3.1 Early Atomic Theories and the Origins of Quantum Theory

What is matter made of? People have wondered about the answer to this question for thousands of years. Around 460 BCE, the Greek philosopher Democritus speculated that matter is composed of elementary particles called atoms. However, it was not until thousands of years later, after collecting a lot of evidence and developing very complex technology, that scientists were able to state with some certainty that matter is composed of atoms. Recently, something very exciting happened. For the first time, scientists are able to "see" individual atoms through a special microscope, called a scanning tunnelling microscope (STM). The STM passes an extremely fine, electrically charged needle over the surface of an object. Changes in the current through the needle indicate changes in the distance between the surface and the needle. These changes indicate the "bumps" of atoms and the "valleys" between them. An STM image of the surface of graphite shows an orderly arrangement of carbon atoms (**Figure 1**). WEB LINK

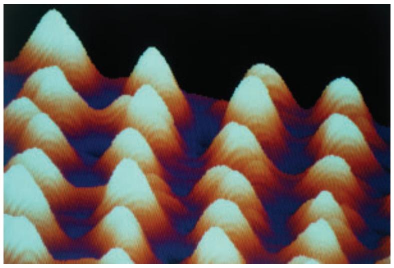

Figure 1 STM image of atoms on the surface of graphite (a form of carbon)

Early Developments in Atomic Structure

To understand chemistry, it helps to be able to visualize matter at the atomic level. Before the invention of the STM, scientists speculated that matter consisted of individual atoms. When Democritus first suggested the existence of atoms, his ideas were based on intuition and reason, not experimentation. For the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms. As new tools to experiment with matter were developed, our understanding of the structure of matter grew. In the late 1700s, French chemist Antoine Lavoisier and others used experimentation to gather the first accurate quantitative measurements of chemical reactions. These measurements were made possible by the invention of instruments that could precisely measure mass and volume. Based on the results of these experiments, John Dalton (1766–1844) proposed the first modern atomic theory: elements consist of atoms, which cannot be created, destroyed, or divided, and atoms of the same element have identical size, mass, and other properties. Dalton's theory, although simple, has stood the test of time extremely well. In the past 200 years, a great deal of experimental evidence has accumulated to support atomic theory.

Figure 2 The English physicist J.J. Thomson (1856–1940) studied electrical discharges in partially evacuated tubes called cathode ray tubes.

electron a negatively charged subatomic particle

Discovering the Electron

The experiments by the English physicist J.J. Thomson (**Figure 2**) were the first to provide evidence for the existence of the **electron**, a negatively charged subatomic particle. In his experiments, Thomson applied high voltage to a partially evacuated tube with a metal electrode at each end. He observed that a ray was produced that started from the negative electrode, or cathode. As a result of these observations, he called his tube a cathode ray tube (**Figure 3(a)**). WEB LINK

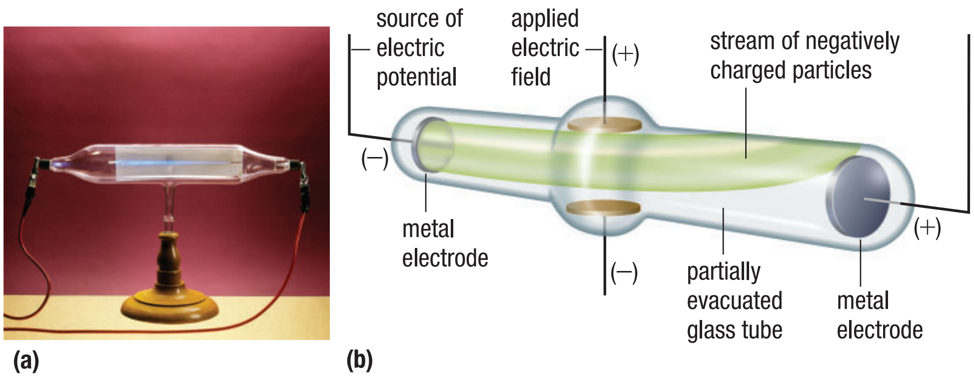

Figure 3 (a) A cathode ray tube under high voltage produces a visible ray. (b) A cathode ray is deflected away from the negative pole in an applied electric field, which is consistent with the ray being composed of a stream of negatively charged particles (electrons).

Thomson also observed that the negative pole of an applied electric field repelled the ray (**Figure 3(b)**). He explained these observations by hypothesizing that the ray was composed of a stream of negatively charged particles, which we now know to be electrons.

By measuring the deflection of the beam of electrons in a magnetic field, Thomson was able to determine the charge-to-mass ratio of an electron, using the formula

$$\frac{e}{m} = -1.76 \times 10^{8}\ \text{C/g}$$

where e represents the charge on the electron in coulombs (C), and m represents the electron mass in grams (g).

One of Thomson's goals in his cathode ray tube experiments was to understand the structure of the atom. He reasoned that since electrons could be produced from electrodes made of various metals, all atoms must contain electrons. Since atoms are electrically neutral, Thomson further reasoned that atoms must also contain a positive charge. Thomson postulated that an atom consists of a diffuse cloud of positive charge with negatively charged electrons embedded randomly in it. This model is sometimes called the "blueberry muffin model"; the electrons are analogous to negatively charged blueberries dispersed in a positively charged muffin (**Figure 4**).

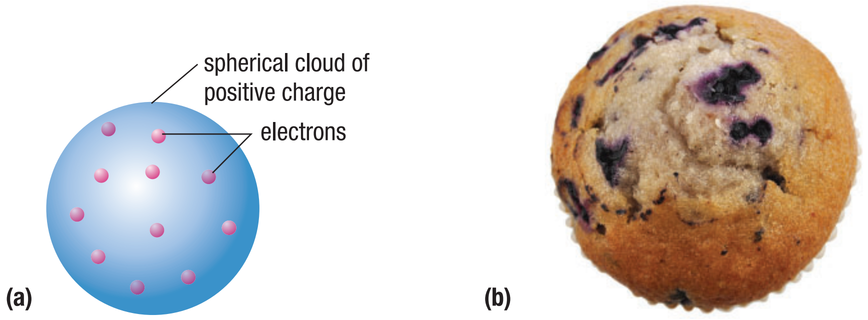

Figure 4 (a) According to Thomson's model, electrons are randomly embedded in a cloud of positive charge. (b) Thomson's model of an atom is sometimes called the "blueberry muffin model." In the model, electrons are represented by the blueberries.

In 1909, scientist Robert Millikan conducted experiments at the University of Chicago in which he used charged oil drops to determine the charge of an electron. Using the apparatus shown in **Figure 5**, Millikan discovered that the fall of charged oil droplets due to gravity could be halted by adjusting the voltage across two charged plates. He was able to calculate the charge on the oil drop from the voltage and the mass of the oil drop. Using this value and the charge-to-mass ratio determined by Thomson, Millikan calculated the mass of an electron to be 9.11×10^{-31} kg.

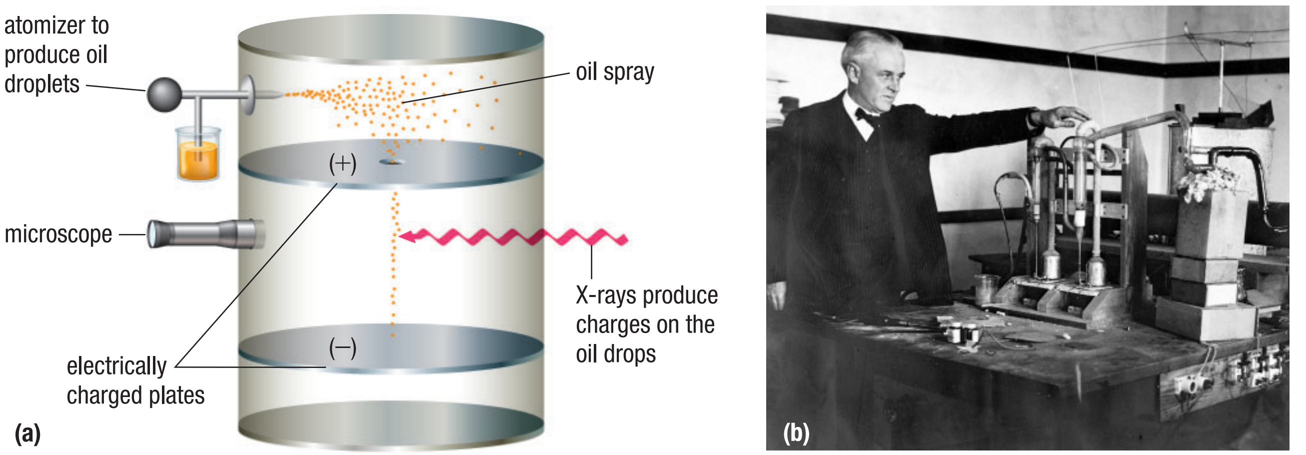

Figure 5 (a) A schematic representation of the apparatus Millikan used to determine the charge of an electron. (b) Robert Millikan using his apparatus

Exploring Radioactivity

In the late nineteenth century, scientists discovered that certain elements emit high levels of energy. In 1896, French scientist Henri Becquerel found that, in the absence of light, a piece of mineral containing uranium produces an image on a photographic plate. He attributed this phenomenon to uranium atoms spontaneously emitting radiation: energy, particles, or waves that travel through space or substances. Elements that emit radiation are said to be radioactive.

radioactivity the spontaneous decay or disintegration of the nucleus of an atom

Today we know that **radioactivity** is the spontaneous decay of the nucleus of an atom. This idea was first proposed by Ernest Rutherford (**Figure 6**). Rutherford showed that radioactivity resulted from the disintegration of atoms. He also discovered the alpha particle and named the beta particle and the gamma ray (**Table 1**).

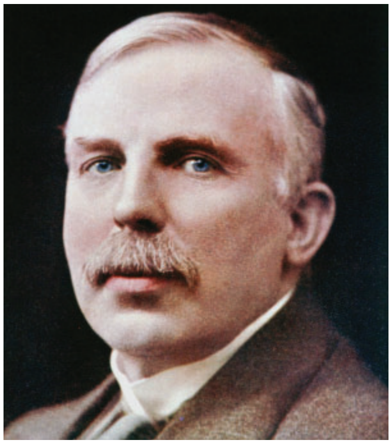

Figure 6 Ernest Rutherford (1871–1937) did much of the early work characterizing radioactivity at McGill University in Montréal, Québec. He received the Nobel Prize in Chemistry in 1908.

Table 1 Characteristics of Three Types of Radioactive Emissions

	Alpha particle	Beta particle	Gamma ray
Symbol	α or ${}^{4}_{2}\alpha$ or ${}^{4}_{2}$He	β or β^- or e	γ
Atomic mass (u)	4	$\frac{1}{2000}$	0
Charge	+2	−1	0
Speed	slow	fast	very fast (speed of light)
Ionizing ability	high	medium	none
Penetrating power	low	medium	high
Stopped by	paper	aluminum	lead

Rutherford's Model of the Atom

In 1911, Rutherford carried out a series of experiments to look for evidence in support of Thomson's "blueberry muffin model" of the atom. Rutherford devised experiments in which positively charged alpha particles were fired at a thin sheet of gold foil. He hypothesized that if Thomson's model was accurate, the massive alpha particles should break through the thin foil like bullets through paper, with only minor deflections (**Figure 7**).

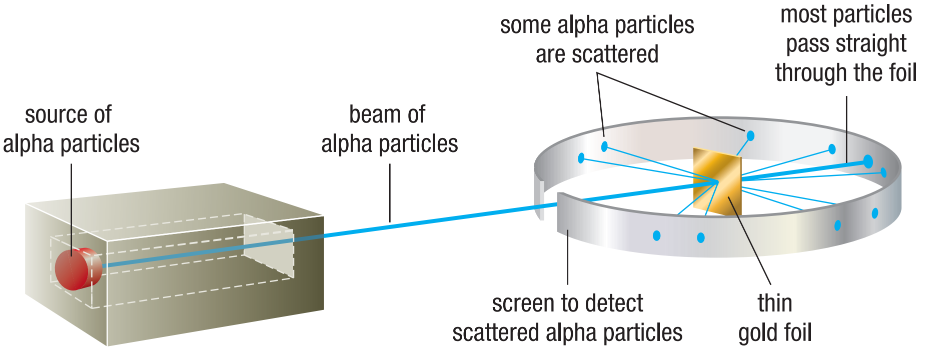

Figure 7 Rutherford's experimental design for the alpha particle bombardment of gold foil

The results of the experiments were very different from what Rutherford had anticipated. Although most of the alpha particles passed straight through the gold foil, some were deflected at various angles while others were reflected back toward the source, never reaching the detector.

Rutherford realized that these experimental results did not support Thomson's model of the atom (**Figure 8(a)**). The only possible explanation was that the observed deflection of alpha particles was caused by a concentrated positive charge at the centre of the atom. Rutherford predicted that the positive charge at the centre of the atom must contain most of the atomic mass, which would account for the deflection of the massive alpha particles. Rutherford also reasoned that since most of the alpha particles passed directly through the foil, the atom must be made up of mostly empty space, and the positive centre must be small in volume relative to the atom (**Figure 8(b)**). The deflected alpha particles must have travelled close to the positively charged centres of the atoms and, since like charges repel, changed paths. The alpha particles that bounced back must have made a direct hit on the much more massive positively charged centres.

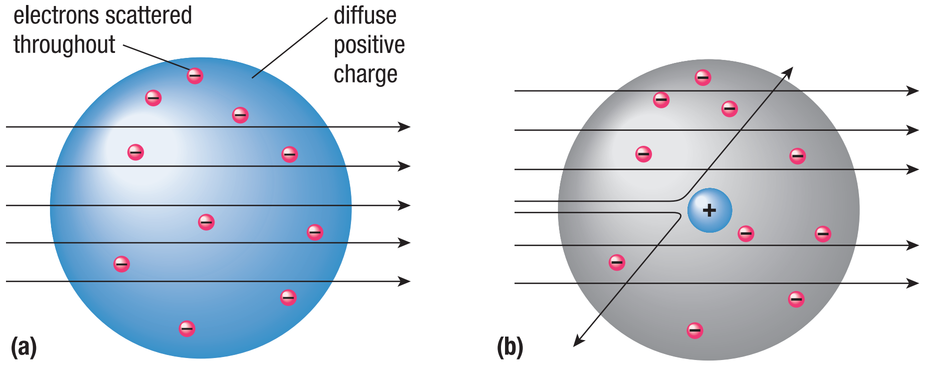

Figure 8 (a) Rutherford predicted that the alpha particles would pass right through the gold foil if Thomson's model was correct. (b) The actual results of Rutherford's experiments revealed that the atom is mostly open space with a small, positively charged centre that contains the bulk of the atomic mass.

Rutherford concluded that these results could be explained only in terms of an atom with a **nucleus**: a dense, positively charged atomic centre. He proposed that electrons move around the nucleus at a relatively far distance, similar to planets orbiting the Sun. Rutherford later named the positive charges in the nucleus **protons**.

nucleus the dense centre of an atom with a positive charge

proton a positively charged subatomic particle

Scientist James Chadwick worked with Rutherford to determine the masses of the nuclei of different elements. In these experiments, he found that the observed masses of the nuclei were not the same as the sum of the masses of the protons. Chadwick concluded that a nucleus must contain not only positively charged protons, but also neutral (uncharged) particles called **neutrons**.

neutron an electrically neutral subatomic particle

Atoms and Isotopes

An atom can be described as consisting of a tiny nucleus with a diameter of about 10^{-15} m and electrons that move around the nucleus at an average distance of about 10^{-10} m. The nucleus is very small compared to the overall size of the atom: if an atom were the size of a sports stadium, the nucleus would be about the size of a ball bearing (**Figure 9**). However, nuclear material is so dense that a ball bearing–sized piece would have a mass of 226 million tonnes!

Figure 9 If the atomic nucleus were the size of this ball bearing, a typical atom would be the size of this stadium.

The nucleus of an atom contains protons, which have a positive charge equal in magnitude to the negative charge of an electron, and neutrons, which have virtually the same mass as a proton but no charge. **Table 2** summarizes the masses and charges of the electron, proton, and neutron.

Table 2 The Mass and Charge of the Electron, Proton, and Neutron

Particle	Mass (kg)	Charge*
electron (e^-)	9.109×10^{-31}	-1
proton (p^+)	1.673×10^{-27}	$+1$
neutron (n^0)	1.675×10^{-27}	none

*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

If all atoms are composed of these same particles, why do different atoms have different chemical properties? The answer lies in the number of electrons in each atom. An electrically neutral atom has the same number of electrons as protons. Electrons constitute nearly all of the volume of an atom, but an insignificant amount of its mass. Electrons of different atoms interact when atoms combine to form molecules. The number of electrons in an atom and their arrangement determine the chemical behaviour of the atom. Neutral atoms of different elements have unique numbers of protons and electrons and, therefore, different chemical properties.

What makes the atoms of a certain element radioactive? You know that a neutral atom by definition has an equal number of protons and electrons in its nucleus. However, the number of neutrons in a neutral atom can differ. Two atoms with the same number of protons but different numbers of neutrons are called **isotopes**.

isotopes atoms with the same number of protons but different numbers of neutrons

atomic number (*Z*) the number of protons in a nucleus

mass number (*A*) the total number of protons and neutrons in a nucleus

The nucleus of each carbon isotope in **Figure 10** has the same **atomic number (*Z*)** which is the number of protons. However, each nucleus has a different **mass number (*A*)** which is the total number of protons and neutrons. The symbols for these two isotopes are written as ${}^{12}_{6}C$ and ${}^{14}_{6}C$. Notice that the atomic number is written as a subscript and the mass number is written as a superscript. These carbon isotopes can also be written as carbon-12 or C-12, and carbon-14 or C-14. Isotopes have almost identical chemical properties because they have the same number of electrons and protons. In nature, most elements contain mixtures of isotopes. In addition to occurring in nature, radioisotopes can be synthesized from certain elements.

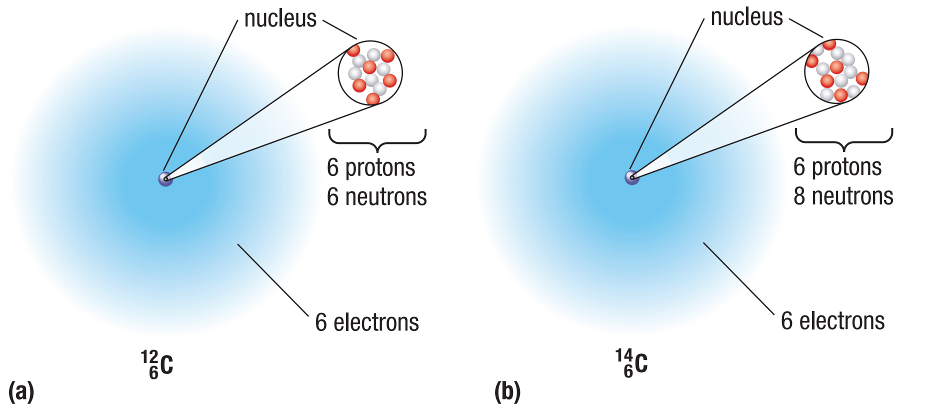

Figure 10 (a) Carbon-12 contains 6 protons and 6 neutrons. (b) Carbon-14 is an isotope of carbon that has 8 neutrons.

Recall that Henri Becquerel observed the spontaneous emission of radiation by uranium. When the nuclei of isotopes are unstable, as is the case for some uranium isotopes, they are radioactive and are called radioisotopes. A **radioisotope** is an isotope with an unstable nucleus, meaning that the nucleus decays and emits radioactive gamma rays and/or subatomic particles. Scientists and engineers use the radiation emitted by radioisotopes in many applications, including carbon dating, nuclear energy, and medicine. For example, carbon-14 is used in archaeological dating.

radioisotope an isotope that emits radioactive gamma rays and/or subatomic particles (for example, alpha and/or beta particles)

The Nature of Matter and Energy

During the first half of the twentieth century, scientists realized that the results of several key experiments were not consistent with the classical theories of physics developed by Isaac Newton and other scientists. To account for the observed behaviour of light and atoms, physicists developed a radical new idea called quantum theory. This new physics provided many surprises, but it also more accurately explains the behaviour of light and matter. WEB LINK

Classical Theories of Light

Light, or light energy, is electromagnetic radiation. Visible light is the portion of this spectrum that can be seen by the human eye. The nature and properties of light have been debated for centuries. Around 300 BCE, Greek philosophers proposed that light existed as a stream of particles. In the seventeenth century, Dutch scientist Christiaan Huygens conducted investigations that led him to theorize that light is a wave. Not all scientists agreed with Huygens. For example, Isaac Newton believed that light was composed of tiny particles, which he called "corpuscles." Investigations continued and new evidence from experiments with refraction, diffraction, and reflection provided a great deal of support for the wave hypothesis proposed by Huygens.

In the mid-nineteenth century, physicist James Maxwell proposed a theory regarding the properties of magnetism, light, and electricity. Maxwell theorized that light could act on charged particles because it existed as an electromagnetic wave made of magnetic and electric fields. Over time, Maxwell's electromagnetic wave theory gained wide acceptance and came to be the classical theory of light. According to Maxwell's theory, light is an electromagnetic wave composed of continuous wavelengths that form a spectrum (**Figure 11**).

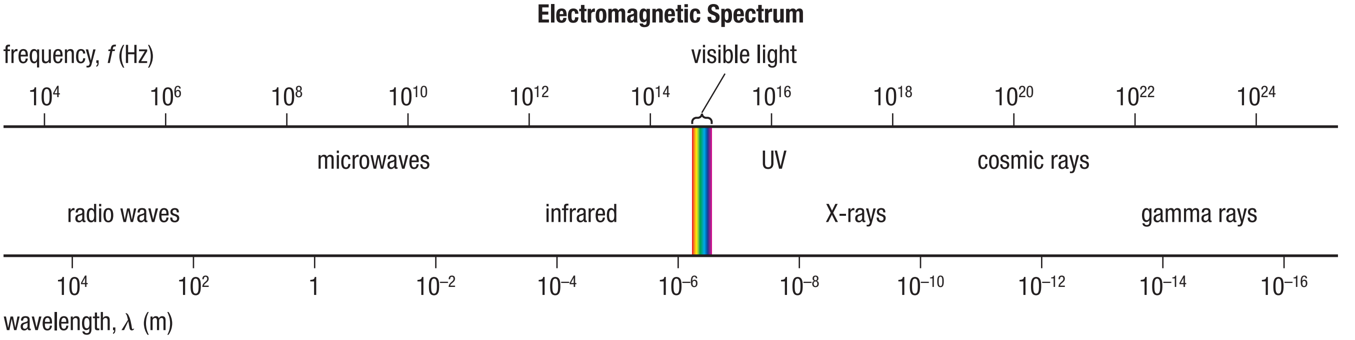

Figure 11 Visible light is only a very narrow band on the electromagnetic spectrum.

At the end of the nineteenth century, matter and energy were considered to be distinct, and unrelated, entities. Matter was thought to be composed of particles that had mass and a specific position in space at a particular time. Light energy was considered to be an electromagnetic wave that had no mass or specific position in space.

However, in 1887 German physicist Heinrich Hertz was attempting to generate electromagnetic waves using induction coils, and instead, discovered the **photoelectric effect**, in which light shining on a metal surface causes the emission of electrons from the metal. Hertz reported the photoelectric effect, but did not attempt to explain it. The discovery of the photoelectric effect had a major impact on the classical theories of light and matter. WEB LINK

photoelectric effect electrons are emitted by matter that absorbs energy from shortwave electromagnetic radiation (for example, visible or UV light)

According to the classical theory of light, the intensity (brightness) of the light shining on the metal should determine the kinetic energy of the electrons emitted. Therefore, the more intense the light, the more energy the emitted electrons should have. However, Hertz's experiments demonstrated that the *frequency* of the light was more important in determining the energy of the emitted electrons (**Figure 12**). Since the classical theory of light and matter could not explain these observations, it began to be viewed as flawed.

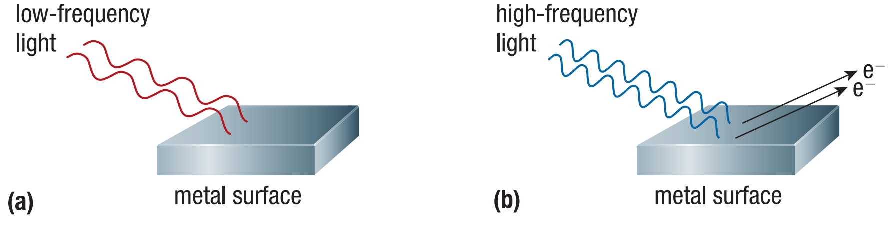

Figure 12 Hertz's experiments showed that light with frequency less than a certain frequency, called the threshold frequency, produces no electrons (a), whereas light with frequency higher than the threshold frequency causes electrons to be emitted from the metal (b).

Investigation 3.1.1

The Photoelectric Effect (page 179)
Einstein was later able to explain the photoelectric effect through experimentation, for which he received a Nobel Prize. In this investigation, you will observe what Einstein observed, which ultimately led to the modern theory of light and atoms.

Planck's Quantum Hypothesis

Figure 13 Max Planck (1858–1947), at right, is regarded as the founder of quantum theory. He studied the light emitted by hot objects. His experiments led him to hypothesize that energy could be gained or transferred in whole-number multiples.

In 1900, German physicist Max Planck (**Figure 13**) was studying the spectra of the radiant energy emitted by solid bodies (called blackbodies) heated to incandescence (glowing). When a solid is heated to very high temperatures, it begins to glow, first red, then white, then blue. The changes in colour and the corresponding light spectra do not depend on the composition of the solid. The intensity of the light of different colours can be measured and plotted on a graph, to produce a curved line (or energy curve). WEB LINK

Classical physics predicted that the energy curve should go up continuously as temperature increases: physicists thought that matter could absorb or emit any quantity of energy. However, Planck's experiments showed that the curve reached a peak and then decreased. The position of the peak correlated to the temperature and moved toward higher light frequencies as an object became hotter. Compare the positions of the peaks for a red-hot and a white-hot object in **Figure 14**. Now compare these to the curved line that would result as predicted by the classical theory of light.

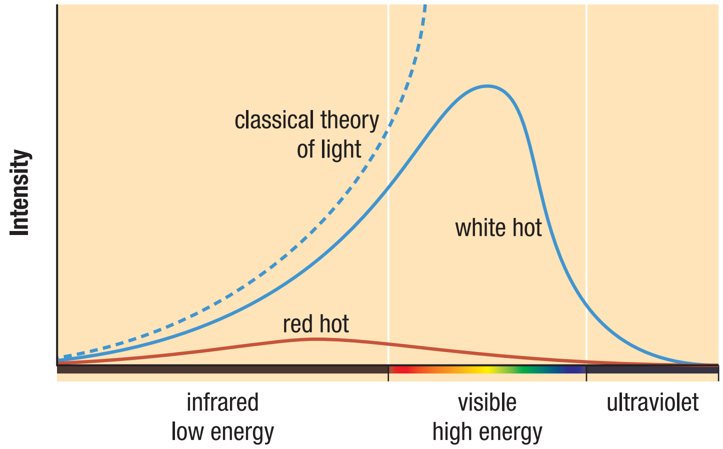

Figure 14 A white-hot wire and a red-hot wire emit light at different colours and intensities. The light emitted does not follow the expected results of the classical theory of light.

Planck accounted for the unexpected results of his heating experiments by postulating that matter can gain or lose energy, E, only in whole-number multiples, according to the equation

$$E = nhf$$

where n is an integer (1, 2, 3, ...), f is the frequency of the radiation and h is Planck's constant. Planck's constant is a constant of nature and has the value 6.63×10^{-34} J·s.

Planck knew that radiation was emitted as atoms vibrated back and forth (oscillated). He hypothesized that the energies from the oscillating atoms in the heated object were multiples of a small quantity of energy. Light was emitted in bursts of this discrete (separate and distinct) quantity of energy rather than as a continuous stream. Albert Einstein later brought Planck's hypothesis to its logical conclusion—the light emitted by a heated solid is quantized. One burst or packet of energy is now known as a **quantum** of energy.

quantum a unit or packet of energy (plural: quanta)

A quantum is a difficult concept. It may help to imagine a quantum of energy as a unit of money. Any value of money can be understood as equal to, for example, a number of pennies, the smallest unit of money. Similarly, that same value of money can be described in terms of other units of money. For example, $2.00 is equal to 200 pennies, but it is also equal to 8 quarters or 20 dimes or 40 nickels. Quanta of light are similar to units of money in that the colours of light emitted are analogous to the value of a particular coin. Infrared light may be thought of as being analogous to a penny, red light to a nickel, blue light to a dime, and ultraviolet light to a quarter.

Heating a solid until it glows in the infrared range is analogous to it emitting pennies of light energy. Similarly, a red-hot solid emits quantities of light energy analogous to nickels, a white-hot solid emits quantities of light energy analogous to dimes, and so on. It is important to keep in mind that there are no intermediate quantities of light energy, just as there are no seven-and-a-half-cent coins.

Planck's results were a surprise to the scientific community. It was now clear that energy can occur only in discrete quanta and, therefore, a system can transfer energy only in whole quanta. Planck's observations (for example, the bell-shaped curves shown in Figure 14) revealed that as the temperature of an object increases, more of the larger quanta and fewer of the smaller quanta of energy are emitted. Also, the colour of the light emitted by a hot object depends on the proportion of the quanta of different energies that are emitted. In this way, light energy seems to have properties similar to particles.

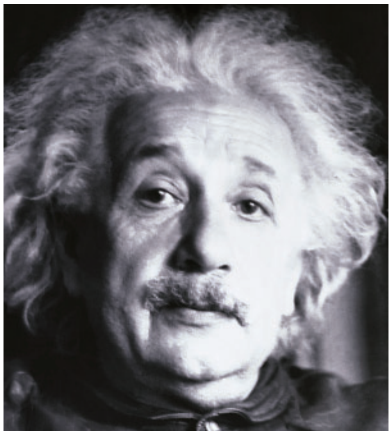

Figure 15 Albert Einstein (1879–1955) received a Nobel Prize in 1921 for a paper explaining the photoelectric effect in terms of quantum theory.

Photons

Investigation and discovery of the photoelectric effect was critical to the development of quantum theory. In 1905, Albert Einstein explained the photoelectric effect by applying Planck's idea of a quantum of energy (**Figure 15**). Einstein suggested that electromagnetic radiation could be viewed as a stream of particles called photons. A **photon** is a unit of light energy. Einstein proposed that an electron was emitted from the surface of the metal because a photon collided with the electron. During the collision, the energy of the photon transferred to the electron. Some of the transferred energy caused the electron to break away from the atom, and the rest was converted to kinetic energy. To free an electron from the atom requires the energy from a minimum of one photon.

photon a unit of light energy

An electron stays in place because of electrostatic forces. If a single electron absorbs a single photon with the right quantity of energy, the electron can escape the metal surface. If a photon does not have enough energy, no electrons can escape the metal no matter how many photons strike it. The kinetic energy of the ejected electrons depends on the frequency of the light used. When the frequency is below a certain level, called the threshold frequency, no electrons are ejected.

Quantum theory has provided explanations for observations, namely, the photoelectric effect and blackbody radiation, that no other theory could explain. For this reason, quantum theory is one of the greatest achievements in modern science. In upcoming sections you will learn about other observations that only quantum theory has been able to explain.

Research This

The Large Hadron Collider—A Smashing Success

Skills: Researching, Analyzing, Communicating, Defining the Issue, Defending a Decision

SKILLS HANDBOOK A5.1

The Large Hadron Collider (LHC) at CERN in Geneva, Switzerland, is the world's most powerful particle accelerator (**Figure 16**). Scientists are using it to investigate how atomic and subatomic particles are structured. A Toroidal LHC ApparatuS (ATLAS) was built to detect the particles and energy present after protons collide. Canadian scientists, including University of Alberta professor James Pinfold, have been working on the ATLAS project alongside scientists from across the globe.

1. Research Canada's participation in the ATLAS project.
2. Research string theory and the grand unified theory.

A. Briefly outline the premises of string theory and the grand unified theory. K/U

B. An enormous amount of money has been spent on LHC and ATLAS projects. Do you think it is worth it? What are the benefits to science and society? T/I A

C. Summarize your research and choose an appropriate, interesting presentation format to share what you learned. T/I C A

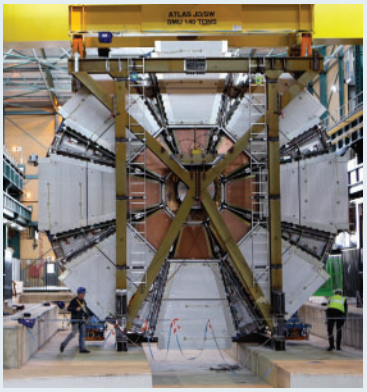

Figure 16

D. Should further investments in these projects and this type of research continue? Explain your reasoning. T/I A

WEB LINK

3.1 Review

Summary

- According to modern atomic theory, the atom has a small, dense nucleus containing protons and neutrons. Electrons reside outside the nucleus in the relatively large remaining atomic volume.
- The atomic number, Z, is the number of protons in an atom's nucleus. The mass number, A, is the total number of protons and neutrons in an atom's nucleus.
- Isotopes of an element have the same atomic number but different mass numbers. Radioisotopes have unstable nuclei that decay and emit radiation.
- According to quantum theory, electromagnetic energy is not continuous; instead, energy exists as packets or quanta, called photons.

Questions

1. For each of the following atoms, identify
   (a) the number of protons and neutrons in the nucleus
   (b) the number of electrons present in the neutral atom for that element K/U
   (i) ^{79}Br (iv) ^{133}Cs
   (ii) ^{81}Br (v) ^{3}H
   (iii) ^{239}Pu (vi) ^{56}Fe
2. Write the atomic symbol ($^{A}_{Z}X$) for each of the following isotopes: K/U
   (a) $Z = 8$; number of neutrons $= 9$
   (b) the isotope of chlorine in which $A = 37$
   (c) $Z = 27$; $A = 60$
   (d) number of protons $= 26$; number of neutrons $= 31$
   (e) the isotope of I with a mass number of 131
   (f) $Z = 3$; number of neutrons $= 4$
3. For each of the following ions, indicate the number of protons and electrons the ion contains: K/U
   (a) Ba^{2+} (d) Rb^{+}
   (b) Zn^{2+} (e) Co^{3+}
   (c) N^{3-} (f) Te^{2-}
4. What is the atomic symbol of an ion with
   (a) 16 protons, 18 neutrons, and 18 electrons?
   (b) 16 protons, 16 neutrons, and 18 electrons? K/U
5. Explain the photoelectric effect. K/U
6. Use a series of diagrams and a few point-form notes to create a flow chart that summarizes the history of atomic theory, beginning with Dalton and ending with Einstein. K/U C
7. Copy **Table 3** in your notebook and complete it. K/U C

Table 3

Symbol	Protons	Neutrons	Electrons	Net charge
$^{238}_{92}U$				0
	20	20		+2
	23	28	20	
$^{89}_{39}Y$				0
	35	44	36	
	26	33		+3
	13	14	10	

8. Scientists record their experimental observations and conclusions in a lab book or journal. Write a journal entry that would reflect the results of Rutherford's gold foil experiment. K/U T/I C
9. According to the latest developments in nuclear theory, protons and neutrons are composed of smaller subatomic particles called quarks. Research quarks and their properties K/U T/I A
   (a) How are quarks named?
   (b) Describe the composition of a proton, and explain how its composition accounts for its charge.
   (c) Which Canadian scientist provided some of the first supporting evidence for the existence of quarks and received a share of the Nobel Prize?
10. The newly updated periodic table includes pie charts for each element. Each pie chart represents the isotopes of that element found in nature, and each pie segment represents the abundance of that isotope in nature. Evaluate the usefulness of this new format compared to the classic table format. K/U T/I A

WEB LINK