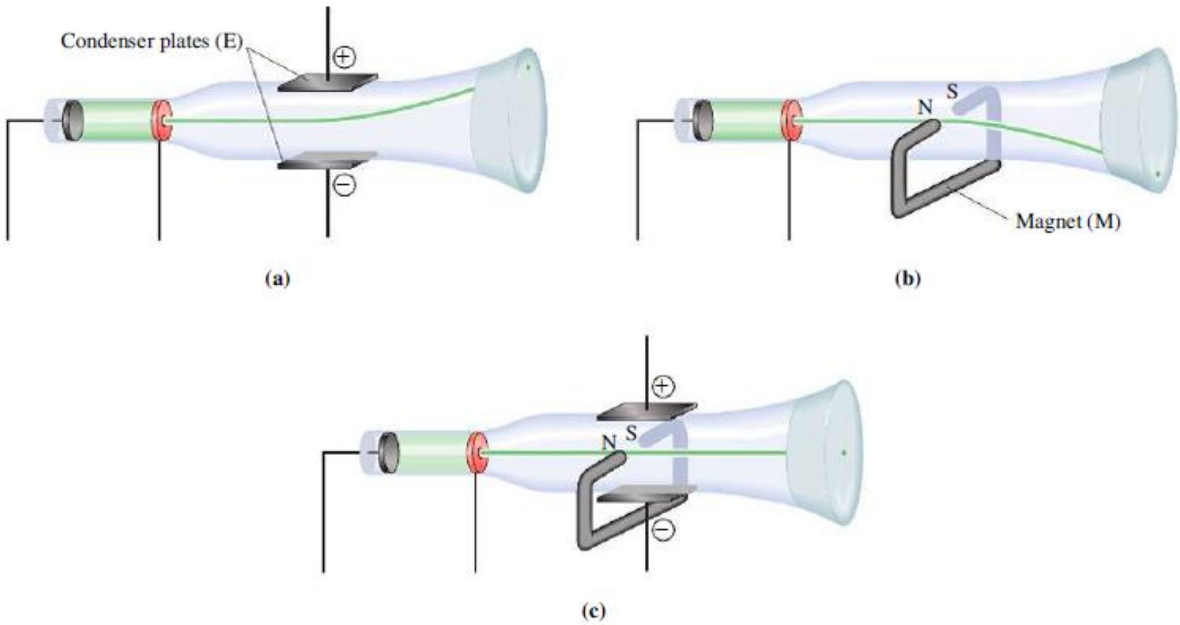

Figure 4. Cathode rays and their properties.

➘ Another significant observation about cathode rays is that they are deflected by electric and magnetic fields in the manner expected for negatively charged particles (Fig. 4a, 4b).

J. J. Thomson

In 1897, J. J. Thomson (1856-1940) established (Fig. 4c):

- The ratio of mass (m) to electric charge (e) for cathode rays, that is, m/e.
- Cathode rays are negatively charged fundamental particles of matter found in all atoms.

➘ Cathode rays subsequently became known as ***electrons***, a term first proposed by George Stoney in 1874.

Robert Millikan

Robert Millikan (1868 1953) determined the electronic charge e through a series of oil-drop experiments (1906 1914), described in Figure 2-8. The currently accepted value of the electronic charge e, expressed in coulombs to five significant figures, is -1.6022×10^{-19} C .By combining this value with an accurate value of the mass-to-charge ratio for an electron, we find that the mass of an electron is 9.1094×10^{-28} g.

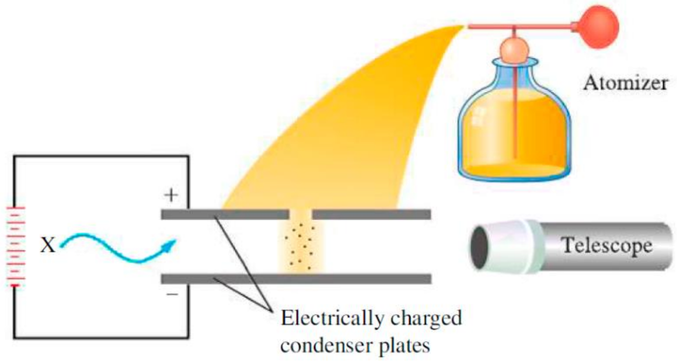

Figure 5. **Millikan's oil-drop experiment:** Ions (charged atoms or molecules) are produced by energetic radiation, such as X-rays (X). Some of these ions become attached to oil droplets, giving them a net charge. The fall of a droplet in the electric field between the condenser plates is speeded up or slowed down, depending on the magnitude and sign of the charge on the droplet. By analyzing data from a large number of droplets, Millikan concluded that the magnitude of the charge, q, on a droplet is an integral multiple of the electric charge, e. That is, q = ne (where n = 1, 2, 3, …).

Once the electron was seen to be a fundamental particle of matter found in all atoms. Thomson's model became the commonly accepted model.

The plum-pudding atomic model

According to Thomson's model (Fig. 6):

- Positive charge (+) necessary to counterbalance the negative charges (–) of electrons.
- Electrons, floated in a diffuse cloud of positive charge.

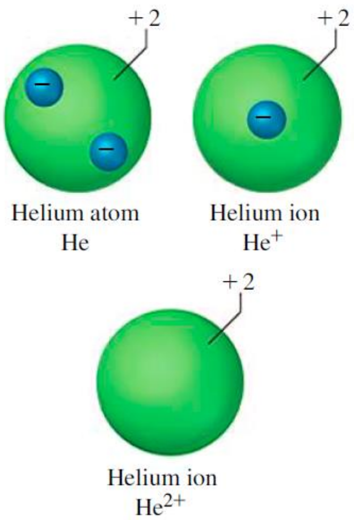

Figure 6. **The plum-pudding atomic model:** According to this model, a helium atom would have a +2 cloud of positive charge and two electrons (–2). If a helium atom loses one electron, it becomes charged and is called an ion. This ion, referred to as He^{+}, has a net charge of 1^{+}. If the helium atom loses both electrons, the He^{2+} ion forms.

X-Rays and Radioactivity

X-ray

In 1895, Wilhelm Roentgen (1845-1923) noticed that when cathode-ray tubes were operating, certain materials *outside* the tubes glowed or fluoresced. He showed that this fluorescence was caused by radiation emitted by the cathode-ray tubes. Because of the unknown nature of this radiation, Roentgen coined the term *X-ray*.

➘ We now recognize the *X-ray* as a form of high-energy electromagnetic radiation.

Antoine Henri Becquerel

Antoine Henri Becquerel (1852-1908) associated X-rays with fluorescence and wondered if naturally fluorescent materials produce X-rays. To test this idea:

- He wrapped a photographic plate with black paper, placed a coin on the paper, covered the coin with a uranium-containing fluorescent material, and exposed the entire assembly to sunlight.
- When he developed the film, a clear image of the coin could be seen. The fluorescent material had emitted radiation (presumably X-rays) that penetrated the paper and exposed the film.
- Becquerel placed the experimental assembly inside a desk drawer for a few days while waiting for the weather to clear.
- He developed the original film and found that the film had become strongly exposed because the uranium-containing material had emitted radiation continuously, even when it was not fluorescing.
- Becquerel had discovered ***radioactivity***.

Ernest Rutherford

Ernest Rutherford (1871-1937) identified two types of radiation from radioactive materials, alpha (α) and beta (β).

> **Alpha particles (α):** Alpha particles carry two fundamental units of positive charge and have essentially the same mass as helium atoms. In fact, alpha particles are identical to He^{2+} ions.
>
> **Beta particles (β):** Beta particles are negatively charged particles produced by changes occurring within the nuclei of radioactive atoms and have the same properties as electrons.

Paul Villard

Paul Villard was discovered a third form of radiation, which is not affected by electric or magnetic fields. This radiation, called *gamma rays* (γ).

Gamma rays (γ): Gamma ray is not made up of particles; it is electromagnetic radiation of extremely high penetrating power.

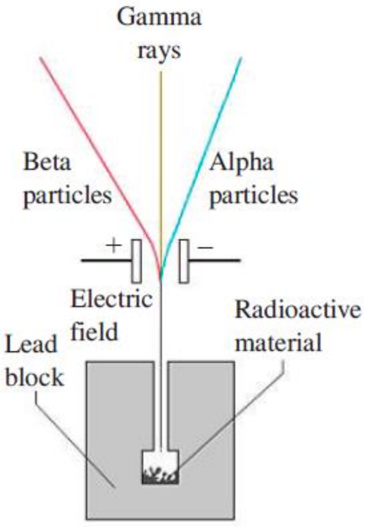

Figure 7. **Three types of radiation from radioactive materials:** The radioactive material is enclosed in a lead block. All the radiation except that passing through the narrow opening is absorbed by the lead. When the escaping radiation is passed through an electric field, it splits into three beams. One beam is undeflected these are gamma rays (γ). A second beam is attracted to the negatively charged plate. These are the positively charged alpha (α) particles. The third beam, of negatively charged beta (β) particles, is deflected toward the positive plate.

The Nuclear Atom

In 1909, Rutherford, with his assistant Hans Geiger, began a line of research using α particles as probes to study the inner structure of atoms using very thin foils of gold.

The apparatus used for these studies is pictured in Figure 8. Alpha particles were detected by the flashes of light they produced when they struck a zinc sulfide screen mounted on the end of a telescope. When Geiger and Ernst Marsden, a student, bombarded very thin foils of gold with particles, they observed the following:

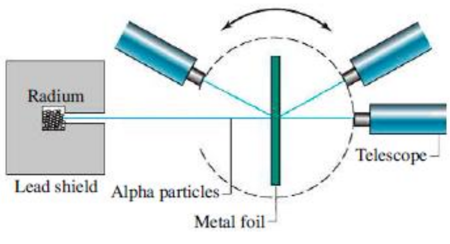

Figure 8. **The scattering of particles by metal foil:** The telescope travels in a circular track around an evacuated chamber containing the metal foil. Most particles pass through the metal foil undeflected, but some are deflected through large angles.

- The majority of particles penetrated the foil undeflected.
- Some α particles experienced slight deflections.
- A few (about 1 in every 20,000) suffered rather serious deflections as they penetrated the foil.

- A similar number did not pass through the foil at all, but bounced back in the direction from which they had come.

Rutherford's Atom Model

By 1911, Rutherford had an explanation. He based his explanation on a model of the atom known as the nuclear atom and having these features:

1. Most of the mass and all of the positive charge of an atom are centered in a very small region called the *nucleus*. The remainder of the atom is mostly *empty space.*
2. The magnitude of the positive charge is different for different atoms and is approximately one-half the atomic weight of the element.
3. There are as many electrons outside the nucleus as there are units of positive charge on the nucleus. The atom as a whole is electrically neutral.

Rutherford's initial expectation and his explanation of the experiments are described in Figure 9.

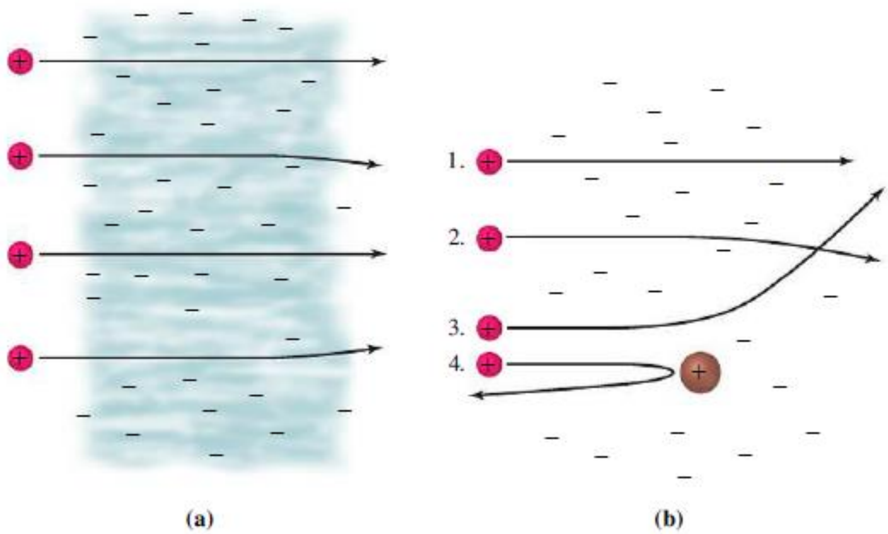

Figure 9. **Explaining the results of α-particle scattering experiments:**

a) Rutherford's expectation was that small, positively charged α particles should pass through the nebulous, positively charged cloud of the Thomson plum-pudding model largely undeflected. Some would be slightly deflected by passing near electrons (present to neutralize the positive charge of the cloud).
b) Rutherford's explanation was based on a nuclear atom. With an atomic model having a small, dense, positively charged nucleus and extranuclear electrons, we would expect the four different types of paths actually observed:
    1. undeflected straight-line paths exhibited by most of the
    2. particles
    3. slight deflections of α particles passing close to electrons
    4. severe deflections of α particles passing close to a nucleus
    5. reflections from the foil of α particles approaching a nucleus head-on

Discovery of Protons and Neutrons

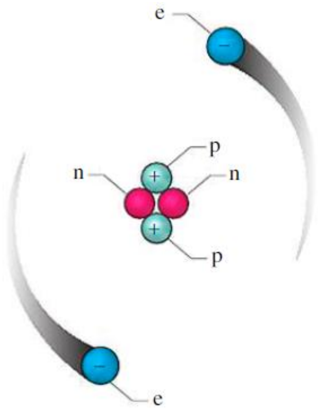

Figure 10. **The nuclear atom illustrated by the helium atom:** In this drawing, electrons are shown much closer to the nucleus than is the case. The actual situation is more like this: If the entire atom were represented by a room, the nucleus would occupy only about as much space as the period at the end of this sentence.

Rutherford s nuclear atom suggested the existence of positively charged fundamental particles of matter in the nuclei of atoms. Rutherford himself discovered these particles, called protons, in 1919 in studies involving the scattering of α particles by nitrogen atoms in air. At about this same time, Rutherford predicted the existence in the nucleus of electrically neutral fundamental particles.

➘ In 1932, James Chadwick showed that a newly discovered penetrating radiation consisted of beams of neutral particles. These particles, called *neutrons,* originated from the nuclei of atoms.

Thus, it has been only for about the past 100 years that we have had the atomic model suggested by Figure 10.

Table 1. Properties of Three Fundamental Particles

	Electric Charge		Mass	
	SI (C)	Atomic	SI (g)	Atomic (u)[a]
Proton	$+1.6022 \times 10^{-19}$	+1	1.6022×10^{-24}	1.0073
Neutron	0	0	1.6749×10^{-24}	1.0087
Electron	-1.6022×10^{-19}	−1	9.1094×10^{-28}	0.00054858

[a] u is the SI symbol for atomic mass unit (abbreviated as amu).

Properties of Protons, Neutrons, and Electrons

Atomic number

The number of protons in a given atom is called the *atomic number*, or the *proton number*, ***Z***. The number of electrons in the atom is also equal to Z because the atom is electrically neutral.

Mass number

The total number of protons and neutrons in an atom is called the *mass number*, ***A***.

Neutron number

The number of neutrons, the neutron number, is $A - Z$.

➘ An electron carries an atomic unit of negative charge, a proton carries an atomic unit of positive charge, and a neutron is electrically neutral. Table 1 presents the charges and masses of protons, neutrons, and electrons in two ways.

The atomic mass unit

The atomic mass unit is defined as exactly 1/2 of the mass of the atom known as carbon-12 (read as carbon twelve). An atomic mass unit is abbreviated as amu and denoted by the symbol u. As we see from Table 1, the proton and neutron masses are just slightly greater than 1 u. By comparison, the mass of an electron is only about 1/2000th the mass of the proton or neutron.

Chemical Elements

Now that we have acquired some fundamental ideas about atomic structure, we can more thoroughly discuss the concept of chemical elements.

- All atoms of a particular element have the same atomic number, Z.
- And, conversely, all atoms with the same number of protons are atoms of the same element.
- The 112 known elements have atomic numbers from $Z = 1$ to $Z = 112$.
- Each element has a name and a distinctive symbol. Chemical symbols are one- or two-letter abbreviations of the name (usually the English name).
- The first (but never the second) letter of the symbol is capitalized;

Example: Carbon, C; Oxygen, O; Neon, Ne; and Silicon, Si.

- Some elements known since ancient times have symbols based on their Latin names, such as Fe for iron (*ferrum*) and Pb for lead (*plumbum*).
- The element sodium has the symbol Na, based on the Latin *natrium* for sodium carbonate.
- Potassium has the symbol K, based on the Latin *kalium* for potassium carbonate.
- The symbol for tungsten, W, is based on the German *wolfram*.
- Elements beyond uranium ($Z = 92$) do not occur naturally and must be synthesized in particle accelerators.

Isotopes

To represent the composition of any particular atom, we need to specify its number of protons (p), neutrons (n), and electrons (e). We can do this with the symbolism.

$$\begin{array}{r} \text{number p + number n} \longrightarrow \\ \text{number p} \longrightarrow \end{array} {}^{A}_{Z}\mathrm{E} \longleftarrow \text{symbol of element}$$

This symbolism indicates that the atom is element E and that it has atomic number *Z* and mass number *A*.

➘ Contrary to what Dalton thought, we now know that atoms of an element do not necessarily all have the same mass.

In 1912, J. J. Thomson measured the mass-to-charge ratios of positive ions formed from neon atoms. From these ratios he deduced that about 91% of the atoms had one mass and that the remaining atoms were about 10% heavier.

$$^{20}_{10}\mathrm{Ne} \qquad ^{21}_{10}\mathrm{Ne} \qquad ^{22}_{10}\mathrm{Ne}$$

➘ Odd-numbered elements tend to have fewer isotopes than do even-numbered elements.

Isotope: Atoms that have the same atomic number (*Z*) but different mass numbers (*A*) are called isotopes.

Percent natural abundance: Natural abundance refers to the abundance of isotopes of a chemical element as naturally found on a planet. Percentage values of these isotopes are called as *percent natural abundances*.

Ions

When atoms lose or gain electrons, for example, in the course of a chemical reaction, the species formed are called *ions* and carry net charges.

- Because an electron is negatively charged, adding electrons to an electrically neutral atom produces a negatively charged ion.
- Removing electrons results in a positively charged ion.
- The <u>number of protons</u> does not change when an atom becomes an ion.

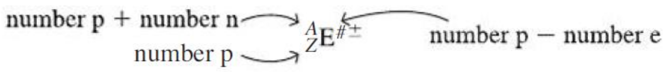

Figure 11. In this expression, #± indicates that the charge is written with the number (#) before the + or – sign. However, when the charge is 1+ or 1–, the number 1 is not included.

An example is the $^{16}O^{2-}$ ion. In this ion, there are 8 protons (atomic number 8), 8 neutrons and 10 electrons ($8 - 10 = -2$).

Atomic Mass

The *atomic mass (weight)* of an element is the average of the isotopic masses, *weighted* according to the naturally occurring abundances of the isotopes of the element.

$$\begin{matrix}\text{at. mass}\\ \text{of an}\\ \text{element}\end{matrix} = \left(\begin{matrix}\text{fractional}\\ \text{abundance of}\\ \text{isotope 1}\end{matrix} \times \begin{matrix}\text{mass of}\\ \text{isotope 1}\end{matrix}\right) + \left(\begin{matrix}\text{fractional}\\ \text{abundance of}\\ \text{isotope 2}\end{matrix} \times \begin{matrix}\text{mass of}\\ \text{isotope 2}\end{matrix}\right) + \ldots$$

The first term on the right side of equation represents the contribution from isotope 1; the second term represents the contribution from isotope 2; and so on.

The fractional abundance, normally represented as a percentage, of each isotope of a given element.

The mass spectrum of carbon shows that 98.93% of carbon atoms are carbon-12 with a mass of exactly 12 u; the rest are carbon-13 atoms with a mass of 13.0033548378 u. Therefore *the atomic mass of naturally occurring carbon*:

$$\begin{aligned}\begin{matrix}\text{at. mass of naturally}\\ \text{occurring carbon}\end{matrix} &= 0.9893 \times 12\text{ u} + (1 - 0.9893) \times 13.0033548378\text{ u}\\ &= 13.0033548378\text{ u} - 0.9893 \times (13.0033548378\text{ u} - 12\text{ u})\\ &= 13.0033548378\text{ u} - 0.9893 \times (1.0033548378\text{ u})\\ &= 13.0033548378\text{ u} - 0.9893\\ &= 12.0107\text{ u}\end{aligned}$$