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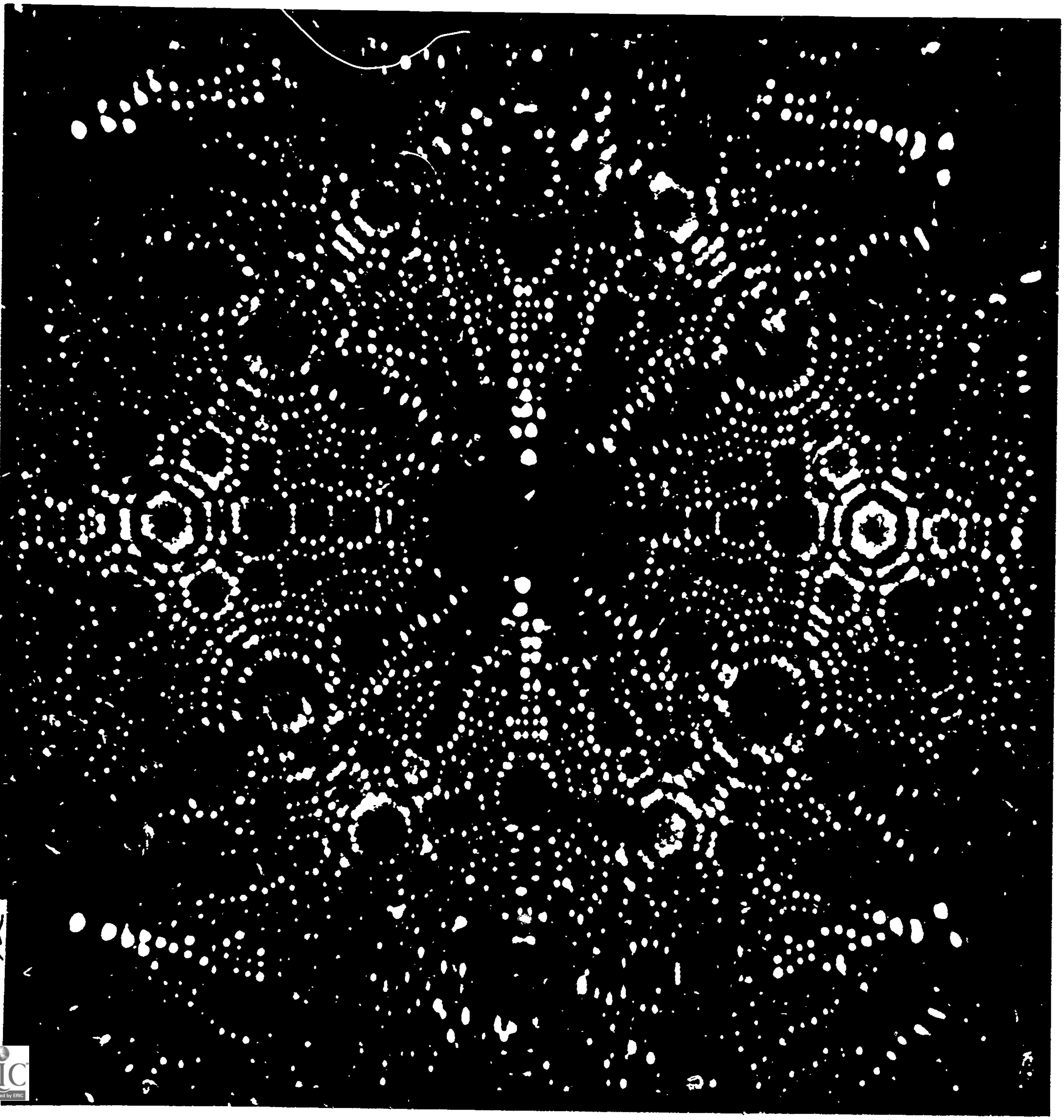
ABSTRACT

Basic atomic theories are presented in this fifth unit of the Project Physics text for use by senior high students. Chemical basis of atomic models in the early years of the 18th Century is discussed n connection with Dalton's theory, atomic properties, and periodic tables. The discovery of electrons is described by using cathode rays, Millikan's experiment, photoelectric effects, x-rays, and Einstein's photon model. Analyses of nucleus are made with a background of gas spectra, Rutherford's model, nuclear charges and sizes, Bohr theory, Franck-Hertz experiment, periodicity of elements, and atomic theory in the early 1920's. Latest ideas about atomic theory are given in terms of results of relativity concepts, particle-like behavior in radiation, wave-like behavior of matter, uncertainty principle, probability interpretation, and physical ideas of quantum mechanics. Historical developments are stressed in the overall explanation. Problems with answers are provided in two categories: study guide and end of section questions. Also included are related illustrations for explanation use and a chart of renowned people's life spans from 1800 to 1950. The work of Harvard Project Physics has been financially supported by: the Carnegie Corporation of New York, the Ford Foundation, the National Science Foundation, the Alfred P. Sloan Foundation, the United States Office of Education, and Harvard University. (CC)

Project Physics **Text** **5**

An Introduction to Physics

Models of the Atom



Project Physics **Text**

An Introduction to Physics 5 Models of the Atom

Authorized Interim Version 1968-69

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Welcome to the study of physics. This volume, more of a student's guide than a text of the usual kind, is part of a whole group of materials that includes a student handbook, laboratory equipment, films, programmed instruction, readers, transparencies, and so forth. Harvard Project Physics has designed the materials to work together. They have all been tested in classes that supplied results to the Project for use in revisions of earlier versions.

The Project Physics course is the work of about 200 scientists, scholars, and teachers from all parts of the country, responding to a call by the National Science Foundation in 1963 to prepare a new introductory physics course for nationwide use. Harvard Project Physics was established in 1964, on the basis of a two-year feasibility study supported by the Carnegie Corporation. On the previous pages are the names of our colleagues who helped during the last six years in what became an extensive national curriculum development program. Some of them worked on a full-time basis for several years; others were part-time or occasional consultants, contributing to some aspect of the whole course; but all were valued and dedicated collaborators who richly earned the gratitude of everyone who cares about science and the improvement of science teaching.

Harvard Project Physics has received financial support from the Carnegie Corporation of New York, the Ford Foundation, the National Science Foundation, the Alfred P. Sloan Foundation, the United States Office of Education and Harvard University. In addition, the Project has had the essential support of several hundred participating schools throughout the United States and Canada, who used and tested the course as it went through several successive annual revisions.

The last and largest cycle of testing of all materials is now completed; the final version of the Project Physics course will be published in 1970 by Holt, Rinehart and Winston, Inc., and will incorporate the final revisions and improvements as necessary. To this end we invite our students and instructors to write to us if in practice they too discern ways of improving the course materials.

The Directors
Harvard Project Physics

An Introduction to Physics 5 Models of the Atom

Prologue

Chapter 17. The Chemical Basis of Atomic Theory

Chap[illegible] 18. Electrons and Quanta

Chapter 19 The Rutherford—Bohr Model of the Atom

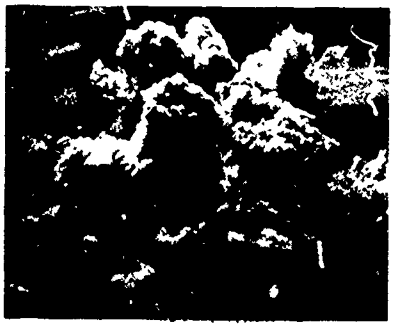
Chapter 20: Some Ideas From Modern Physical Theories

Prologue In the earlier units of this course we studied the motion of bodies: bodies of ordinary size, such as we deal with in everyday life, and very large bodies, such as planets. We have seen how the laws of motion and gravitation were developed over many centuries and how they are used. We have learned about conservation laws, about waves, about light, and about electric and magnetic fields. All that we have learned so far can be used to study a problem which has bothered people for many centuries: the problem of the nature of matter. The phrase, "the nature of matter," may seem simple to us now, but its meaning has been changing and growing over the centuries. The phrase really stands for the questions men ask about matter at any given date in the development of science; the kind of questions and the methods used to find answers to these questions are continually changing. For example, during the nineteenth century the study of the nature of matter consisted mainly of chemistry; in the twentieth century the study of matter has moved into atomic and nuclear physics.

The photographs on these two pages illustrate some of the variety of forms of matter: large and small, stable and shifting, animate and inanimate.

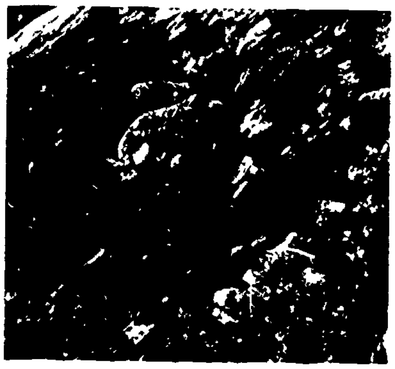
microscopic crystals

Since 1800 progress has been so rapid that it is easy to forget that people have theorized about matter for more than 2500 years. In fact some of the questions for which answers have been found only during the last hundred years were asked more than two thousand years ago. Some of the ideas we consider new and exciting, such as the atomic constitution of matter, were debated in Greece in the fifth and fourth centuries B.C. In this prologue we shall, therefore, review briefly the development of ideas concerning the nature of matter up to about 1800. This review will set the stage for the four chapters of Unit 5, which will be devoted, in greater detail, to the progress made since 1800 on the problem of the constitution of matter. It will be shown in these chapters that matter is made up of atoms and that atoms have structures about which a great deal of information has been obtained.



condensed water vapor

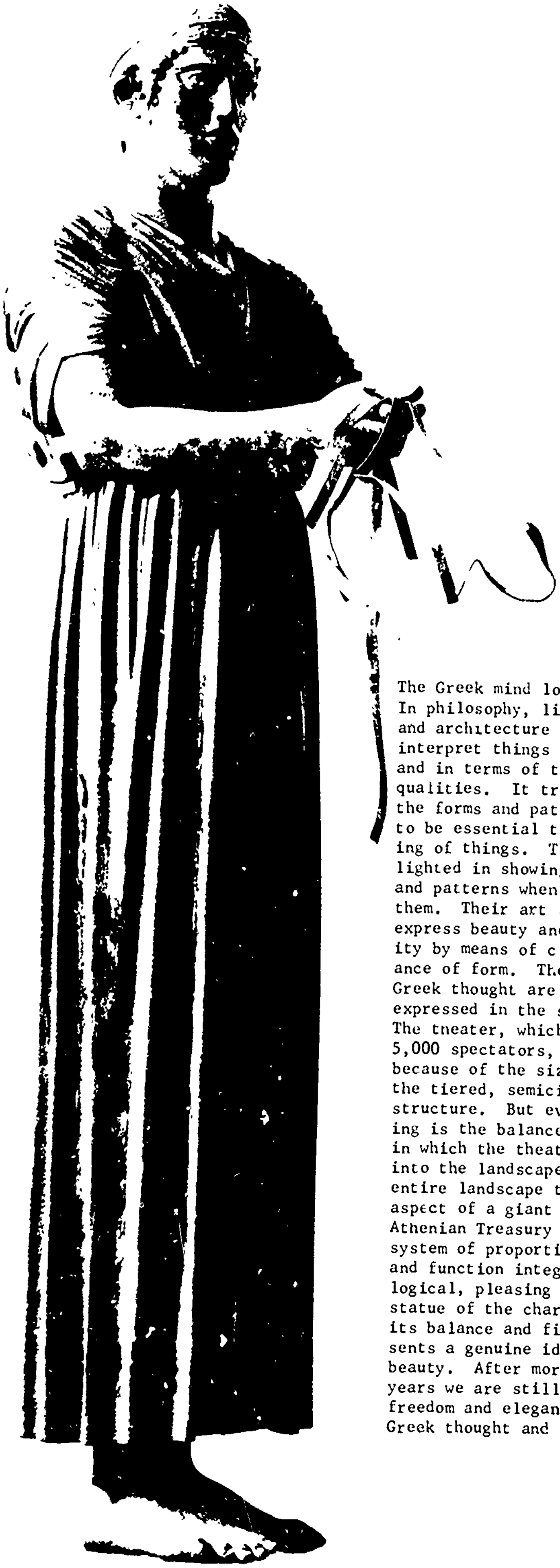
Long before men started to develop the activities we call science, they were acquainted with snow, wind, rain, mist and cloud; with heat and cold; with salt and fresh water; wine, milk, blood and honey; ripe and unripe fruits; fertile and infertile seeds. They saw that plants, animals and men were born, that they grew and matured and that they aged and died. Men noticed that the world about them was continually changing and yet, on a large scale, it seemed to remain much the same. The causes of these changes and of the apparent continuity of nature were unknown. So men invented gods and demons who controlled nature. Myths grew up around the creation of the world and its contents, around



toad on log

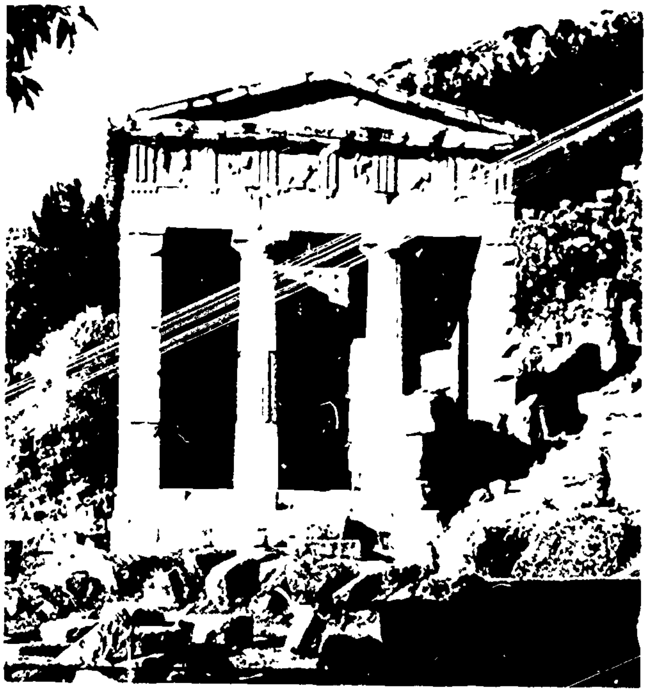
See "Structure, Substructure, Superstructure" in Project Physics Reader 5.

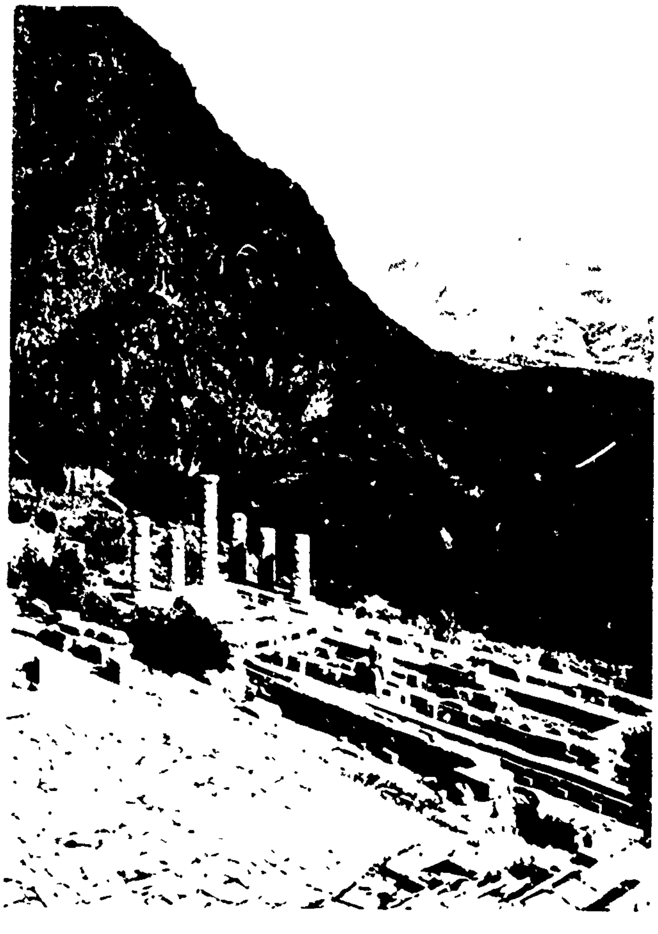
Monolith—The Face of Half Dome, 1927 (photo by Ansel Adams)



Greek Ideas of Order

The Greek mind loved clarity. In philosophy, literature, art and architecture it sought to interpret things with precision and in terms of their lasting qualities. It tried to discover the forms and patterns thought to be essential to an understanding of things. The Greeks delighted in showing these forms and patterns when they found them. Their art and architecture express beauty and intelligibility by means of clarity and balance of form. These aspects of Greek thought are beautifully expressed in the shrine of Delphi. The theater, which could seat 5,000 spectators, impresses us because of the size and depth of the tiered, semicircular seating structure. But even more striking is the balanced, orderly way in which the theater is shaped into the landscape so that the entire landscape takes on the aspect of a giant theater. The Athenian Treasury has an orderly system of proportions, with form and function integrated into a logical, pleasing whole. The statue of the charioteer, with its balance and firmness, represents a genuine ideal of male beauty. After more than 2,000 years we are still struck by the freedom and elegance of ancient Greek thought and expression.





Basing his ideas on the tradition of atomists dating back to the greek philosophers, Democritus and Leucippus, Lucretius wrote in his poem, De rerum natura (Concerning the Nature of Things), "...Since the atoms are moving freely through the void, they must all be kept in motion either by their own weight or on occasion by the impact of another atom. For it must often happen that two of them in their course knock together and immediately bounce apart in opposite directions, a natural consequence of their hardness and solidity and the absence of anything behind to stop them.

"As a further indication that all particles of matter are on the move, remember that the universe is bottomless: there is no place where the atoms could come to rest. As I have already shown by various arguments and proved conclusively, space is without end or limit and spreads out immeasurably in all directions alike.

"It clearly follows that no rest is given to atoms in their course through the depths of space. Driven along in an incessant but variable movement, some of them bounce far apart after a collision while others recoil only a short distance from the impact. From those that do not recoil far, being driven into a closer union and held there by the entanglement of their own interlocking shapes, are composed firmly rooted rock, the stubborn strength of steel and the like. Those others that move freely through larger tracts of space, springing far apart and carried far by the rebound—these provide for us thin air and blazing sunlight. Besides these, there are many other atoms at large in empty space which have been thrown out of compound bodies and have nowhere even been granted admittance so as to bring their motions into harmony."

the changes of the seasons, around the events man could see happening but could not understand.

Over a long period of time men developed some control over nature: they learned how to smelt ores, to make weapons and tools, to produce gold ornaments, glass, perfumes, medicines and beer. Eventually, in Greece, about the year 600 B.C., philosophers—the lovers of wisdom started to look for rational explanations of natural events, that is, explanations that did not depend on the whims of gods or demons. They sought to discover the enduring, unchanging things out of which the world is made. They started on the problem of explaining how these enduring things can give rise to the changes that we perceive. This was the beginning of man's attempts to understand the material world - the nature of matter.

This gold earring, made in Greece about 600 B.C., shows the great skill with which ancient artisans worked metals.
Museum of Fine Arts, Boston

The earliest Greek philosophers thought that all the different things in the world were made out of a single basic substance, or stuff. Some thought that water was the fundamental substance and that all other substances were derived from it. Others thought that air was the basic substance; still others favored fire. But neither water, air nor fire was satisfactory; no one substance seemed to have enough different properties to give rise to the enormous variety of substances in the world. According to another view, introduced by Empedocles around 450 B.C., there are four basic types of matter: earth, air, fire and water; all material things were made out of them. Change comes about through the mingling and separation of these four basic materials which unite in different proportions to produce the familiar objects around us; but the basic materials were supposed to persist through all these changes. This theory was the first appearance in our scientific tradition of a model of matter according to which all material things are just different arrangements of a few eternal substances, or elements.

The first atomic theory of matter was introduced by the Greek philosopher Leucippus, born about 500 B.C., and his pupil Democritus, who lived from about 460 B.C. to 370 B.C. Only scattered fragments of the writings of these philosophers remain, but their ideas are discussed in considerable detail by Aristotle (384-322 B.C.), by another Greek philosopher, Epicurus (341-270 B.C.) and by the Latin poet Lucretius (100-55 B.C.). It is to these men that we owe most of our knowledge of ancient atomism.

The theory of the atomists was based on a number of assumptions: (1) that matter is eternal, and that no material thing can come from nothing, nor can anything material pass into nothing; (2) that material things consist of very minute, but not infinitely small, indivisible particles— the word "atom" meant "uncuttable" in Greek and, in discussing the ideas of the early atomists, we could use the word "indivisibles" instead of the word "atoms"; (3) that all atoms are of the same kind, that is, of the same substance, but differ in size, shape and position; (4) that the atoms exist in otherwise empty space (void), which separates them, and because of this space they are capable of movement; (5) that the atoms are in ceaseless motion although the nature and cause of the atomic motions are not clear. In the course of their motions atoms come together and form combinations which are the material substances we know. When the atoms forming these combinations separate, the substances break up. Thus, the combinations and separations of atoms give rise to the changes which take place in the world. The combinations and separations take place in accord with natural laws which are not known, but do not require the action of gods or demons or other supernatural powers.

With the above assumptions, the ancient atomists were able to work out a consistent story of change, of what they sometimes called "coming-to-be" and "passing-away." They could not prove experimentally that their theory was correct, and they had to be satisfied with a rational explanation based on assumptions that seemed reasonable to them. The theory was a "likely story," but it was not useful for the prediction of new phenomena.

The atomic theory was criticized severely by Aristotle, who argued, on logical grounds, that no vacuum or void could exist and that the ideas of atoms with their inherent motion must be rejected. For a long time Aristotle's argument against the void was convincing. Not until the seventeenth century did Torricelli's experiments (described in Chapter 12) show that a vacuum could indeed exist. Aristotle also argued that matter is continuous and infinitely divisible so that there can be no atoms.

Aristotle developed a theory of matter as part of his grand scheme of the universe, and this theory, with some modifications, was thought to be satisfactory by most philosophers of nature for nearly two thousand years. His theory of matter was based on the four basic substances

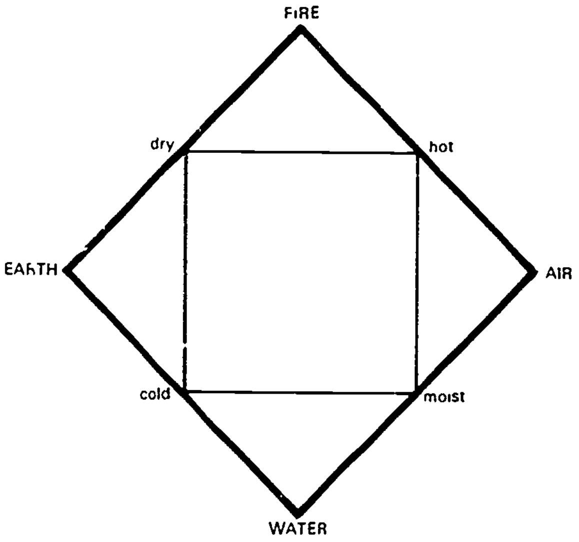
According to Aristotle in his Metaphysics, "There is no consensus concerning the number or nature of these fundamental substances. Thales, the first to think about such matters, held that the elementary substance is clear liquid....He may have gotten this idea from the observation that only moist matter can be wholly integrated into an object—so that all growth depends on moisture....

"Anaximenes and Diogenes held that colorless gas is more elementary than clear liquid, and that, indeed, it is the most elementary of all simple substances. On the other hand, Hippasus of Metapontum and Heraclitus of Ephesus said that the most elementary substance is heat. Empedocles spoke of four elementary substances, adding dry dust to the three already mentioned...Anaxagoras of Clazomenae says that there are an infinite number of elementary constituents of matter...." [From a translation by D. E. Gershenson and D. A. Greenberg.]

or "elements," earth, air, fire and water, and four "qualities," cold, hot, moist and dry. Each element was characterized by two qualities. Thus the element

earth is dry and cold
water is cold and moist
air is moist and hot
fire is hot and dry.

According to Aristotle, it is always the first of the two qualities which predominates. The elements are not unchangeable; any one of them may be transformed into any other because of one or both of its qualities changing into opposites. The transformation takes place most easily between two elements having one quality in common; thus earth is transformed into water when dryness changes into moistness. Aristotle worked out a scheme of such possible transformations which can be shown in the following diagram:



Earth can also be transformed into air if both of the qualities of earth (dry, cold) are changed into their opposites (moist, hot). Water can be transformed into fire if both of its qualities (cold, moist) are changed into their opposites (hot, dry).

Aristotle was also able to explain many natural phenomena by means of his ideas. Like the atomic theory, Aristotle's theory of coming-to-be and passing-away was consistent, and constituted a model of the nature of matter. It had certain advantages over the atomic theory: it was based on elements and qualities that were familiar to people; it did not involve the use of atoms, which couldn't be seen or otherwise perceived, or of a void, which was difficult to imagine. In addition, Aristotle's theory provided some basis for further experimentation: it supplied what seemed like a rational basis for the possibility of changing one material into another.

During the period 300 A.D. to about 1600 A.D., atomism declined although it did not die out completely. Christian, Hebrew and Moslem theologians considered atomists to be "atheistic" and "materialistic" because they claimed that everything in the universe can be explained in terms of matter and motion. The atoms of Leucippus and Democritus moved through empty space, devoid of spirit, and wi definite plan or purpose. Such an idea was contrary to the beliefs of the major religions.

About 300 or 400 years after Aristotle, a kind of research called *alchemy* appeared in the Near and Far East. Alchemy in the Near East was a combination of Aristotle's ideas about matter with methods of treating ores and metals. One of the aims of the alchemists was to change, or transmute, ordinary metals into gold. Although they failed to do this, alchemy (along with metallurgy) was a forerunner of chemistry. The alchemists studied many of the properties of substances that are now classified as chemical properties. They invented many of the pieces of chemical apparatus that are still used, such as reaction vessels (retorts) and distillation flasks. They studied such processes as calcination, distillation, fermentation and sublimation. In this sense alchemy may be regarded as the chemistry of the Middle Ages. But alchemy left unsolved some of the fundamental questions. At the opening of the eighteenth century the most important of these questions were: first, what is a chemical element; second, what is the nature of chemical composition and chemical change, especially burning; third, what is the chemical nature of the so-called elements, air, fire and water. Until these questions were answered, it was impossible to make real progress in finding out what matter is. One result was that the "scientific revolution" of the seventeenth century, which clarified the problems of astronomy and dynamics, did not reach chemistry until the eighteenth century.

Laboratory of a 16th-century alchemist.

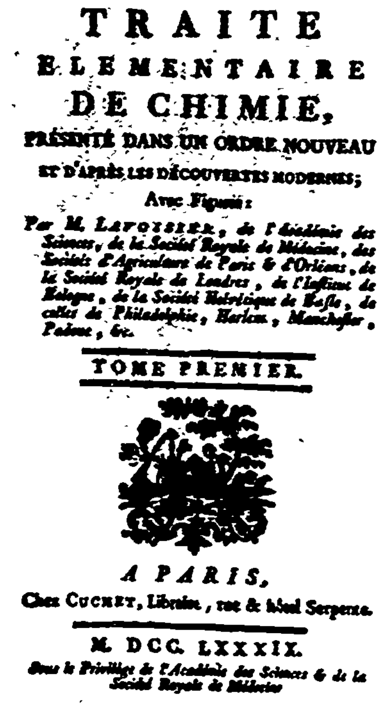
During the seventeenth century, however, some forward steps were made which supplied a basis for future progress on the problem of matter. The Copernican and Newtonian revolutions undermined the authority of Aristotle to such an extent that his ideas about matter were also questioned. Atomic concepts were revived because atomism offered a way of looking at things that was very different from Aristotle's ideas. As a result theories involving "atoms," "particles" or "corpuscles" were again considered seriously. Boyle's models of a gas (Chapter 11) were based on the idea of "gas particles." Newton also discussed the behavior of a gas (and even of light!) by supposing it to consist of particles. Thus, the stage was set for a general revival of atomic theory.

In the eighteenth century, chemistry became more quantitative as the use of the balance was increased. Many

One of those who contributed greatly to the revival of atomism was Pierre Gassendi (1592-1655), a French priest and philosopher. He avoided the criticism of atomism as atheistic by saying that God also created the atoms and bestowed motion upon them. Gassendi accepted the physical explanations of the atomists, but rejected their disbelief in the immortality of the soul and in Divine Providence. He was thus able to provide a philosophical justification of atomism which met some of the serious religious objections.

new substances were isolated and their properties examined. The attitude that grew up in the latter half of the century was exemplified by that of Henry Cavendish (1731-1810), who, according to a biographer, regarded the universe as consisting

> ...solely of a multitude of objects which could be weighed, numbered, and measured; and the vocation to which he considered himself called was to weigh, number, and measure as many of those objects as his alloted threescore years and ten would permit....He weighed the Earth; he analysed the Air; he discovered the compound nature of Water; he noted with numerical precision the obscure actions of the ancient element Fire.


TRAITE
ELEMENTAIRE
DE CHIMIE,
PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;
Avec Figures:
Par M. Lavoisier, de l'Académie des Sciences, de la Société Royale de Médecine, des Sociétés d'Agriculture de Paris & d'Orléans, de la Société Royale de Londres, de l'Institut de Bologne, de la Société Helvétique de Basle, de celles de Philadelphie, Harlem, Manchester, Padoue, &c.
TOME PREMIER.
A PARIS,
Chez Cuchet, Libraire, rue & hôtel Serpente.
M. DCC. LXXXIX.
Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine

Title page of Lavoisier's Traité Elémentarie de Chimie (1789)

Eighteenth-century chemistry reached its peak in the work of Lavoisier (1743-1794), who worked out the modern views of combustion, established the law of conservation of mass (see Chapter 9), explained the elementary nature of hydrogen and oxygen and the composition of water, and emphasized the quantitative aspects of chemistry. His famous book, Traité Elémentaire de Chimie (or Elements of Chemistry), published in 1789, established chemistry as a modern science. In it, he analyzed the idea of element in a way which is very close to our modern views:

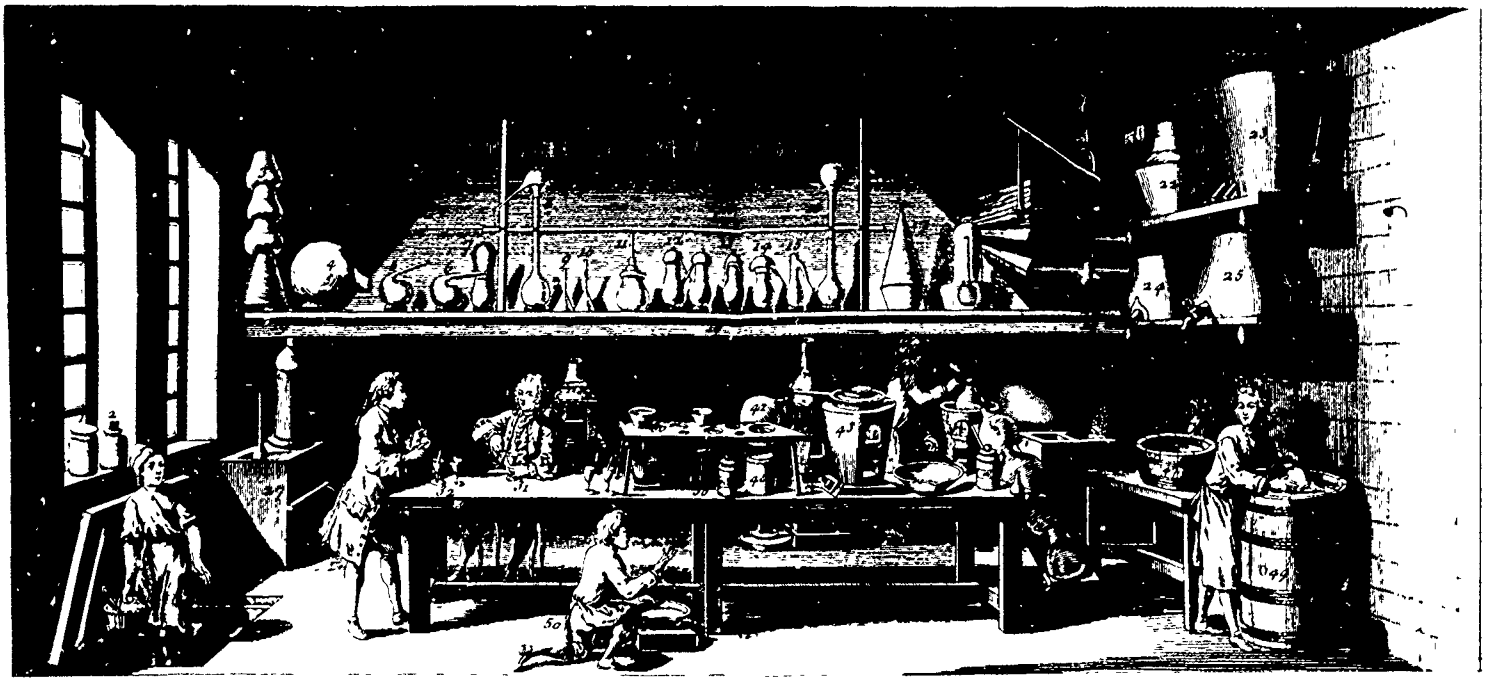
> ...if, by the term elements we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable that we know nothing at all about them; but if we apply the term elements, or principles of bodies, to express our ide[illegible] the last point which analysis is capable [illegible]ing, we must admit as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. Not that we are entitled to affirm that these substances we consider as simple may not be compounded of two, or even of a greater number of principles; but since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so.

During the latter half of the eighteenth century and the early years of the nineteenth century great progress was made in chemistry because of the increasing use of quantitative methods. Chemists found out more and more about the composition of substances. They separated many elements and showed that nearly all substances are compounds—combinations—of chemical elements. They learned a great deal about how elements combine to form compounds and how compounds can be broken down into the elements of which they are composed. This information made it possible for chemists to establish certain laws of chemical combination. Then chemists sought an explanation for these laws.

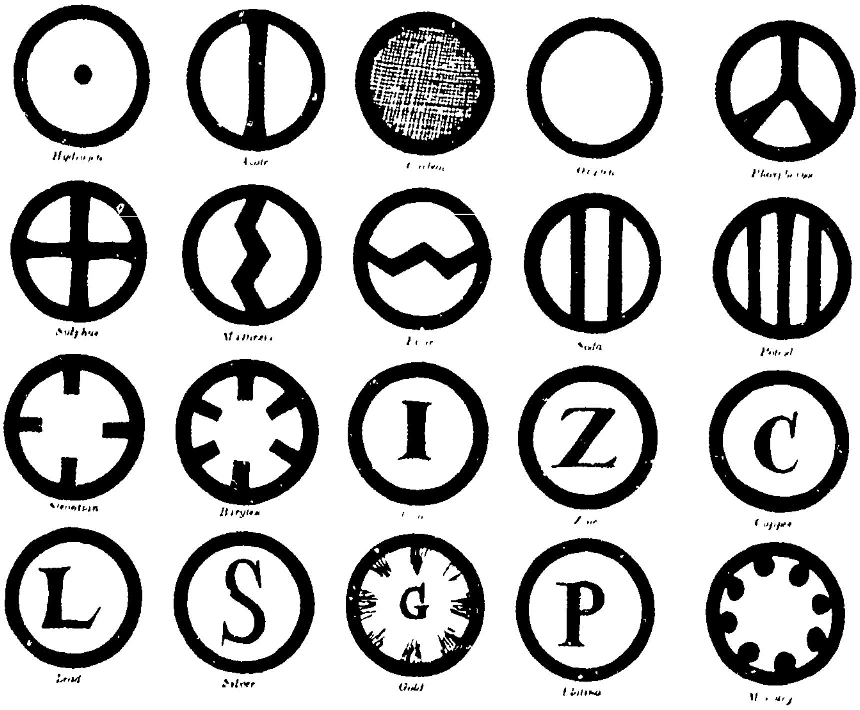
During the first ten years of the nineteenth century, John Dalton, an English chemist, introduced a modified form of the old Greek atomic theory to account for the laws of chemical combination. It is here that the modern story of the atom begins. Dalton's theory was an improvement over that of Democritus, Epicurus and Lucretius because it opened the way for the quantitative study of the atom in the nineteenth century. Today the existence of the atom is no longer a topic of speculation. There are many kinds of experimental evidence, not only for the existence of atoms but also for their structure. This evidence, which began to accumulate about 150 years ago, is now convincing. In this unit we shall trace the discoveries and ideas that produced this evidence.

The first mass of convincing evidence for the existence of atoms and the first clues to the nature of atoms came from chemistry. We shall, therefore, start with chemistry in the early years of the nineteenth century; this is the subject of Chapter 17. We shall see that chemistry raised certain questions about atoms which could only be answered by physics. Physical evidence, accumulated in the nineteenth century and the early years of the twentieth century, made it possible to propose atomic models of atomic structure. This evidence and the earlier models will be discussed in Chapters 18 and 19. The latest ideas about atomic theory will be discussed in Chapter 20.

A chemical laboratory of the 18th century



Chapter 17 The Chemical Basis of Atomic Theory



Dalton's symbols of the elements

17.1 Dalton's atomic theory and the laws of chemical combination.

The atomic theory of John Dalton appeared in his treatise, *A New System of Chemical Philosophy*, published in two parts, in 1808 and 1810. The main postulates of his theory were:

(1) Matter consists of indivisible atoms.

> ...matter, though divisible in an *extreme degree*, is nevertheless not *infinitely* divisible. That is, there must be some point beyond which we cannot go in the division of matter. The existence of these ultimate particles of matter can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements. I have chosen the word *atom* to signify these ultimate particles....

(2) Each element consists of a characteristic kind of identical atoms. There are consequently as many different kinds of atoms as there are elements. The atoms of an element "are perfectly alike in weight and figure, etc."

(3) Atoms are unchangeable.

(4) When different elements combine to form a compound, the smallest portion of the compound consists of a grouping of a definite number of atoms of each element.

(5) In chemical reactions, atoms are neither created nor destroyed, but only rearranged.

Dalton's theory really grew out of his interest in meteorology and his research on the composition of the atmosphere. He tried to explain many of the physical properties of gases in terms of atoms. At first he assumed that the atoms of all the different elements had the same size. But this assumption didn't work and he was led to think of the atoms of different elements as being different in size or in mass. In keeping with the quantitative spirit of the time, he tried to determine the numerical values for the differences in mass. But—before considering how to determine the masses of atoms of the different elements, let us see how Dalton's postulates make it possible to account for the laws of chemical combination.

Meteorology is a science that deals with the atmosphere and its phenomena—weather forecasting is one branch of meteorology.

We consider first the law of conservation of mass. In 1774, Lavoisier studied the reaction between tin and oxygen in a closed and sealed container. When the tin is heated in air, it reacts with the oxygen in the air to form a compound, tin oxide, which is a white powder. Lavoisier weighed the sealed container before and after the chemical reaction and found that the mass of the container and its contents was the same before and after the reaction. A modern example of a similar reaction is the flashing of a photographic flash bulb containing magnesium. The flash bulb is an isolated system containing two elements, magnesium (in the form of a wire) and oxygen gas, sealed in a closed container. When an electric current passes through the wire, a chemical reaction occurs with a brilliant flash. Magnesium and oxygen disappear, and a white powder, magnesium oxide, is formed. Comparison of the mass after the reaction with the mass before the reaction shows that there is no detectable change in mass; the mass is the same before and after the reaction. Careful work by many experimenters on many chemical reactions has shown that mass is neither destroyed nor created, in any detectable amount, in a chemical reaction. This is the law of conservation of mass.

See "Failure and Success" in Project Physics Reader 5.

According to Dalton's theory (postulates 4 and 5) chemical changes are only the rearrangements of unions of atoms. Since atoms are unchangeable (according to postulate 3) rearranging them cannot change their masses. Hence, the total mass of all the atoms before the reaction must equal the total mass of all the atoms after the reaction. Dalton's atomic theory, therefore, accounts in a simple and direct way for the law of conservation of mass.

A second law of chemical combination which could be explained easily with Dalton's theory is the law of definite proportions. This law states that a particular chemical compound always contains the same elements united in the same proportions by weight. For example, the ratio of the masses of oxygen and hydrogen which combine to form water is always 7.94 to 1, that is,

$$\frac{\text{mass of oxygen}}{\text{mass of hydrogen}} = \frac{7.94}{1}.$$

If there is more of one element present, say 10 grams of oxygen and one gram of hydrogen, only 7.94 grams of oxygen will combine with the hydrogen. The rest of the oxygen, 2.06 grams, remains uncombined.

The fact that elements combine in fixed proportions means also that each chemical compound has a certain definite composition. Thus, by weight, water consists of 88.8 percent oxygen and 11.2 percent hydrogen. The decomposition of sodium chloride (common salt) always gives the results: 39 percent sodium and 61 percent chlorine by weight. This is another way of saying that 10 grams of sodium always combine with 15.4 grams of chlorine to form sodium chloride. Hence, the law of definite proportions is also referred to as the law of definite composition.

Now let us see how Dalton's theory can be applied to a chemical reaction, say, to the formation of water from oxygen and hydrogen. First, according to Dalton's second postulate, all the atoms of oxygen have the same mass; all the atoms of hydrogen have the same mass, which is different from the mass of the oxygen atoms. To express the mass of the oxygen entering into the reaction, we multiply the mass of a single oxygen atom by the number of oxygen atoms:

$$\text{mass of oxygen} = \left(\begin{matrix}\text{mass of 1}\\\text{oxygen atom}\end{matrix}\right) \times \left(\begin{matrix}\text{number of}\\\text{oxygen atoms}\end{matrix}\right).$$

Similarly, the mass of hydrogen entering into the reaction is equal to the product of the number of hydrogen atoms entering into the reaction and the mass of one hydrogen atom:

$$\text{mass of hydrogen} = \left(\begin{matrix}\text{mass of 1}\\\text{hydrogen atom}\end{matrix}\right) \times \left(\begin{matrix}\text{number of}\\\text{hydrogen atoms}\end{matrix}\right).$$

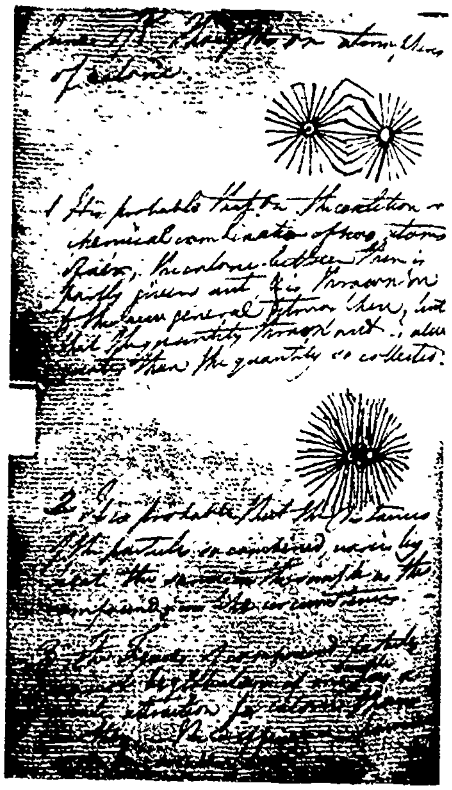
To get the ratio of the mass of oxygen entering into the reaction to the mass of hydrogen entering into the reaction, we divide the first equation by the second equation:

$$\frac{\text{mass of oxygen}}{\text{mass of hydrogen}} = \frac{\left(\begin{matrix}\text{mass of 1}\\\text{oxygen atom}\end{matrix}\right)}{\left(\begin{matrix}\text{mass of 1}\\\text{hydrogen atom}\end{matrix}\right)} \times \frac{\left(\begin{matrix}\text{number of}\\\text{oxygen atoms}\end{matrix}\right)}{\left(\begin{matrix}\text{number of}\\\text{hydrogen atoms}\end{matrix}\right)}.$$

Now, the masses of the atoms do not change (postulate 3), so the first ratio on the right side of the resulting equation has a certain unchangeable value. According to postulate 4, the smallest portion of the compound, water (now called a <u>molecule</u> of water) consists of a definite number of atoms of each element. Hence the numerator of the second ratio on the right side of the equation has a definite value, and the denominator has a definite value, so the ratio has a definite value. The product of the two ratios on the right hand side therefore, has a certain definite value. This equation then tells us that the ratio of the masses of oxygen and hydrogen that combine to form water must have a certain definite value. But this is just the law of definite proportions or definite composition. Thus, Dalton's theory also accounts for this law of chemical combination.

There are other laws of chemical combination which are explained by Dalton's theory. Because the argument would

John Dalton (1766-1844). His first love was meteorology and he kept careful daily weather records for 46 years—a total of 200,000 observations. He was the first to describe color blindness in a publication, and was color-blind himself, not exactly an advantage for a chemist who had to see color changes in chemicals (his color blindness may help to explain why Dalton was a rather clumsy and slipshod experimenter). But his accomplishments rest not upon successful experiments, but upon his interpretation of the work of others. Dalton's notion that all elements were composed of extremely tiny, indivisible and indestructible atoms, and that all substances are composed of combinations of these atoms was accepted by most chemists with surprisingly little opposition. There were many attempts to honor him, but being a Quaker, he shunned any form of glory. When he received a doctor's degree from Oxford, his colleagues wanted to present him to King William IV. He had always resisted such a presentation because he would not wear court dress. However, his Oxford robes would satisfy the protocol. Unfortunately, they were scarlet and a Quaker could not wear scarlet. But Dalton could see no scarlet and was presented to the king in robes which he saw as gray.



A page from Dalton's notebook, showing his representation of two adjacent atoms (top) and of a molecule or "compound atom" (bottom)

get complicated and nothing really new would be added, we shall not discuss them.

Dalton's interpretation of the experimental facts of chemical combination made possible several important conclusions: (1) that the differences between one chemical element and another would have to be described in terms of the differences between the atoms of which these elements were made up; (2) that there were, therefore, as many different types of atoms as there were chemical elements; (3) that chemical combination was the union of atoms of different elements into molecules of compounds. Dalton's theory also showed that the analysis of a large number of chemical compounds could make it possible to assign relative mass values to the atoms of different elements. This possibility will be discussed in the next section.

Q1 What did Dalton assume about the atoms of an element?

Q2 What two experimental laws did Dalton's assumptions explain?

17.2 The atomic masses of the elements. One of the most important concepts to come from Dalton's work is that of atomic mass and the possibility of determining numerical values for the masses of the atoms of different elements. Dalton had no idea of the actual masses of atoms except that he thought they were very small. In addition, reasonable estimates of atomic size did not appear until about 50 years after Dalton published his theory. They came from the kinetic theory of gases and indicated that atoms (or molecules) had diameters of the order of 10^{-10} meter. Atoms are thus much too small for mass measurements to be made on single atoms. But relative values of atomic masses can be found by using the law of definite proportions and experimental data on chemical reactions.

To see how this could be done we return to the case of water, for which, as we saw in the last section, the ratio of the mass of oxygen to the mass of hydrogen is 7.94:1. Now, if we knew how many atoms of oxygen and hydrogen are contained in a molecule of water we could find the ratio of the mass of the oxygen atom to the mass of the hydrogen atom. Dalton didn't know the numbers of oxygen and hydrogen atoms in a molecule of water. He therefore made an assumption. As scientists often do, he made the simplest assumption, namely, that one atom of oxygen combines with one atom of hydrogen to form one "compound atom" (molecule) of water. By this reasoning Dalton concluded that the oxygen atom is 7.94 times more massive than the hydrogen atom.

SG 17.4
SG 17.5

More generally, Dalton assumed that when only one compound of two elements, A and B, exists, one atom of A always combines with one atom of B. Although Dalton could then find values of the relative masses of different atoms later work showed that Dalton's assumption of one to one ratios was often incorrect. For example, it was found that one atom of oxygen combines with two atoms of hydrogen to form one molecule of water, so the ratio of the mass of an oxygen atom to the mass of a hydrogen atom is 15.88 instead of 7.94. By studying the composition of water as well as many other chemical compounds, Dalton found that the hydrogen atom appeared to have less mass than the atoms of any other elements. Therefore, he proposed to express the masses of atoms of all other elements in terms of the mass of the hydrogen atom. Dalton defined the relative atomic mass of an element as the mass of an atom of that element compared to the mass of a hydrogen atom. This definition could be used by chemists in the nineteenth century even before the masses of individual atoms could be measured directly. All that was needed was the ratios of masses of atoms; these ratios could be found by measuring the masses of substances in chemical reactions (see Sec. 17.1). For example, we can say that the mass of a hydrogen atom is "one atomic mass unit" (1 amu). Then, if we know that an oxygen atom has a mass 15.38 times as great as that of a hydrogen atom, we can say that the atomic mass of oxygen is 15.88 atomic mass units. The system of atomic masses used in modern physical science is based on this principle, although it differs in details (and the standard for comparison is now carbon instead of oxygen).

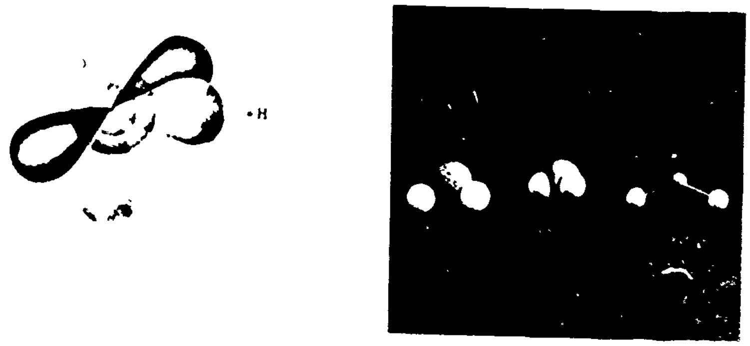
During the nineteenth century chemists extended and improved Dalton's ideas. They studied many chemical reactions quantitatively, and developed highly accurate methods for determining relative atomic and molecular masses. More elements were isolated and their relative atomic masses determined. Because oxygen combined readily with many other elements chemists decided to use oxygen rather than hydrogen as the standard for atomic masses. Oxygen was assigned an atomic mass of 16 so that hydrogen could have an atomic mass close to one. The atomic masses of other elements could be obtained, relative to that of oxygen, by applying the laws of chemical combination to the compounds of the elements with oxygen. By 1872, 63 elements had been identified and their atomic masses determined. They are listed in Table 17.1, which gives modern values for the atomic masses. This table contains much valuable information, which we shall consider at greater length in Sec. 17.4. (The special marks, circles and rectangles, will be useful then.)

The progress made in identifying elements in the 19th century may be seen in the following table.

Year	Total number of elements identified
1720	14
1740	15
1760	17
1780	21
1800	31
1820	49
1840	56
1860	60
1880	69
1900	83

Q3 Was the simplest chemical formula necessarily correct?

Q4 Why did Dalton choose hydrogen as the unit of atomic mass?



Several different representations of a water molecule.

Table 17.1 Elements known by 1872

Name	Symbol	Atomic Mass*
hydrogen	H	1.0
☐ lithium	Li	6.9
beryllium	Be	9.0
boron	B	10.8
carbon	C	12.0
nitrogen	N	14.0
oxygen	O	16.0
○ fluorine	F	19.0
☐ sodium	Na	23.0
magnesium	Mg	24.3
aluminum	Al	27.0
silicon	Si	28.1
phosphorus	P	31.0
sulfur	S	32.1
○ chlorine	Cl	35.5
☐ potassium	K	39.1
calcium	Ca	40.1
titanium	Ti	47.9
vanadium	V	50.9
chromium	Cr	52.0
manganese	Mn	54.9
iron	Fe	55.8
cobalt	Co	58.9
nickel	Ni	58.7
copper	Cu	63.5
zinc	Zn	65.4
arsenic	As	74.9
selenium	Se	79.0
○ bromine	Br	79.9
☐ rubidium	Rb	85.5
strontium	Sr	87.6
yttrium	Yt	88.9
zirconium	Zr	91.2
niobium	Nb	92.9
molybdenum	Mo	95.9
ruthenium	Ru	101.1(104)
rhodium	Rh	102.9(104)
palladium	Pd	106.4
silver	Ag	107.9

Name	Symbol	Atomic Mass*
cadmium	Cd	112.4
indium	In	114.8(113)
tin	Sn	118.7
antimony	Sb	121.7
tellurium	Te	127.6(125)
○ iodine	I	126.9
☐ cesium	Cs	132.9
barium	Ba	137.3
didymium(**)	Di	--- (138)
cerium	Ce	140.1
erbium	Er	167.3(178)
lanthanum	La	138.9(180)
tantalum	Ta	180.9(182)
tungsten	W	183.9
osmium	Os	190.2(195)
iridium	Ir	192.2(197)
platinum	Pt	195.1(198)
gold	Au	197.0(199)
mercury	Hg	200.6
thallium	Tl	204.4
lead	Pb	207.2
bismuth	Bi	209.0
thorium	Th	232.0
uranium	U	238.0(240)

* Atomic masses given are modern values. Where these differ greatly from those accepted in 1872, the old values are given in parentheses.

** Didymium (Di) was later shown to be a mixture of two different elements, namely praseodymium (Pr; atomic mass 140.9) and neodymium (Nd; atomic mass 144.2).

○ halogens ☐ alkaline metals

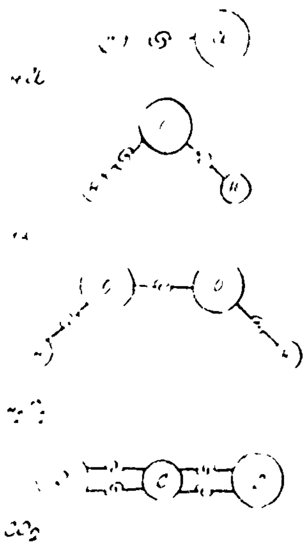
17.3 Other properties of the elements: valence. In addition to the atomic masses, many other properties of the elements and their compounds were determined. Among these properties were: melting point, boiling point, density, electrical conductivity, thermal conductivity (the ability to conduct heat), specific heat (the amount of heat needed to change the temperature of one gram of a substance by 1°C), hardness, refractive index and others. The result was that by 1870 an enormous amount of information was available about a large number of elements and their compounds.

One of the most important properties that chemists studied was the combining ability or combining capacity of an element. This property, which is called valence,

In the thirteenth century a great theologian and philosopher, Albertus Magnus (Albert the Great) introduced the idea of affinity to denote an attractive force between substances that causes them to enter into chemical combination. It was not until 600 years later that it became possible to replace this qualitative notion by quantitative concepts. Valence is one of these quantitative concepts.

plays an important part in our story. As a result of studies of chemical compounds, chemists were able to assign formulas to the molecules of compounds. These formulas show how many atoms of each element are contained in a molecule. For example, water has the familiar formula H_2O, which indicates that the smallest piece of water that exists as water contains two atoms of hydrogen and one atom of oxygen. Hydrogen chloride (hydrochloric acid) has the formula HCl: one atom of hydrogen combines with one atom of chlorine. Common salt may be represented by the formula NaCl: this indicates that one atom of sodium combines with one atom of chlorine to form sodium chloride. Another salt, calcium chloride (which is used to melt ice on roads), has the formula $CaCl_2$: one atom of calcium combines with two atoms of chlorine to form this compound. Carbon tetrachloride, a common compound of chlorine used for dry cleaning, has the formula CCl_4 where C stands for a carbon atom which combines with four chlorine atoms. Another common substance, ammonia, has the formula NH_3: in this case one atom of nitrogen combines with three atoms of hydrogen.

There are especially important examples of combining capacity among the gaseous elements. For example, hydrogen occurs in nature in the form of molecules each of which contains two hydrogen atoms. The molecule of hydrogen consists of two atoms and has the formula H_2. Similarly chlorine has the molecular formula Cl_2. Chemical analysis always gives these results. It would be wrong to try to assign the formula H_3 or H_4 to a molecule of hydrogen, or Cl, Cl_3 or Cl_4 to a molecule of chlorine. These formulas would just not agree with the results of experiments on the composition and properties of hydrogen or chlorine.


Representations of molecules formed from "atoms with hooks."

The above examples indicate that different elements have different capacities for chemical combination. It was natural for chemists to seek an explanation for these differences. They asked the question: why does a substance have a certain molecular formula and not some other formula? An answer would be possible were we to assume that each species of atom is characterized by some particular combining capacity, or valence. At one time valence was considered as though it might represent the number of hooks possessed by a given atom, and thus the number of links that an atom could form with others of the same or different species. If hydrogen and chlorine atoms each had just one hook (that is, a valence of 1) we would readily understand how it is that molecules like H_2, Cl_2 and HCl are stable, while certain other species like H_3, H_2Cl, HCl_2 and Cl_3 don't exist at all. And if the hydrogen atom is thus assigned a valence of 1, the formula of water (H_2O) requires that the oxygen atom has two hooks or a valence of 2. The formula NH_3 for ammonia leads us to assign a valence of three to nitrogen; the formula CH_4 for methane leads us to assign a valence of 4 to carbon; and so on. Proceeding in this fashion, we can assign a valence number to each of the known elements. Sometimes complications arise as, for example, in the case of sulfur. In H_2S the sulfur atom seems to have a valence of 2, but in such a compound as sulfuric acid (H_2SO_4) sulfur seems to have a valence of 6. In this case and others, then, we may have to assign two (or even more) valence numbers to a single species of atom. At the other extreme of possibilities are those elements, for example, helium, neon and argon, which have not been found as parts of compounds--and to these elements we may appropriately assign a valence of zero.

The atomic mass and valence are numbers that can be assigned to an element; they are "numerical characterizations" of the atoms of the element. There are other numbers which represent properties of the atoms of the elements, but atomic mass and valence were the two most important to nineteenth-century chemists. These numbers were used in the attempt to find order and regularity among the elements—a problem which will be discussed in the next section.

Q6 At this point we have two numbers which are characteristic of the atoms of an element. What are they?

Q7 Assume the valence of oxygen is 2. In each of the following molecules, give the valence of the atoms other than oxygen: CO, CO_2, NO_3, Na_2O and MnO.

17.4 The search for order and regularity among the elements.

By 1872 sixty-three elements were known; they are listed in Table 17.1 with their atomic masses and chemical symbols. Sixty-three elements are many more than Aristotle's four; and chemists tried to make things simpler by looking for ways of organizing what they had learned about the elements. They tried to find relationships among the elements—a quest somewhat like Kepler's earlier search for rules that would relate the motions of the planets of the solar system.

See "Looking for a New Law" in Project Physics Reader 5.

Relationships did indeed appear: there seemed to be families of elements with similar properties. One such family consists of the so-called alkali metals—lithium, sodium, potassium, rubidium and cesium—listed here in order of increasing atomic mass. We have placed these elements in boxes in Table 17.1. All these metals are similar physically: they are soft and have low melting points. The densities of these metals are very low; in fact, lithium, sodium and potassium are less dense than water. The alkali metals are also similar chemically: they all have valence 1; they all combine with the same elements to form similar compounds. Because they form compounds readily with other elements; they are said to be highly reactive. They do not occur free in nature, but are always found in combination with other elements.

In 1829 the German chemist Johann Wolfgang Döbereiner noticed that elements often formed groups of three members with similar chemical properties. He identified the "triads": chlorine, bromine and iodine; calcium, strontium and barium; sulfur, selenium and tellurium; iron, cobalt and manganese. In each "triad," the atomic mass of the middle member was approximately the arithmetical average of the masses of the other two elements.

Another family of elements, called the halogens, includes, in order of increasing atomic mass, fluorine, chlorine, bromine and iodine. The halogens may be found in Table 17.1 just above the alkali metals, and they have been circled. It turns out that each halogen precedes an alkali metal in the list, although the order of the listing was simply by atomic mass.

Although these four halogen elements exhibit some marked dissimilarities (for example, at 25°C the first two are gases, the third a liquid, the last a volatile solid) they have much in common. They all combine violently with many metals to form white, crystalline salts (halogen means "salt-former") having similar formulas, such as NaF, NaCl, NaBr and NaI, or MgF_2, $MgCl_2$, $MgBr_2$ and MgI_2. From much similar evidence chemists noticed that all four members of the family seem to have the same valence with respect to any other particular element. All four elements form simple compounds with hydrogen (HF, HCl, HBr, HI) which dissolve in water and form acids. All four, under ordinary conditions, exist as diatomic molecules, that is, each molecule contains two atoms.

In 1865 the English chemist J. A. R. Newlands pointed out that the elements could usefully be listed simply in the order of increasing atomic mass. For when this was done, a curious fact became evident: not only were the atomic masses of the elements within any one family regularly spaced, as Döbereiner had suggested, but there was also in the whole list a periodic recurrence of elements with similar properties: "...the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music." Newlands' proposal was met with skepticism. One chemist even suggested that Newlands might look for similar patterns in an alphabetical list of elements.

The elements which follow the alkali metals in the list also form a family, the one called the alkaline earth family; this family includes beryllium, magnesium, calcium, strontium and barium. Their melting points and densities are higher than those of the alkali metals. The alkaline earths all have a valence of two, and are said to be divalent. They react easily with many elements but not as easily as do the alkali metals.

The existence of these families of elements encouraged chemists to look for a systematic way of arranging the elements so that the members of a family would group together. Many schemes were suggested; the most successful was that of the Russian chemist, D.I. Mendeleev.

Q7 What are three properties of elements which recur systematically with increasing atomic mass?

17.5 Mendeleev's periodic table of the elements. Mendeleev, examining the properties of the elements, came to the conconclusion that the atomic masses supplied the fundamental "numerical characterization" of the elements. He discovered that if the elements were arranged in a table in the order of their atomic masses—but in a special way—the different families appeared in columns of the table. In his own words:

Although chemically similar elements did occur at periodic intervals, Newlands did not realize that the number of elements in a period changed if one continued far enough. This was recognized by Mendeleev.

> The first attempt which I made in this way was the following: I selected the bodies with the lowest atomic weights and arranged them in the order of the size of their atomic weights. This showed that there existed a period in the properties of the simple bodies, and even in terms of their atomicity the elements followed each other in the order of arithmetic succession of the size of their atoms:
>
> Li=7 Be=9.4 B=11 C=12 N=14 O=16 F=19
> Na=23 Mg=24 Al=27.4 Si=28 P=31 S=32 Cl=35.3
> K=39 Ca=40 . . . . Ti=50 V=51 et cetera

In this table, hydrogen was omitted because of its unique properties. Helium and the other elements of the family of noble gases had not yet been discovered.

Mendeleev set down seven elements, from lithium to fluorine, in the order of increasing atomic masses, and then wrote the next seven, from sodium to chlorine, in the second row. The periodicity of chemical behavior is already evident before we go on to write the third row. In the first vertical column are the first two alkali metals. In the seventh column are the first two halogens. Indeed, within each of the columns the elements are chemically similar, having, for example, the same characteristic valence.

When Mendeleev added a third row of elements, potassium (K) came below elements Li and Na, which are members of the same family and have the same valence, namely, 1. Next in the row is Ca, divalent like Mg and Be above it. In the next space to the right, the element of next higher atomic mass should appear. Of the elements known at the time, the next heavier was titanium (Ti), and it was placed in this space under Al and B by various workers who had tried to develop such schemes. Mendeleev, however, recognized that Ti has chemical properties similar to those of

Dmitri Ivanovich Mendeleev (men-deh-lay'-ef) (1834-1907) received his first science lessons from a political prisoner who had been banished to Siberia by the Czar. Unable to get into college in Moscow, he was accepted in St. Petersburg, where a friend of his father had some influence. In 1866 he became a professor of chemistry there; in 1869 he published his first table of the sixty-three known elements arranged according to atomic mass. His paper was translated into German at once and was made available to all scientists. Mendeleev came to the United States, where he studied the oil fields of Pennsylvania in order to advise his country on the development of the Caucasian resources.

C and Si and therefore should be put in the fourth vertical column (the pigment, titanium white, TiO_2, has a formula comparable to CO_2 and SiO_2, and all three elements show a valence of 4). Then if the classification is to be complete, there should exist a hitherto unsuspected element with atomic mass between that of Ca (40) and Ti (50) and with a valence of 3. Here was a definite prediction, and Mendeleev found other cases of this sort among the remaining elements.

Table 17.2 is Mendeleev's periodic system or "periodic table" of the elements, proposed in 1872. We note that he distributed the 63 elements then known (with 5 in doubt) in 12 horizontal rows or series, starting with hydrogen at the top left, and ending with uranium at the bottom right. All are written in order of increasing

GROUP→		I	II	III	IV	V	VI	VII	VIII
Higher oxides and hydrides		R_2O —	RO —	R_2O_3 —	RO_2 H_4R	R_2O_5 H_3R	RO_3 H_2R	R_2O_7 HR	RO_4 —
SERIES	1	H(1)							
	2	Li(7)	Be(9.4)	B(11)	C(12)	N(14)	O(16)	F(19)	
	3	Na(23)	Mg(24)	Al(27.3)	Si(28)	P(31)	S(32)	Cl(35.5)	
	4	K(39)	Ca(40)	—(44)	Ti(48)	V(51)	Cr(52)	Mn(55)	Fe(56), Co(59), Ni(59), Cu(63)
	5	[Cu(63)]	Zn(65)	—(68)	—(72)	As(75)	Se(78)	Br(80)	
	6	Rb(85)	Sr(87)	?Yt(88)	Zr(90)	Nb(94)	Mo(96)	—(100)	Ru(104), Rh(104), Pd(106), Ag(108)
	7	[Ag(108)]	Cd(112)	In(113)	Sn(118)	Sb(122)	Te(125)	I(127)	
	8	Cs(133)	Ba(137)	?Di(138)	?Ce(140)	—	—	—	
	9	—	—	—	—	—	—	—	
	10	—	—	?Er(178)	?La(180)	Ta(182)	W(184)	—	Os(195), Ir(197), Pt(198), Au(199)
	11	[Au(199)]	Hg(200)	Tl(204)	Pb(207)	Bi(208)	—	—	
	12	—	—	—	Th(231)	—	U(240)		

Table 17.2 Periodic classification of the elements; Mendeleev, 1872.

atomic mass (Mendeleev's values given in parentheses), but are so placed that elements with similar chemical properties are in the same vertical column or *group*. Thus in Group VII are all the halogens; in Group VIII, only metals that can easily be drawn to form wires; in Groups I and II, metals of low densities and melting points; and in Group I, the family of alkali metals.

Table 17.2 shows many gaps. But, as Mendeleev realized, it revealed an important generalization:

> For a true comprehension of the matter it is very important to see that all aspects of the distribution of the elements according to the order of their atomic weights express essentially one and the same fundamental dependence—*periodic properties*.

By this is meant that in addition to the gradual change in physical and chemical properties within each vertical group, there is also a periodic change of properties in the horizontal sequence, beginning with hydrogen and ending with uranium.

This *periodic law* is the heart of the matter. We can best illustrate it as Lothar Meyer did, by drawing a curve showing the values of some physical quantity as a function of atomic mass. Figure 17.1 is a plot of the *atomic volumes* of the elements. This atomic volume is defined as the atomic mass of the substance divided by its density in the liquid or solid state. Each circled point on this graph represents an element; a few of the points have been labeled with the identifying chemical symbols. Viewed as a whole, the graph demonstrates a striking periodicity: as the mass increases the atomic volume first drops, then

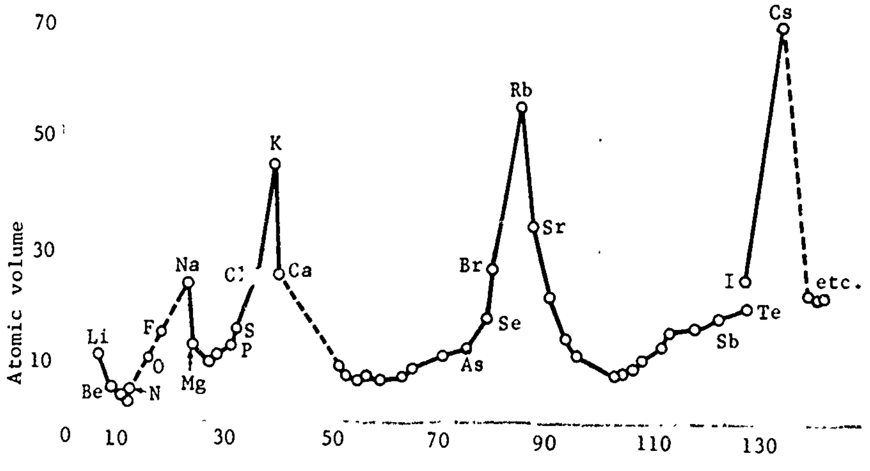


Fig. 17.1 The atomic volumes of elements graphed against their atomic masses

increases to a sharp maximum, drops off again and increases to another sharp maximum, and so on. And at the successive peaks we find Li, Na, K, Rb, Cs, the members of the family of alkali metals. On the left-hand side of each peak, there is one of the halogens.

In 1864, the German chemist Lothar Meyer wrote a chemistry textbook. In this book, he considered how the properties of the chemical elements might depend on their atomic masses. He later found that if he plotted the atomic volume against the atomic mass, the line drawn through the plotted points rose and fell in two short periods, then in two long periods. This was exactly what Mendeleev had discovered in connection with valence. Mendeleev published his result in 1869; Meyer published his in 1870. Meyer, as he himself later admitted, lacked the courage to predict the discovery of unknown elements. Nevertheless, Meyer should be given part of the credit for the idea of the periodic table.

Mendeleev's periodic table of the elements not only provided a remarkable correlation of the elements and their properties, it also enabled him to predict that certain unknown elements must exist and what many of their properties should be. To estimate physical properties of a missing element, Mendeleev averaged the properties of its nearest neighbors in the table: those to right and left, above and below. A striking example of Mendeleev's success in using the table in this way is his set of predictions concerning the gap in Series 5 Group IV. This was a gap in Group IV, which contained elements with properties resembling those of carbon and silicon. Mendeleev assigned the name "eka-silicon" (Es) to the unknown element. His predictions of the properties of this element are listed in the left-hand column that follows. In 1887, this element was isolated and identified (it is now called "germanium"); its properties are listed in the right-hand column.

"The following are the properties which this element should have on the basis of the known properties of silicon, tin, zinc, and arsenic.	The predictions in the left column were made by Mendeleev in 1871. In 1887 an element (germanium) was discovered which was found to have the following properties:
Its atomic [mass] is nearly 72,	Its atomic mass is 72.5.
it forms a higher oxide EsO_2,...	It forms an oxide GeO_2, and
Es gives volatile organo-metallic compounds; for instance...$Es(C_2H_5)_4$,	forms an organo-metallic compound $Ge(C_2H_5)_4$
which boil at about 160°, etc.;	which boils at 160° C, and
also a volatile and liquid chloride, $EsCl_4$, boiling at about 90°	forms a liquid chloride $GeCl_4$ which boils at 83° C
and of specific gravity about 1.9....	and has a specific gravity of 1.9.
the specific gravity of Es will be about 5.5, and EsO_2 will have a specific gravity of about 4.7, etc...."	The specific gravity of germanium is 5.5 and the specific gravity of GeO_2 is 4.7.

Mendeleev's predictions are remarkably close to the properties actually found.

The daring of Mendeleev is shown in his willingness to venture detailed numerical predictions; the sweep and power of his system is shown above in the remarkable accuracy of those predictions. In similar fashion, Mendeleev described the properties to be expected for the then unknown elements in Group III, Period 4 and in Group III, Period 5, elements now called gallium and

17 5

scandium, and again his predictions turned out to be remarkably accurate.

Even though not every aspect of Mendeleev's work yielded such successes, these were indeed impressive results. Successful numerical predictions like these are among the most desired results in physical science.

[illegible] What was the basic ordering principle in Mendeleev's table?

[illegible] What reasons led him to violate that principle?

[illegible] How did he justify leaving gaps in the table?

17.6 The modern periodic table. The periodic table has had an important place in chemistry and physics for nearly one hundred years. It presented a serious challenge to any theory of the atom proposed after about 1880: the challenge of providing an explanation for the order among the elements expressed by the table. A successful model of the atom must provide a physical explanation for the of the elements. In Chapter 19 we shall see how one model of the atom—the Bohr model—met this challenge.

Since 1872 many changes have had to be made in the periodic table, but they have been changes in detail rather than in general ideas. None of these changes has affected the basic feature of periodicity among the properties of the elements. A modern form of the table is shown in Table 17.3.

Table 17.3 A modern form of the periodic table of the elements. The number above the symbol is the chemist's atomic weight, the number below the symbol is the atomic number.

Group→ Period↓	I	II											III	IV	V	VI	VII	0
1	1 0080 H 1																	4 0026 He 2
2	6 939 Li 3	9 012 Be 4											10 811 B 5	12 011 C 6	14 007 N 7	15 999 O 8	18.998 F 9	20 183 Ne 10
3	22 990 Na 11	24 31 Mg 12											26 98 Al 13	28 09 Si 14	30 97 P 15	32 06 S 16	35 45 Cl 17	39 95 Ar 18
4	39 10 K 19	40 08 Ca 20	44 96 Sc 21	47 90 Ti 22	50 94 V 23	52 00 Cr 24	54 94 Mn 25	55 85 Fe 26	58 93 Co 27	58 71 Ni 28	63 54 Cu 29	65 37 Zn 30	69 72 Ga 31	72 59 Ge 32	74 92 As 33	78 96 Se 34	79 91 Br 35	83 80 Kr 36
5	85 47 Rb 37	87 62 Sr 38	88 91 Y 39	91 22 Zr 40	92 91 Nb 41	95 94 Mo 42	(99) Tc 43	101 07 Ru 44	102 91 Rh 45	106 4 Pd 46	107 87 Ag 47	112.40 Cd 48	114 82 In 49	118 69 Sn 50	121 75 Sb 51	127 60 Te 52	126 9 I 53	131 30 Xe 54
6	132 91 Cs 55	137 34 Ba 56	* 57-71	178 49 Hf 72	180 95 Ta 73	183 85 W 74	186 2 Re 75	190 2 Os 76	192 2 Ir 77	195 09 Pt 78	196 97 Au 79	200 59 Hg 80	204 37 Tl 81	207 19 Pb 82	208 98 Bi 83	210 Po 84	(210) At 85	222 Rn 86
7	(223) Fr 87	226 05 Ra 88	† 89															

*Rare-earth metals	138 91 La 57	140 12 Ce 58	140 91 Pr 59	144 27 Nd 60	(147) Pm 61	150 35 Sm 62	151 96 Eu 63	157.25 Gd 64	158 92 Tb 65	162 50 Dy 66	164 93 Ho 67	167 26 Er 68	168 93 Tm 69	173 04 Yb 70	174 97 Lu 71
† Actinide metals	227 Ac 89	232 04 Th 90	231 Pa 91	238 03 U 92	(237) Np 93	(242) Pu 94	(243) Am 95	(245) Cm 96	(249) Bk 97	(249) Cf 98	(253) E 99	(255) Fm 100	(256) Mv 101	(253) No 102	(257) Lw 103

One difference between the modern and older tables is that new elements have been added. Forty new elements have been identified since 1872, so that the table now contains 103 elements. Some of these new elements are especially interesting, and we shall need to know something about them.

Although Mendeleev's table had eight columns, the column labelled VIII did not contain a family of elements. It contained the "transition" elements which are now in the long series (periods) labelled 4,5 and 6 in Table 17.3. The group labelled "0" in Table 17.3 does consist of a family of elements, the noble gases, which do have similar properties.

Comparison of the modern form of the table with Mendeleev's table shows that the modern table contains eight groups, or families, instead of seven. The additional group is labeled "zero." In 1894, the British scientists Lord Rayleigh and William Ramsay discovered that about 1 percent of our atmosphere consists of a gas that had previously escaped detection. It was given the name argon (symbol Ar). Argon does not seem to enter into chemical combination with any other elements, and is not similar to any of the groups of elements in Mendeleev's original table. Other elements similar to argon were also discovered: helium (He), neon (Ne), krypton (Kr), xenon (Xe), and radon (Rn). These elements are considered to form a new group or family of elements, called the "noble gases." (In chemistry, elements such as gold and silver that react only rarely with other elements were called "noble" and all the members of the new family are gases at room temperature.) Each noble gas (with the exception of argon) has an atomic mass slightly smaller than that of a Group I element. The molecules of the noble gases contain only one atom, and until only a few years ago no compound of any noble gas was known. The group number zero was thought to correspond to the chemical inertness, or zero valence of the members of the group. In 1963, some compounds of xenon and krypton were produced, so that these elements are not really inert. These compounds are not found in nature, and are unstable when they are made in the laboratory. The noble gases are certainly less liable to react chemically than any other elements and their position in the table does correspond to their "reluctance" to react.

Helium was first detected in the spectrum of the sun in 1868 (Chapter 19). Its name comes from <u>helios</u>, the Greek word for the sun. It was not discovered on earth until 1895, when Ramsay found it in a uranium-containing mineral (Chapter 21). Almost all the helium in the world comes from natural gas wells in Texas, Kansas and Oklahoma. Helium is lighter than air, and is widely used in balloons and blimps instead of highly flammable hydrogen.

In addition to the noble gases, two other sets of elements had to be included in the table. After the fifty-seventh place, room had to be made for a whole set of 14 chemically almost indistinguishable elements, known as the <u>rare earths</u> or lanthanide series. Most of these elements were unknown in Mendeleev's time. Similarly, a set of 14 very similar elements, forming what is called the <u>actinide</u> series, belongs immediately after actinium at the eighty-ninth place. These elements are shown in two rows below the main table. No more additions are now expected within the table. There are no known gaps, and we shall see in Chapters 19 and 20 that according to the best theory of the atom now available, no new gaps should appear.

Besides the addition of new elements to the periodic table, there have also been some changes of a more general type. As we have seen, Mendeleev arranged the elements in order of increasing atomic mass. In the late nineteenth century, however, this basic scheme was found to break down in several places. For example, the chemical properties of argon (Ar) and potassium (K) demand that they should be placed in the eighteenth and nineteenth positions, whereas on the basis of their atomic masses alone (39.948 for argon, 39.102 for potassium), their positions should be reversed. Other reversals of this kind have been found necessary, for example, for the fifty-second element, tellurium (at. mass = 127.60) and the fifty-third, iodine (at. mass = 126.90). The consecutive integers that indicate the number for the best position for the element, according to its chemical properties, are called the atomic numbers; the atomic number is usually denoted by the symbol Z· thus for hydrogen, $Z = 1$; for uranium, $Z = 92$. The atomic numbers of all the elements are given in Table 17.3. In Chapter 19 we shall see that the atomic number has a fundamental physical meaning related to atomic structure.

The need for reversals in the periodic table of the elements would have been a real catastrophe to Mendeleev. He confidently expected, for example, that the atomic mass of tellurium (modern value = 127.60, fifty-second place), when more accurately determined, would turn out to be lower than that of iodine (modern value = 126.90, fifty-third place) and, in fact, in 1872 (see Table 17.2) he had convinced himself that the correct atomic mass of tellurium was 125! Mendeleev overestimated the necessity of the periodic law in every detail, particularly as it had not yet received a physical explanation. Although the reversals in the sequence of elements have proved to be real (e.g., tellurium, in fifty-second place, does have a higher atomic mass than iodine, in fifty-third place in the periodic table), their existence did not invalidate the scheme. Satisfactory explanations for these reversals have been found in modern atomic physics.

Q11 What is the "atomic number" of an element?

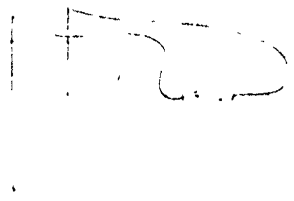
17.7 Electricity and matter: qualitative studies. While chemists were applying Dalton's atomic theory, another development was taking place which opened an important path to our understanding of the atom. Sir Humphry Davy and Michael Faraday made discoveries which showed that electricity and matter are intimately related. Their work marked the beginning of electrochemistry. Their discoveries had to do with the breaking down, or decomposition, of chemical compounds by electric currents. This process is called electrolysis.

The study of electrolysis was made possible by the invention of the electric cell by the Italian scientist Alessandro Volta, in 1800. Volta's cell consisted of a pair of zinc and copper discs, separated from each other by a sheet of paper moistened with a weak salt solution. As a result of chemical changes occurring in the cell, an electric potential difference is established across the cell. A battery usually consists of several similar cells connected together.

A battery has two terminals, one positively charged and the other negatively charged. When the terminals are connected to each other, outside the battery, by means of certain materials, there is an electric current in the battery and the materials. We say that we have a circuit. The connecting materials in which the current exists are called conductors of electricity. Thus, the battery can produce and maintain an electric current. It is not the only device that can do so, but it was the first source of steady currents.

Not all substances are electrical conductors. Among solids, the metals are the best conductors. Some liquids conduct electricity. Pure distilled water is a poor conductor. But when certain substances such as acids or salt are dissolved in water, the resulting solutions are good electrical conductors. Gases are not conductors under normal conditions, but can be made electrically conducting in the presence of strong electric fields, or by other methods. The conduction of electricity in gases, vital to the story of the atom, will be discussed in Chapter 18.

Fig. 17.2



Within a few weeks after Volta's announcement of his discovery it was found that water could be decomposed into oxygen and hydrogen by the use of electric currents. Figure 17.2 is a diagram of an electrolysis apparatus. The two terminals of the battery are connected, by conducting wires, to two thin sheets of platinum. When these platinum sheets are immersed in ordinary water, bubbles of oxygen appear at one sheet and bubbles of hydrogen at the other. Adding a small amount of certain acids speeds up the reaction without changing the products. Hydrogen and oxygen gases are formed in the proportion of 7.94 grams of oxygen to 1 gram of hydrogen, which is exactly the proportion in which these elements combine to form water. Water had previously been impossible to decompose, and had been regarded—from ancient times until after 1750—as an element. Thus the ease with which water was separated into its elements by electrolysis dramatized the chemical use of electricity, and stimulated many other investigations of electrolysis.

This can be explained by assuming that some of the water molecules come apart, leaving the hydrogen atoms with a + charge and the oxygen atoms with a - charge; the hydrogen atoms would be attracted to the - plate and the oxygen to the + plate. Faraday called the charged atoms ions (after the Greek word for "wanderers"). Solutions of such charged particles are said to be ionized.

Among these investigations, some of the most successful were those of the young English chemist Humphry Davy. Perhaps the most striking of Davy's successes were those he achieved when, in 1807, he studied the effect of the current from a large electric battery on soda and potash. Soda and potash were materials of commercial importance (for example, in the manufacture of glass, soap and gunpowder) and had been completely resistant to every earlier attempt to decompose them. Soda and potash were thus regarded as true chemical elements—up to the time of Davy's work. When electrodes connected to a powerful battery were touched to a solid lump of soda, or to a lump of potash, part of the solid was heated to its melting point. At one electrode gaseous oxygen was released violently; at the other electrode small globules of molten metal appeared which burned brightly and almost explosively in air. When the electrolysis was done in the absence of air, the metallic material could be obtained. Sodium and potassium were discovered in this way. The metallic element sodium was obtained from soda (in which it is combined as sodium hydroxide) and the metallic element potassium obtained from potash (in which it is combined as potassium hydroxide). In the immediately succeeding years electrolytic trials made on several hitherto undecomposed "earths" yielded the first samples ever obtained of such metallic elements as magnesium, strontium and barium: there were also many other demonstrations of the striking changes produced by the chemical activity of electricity.

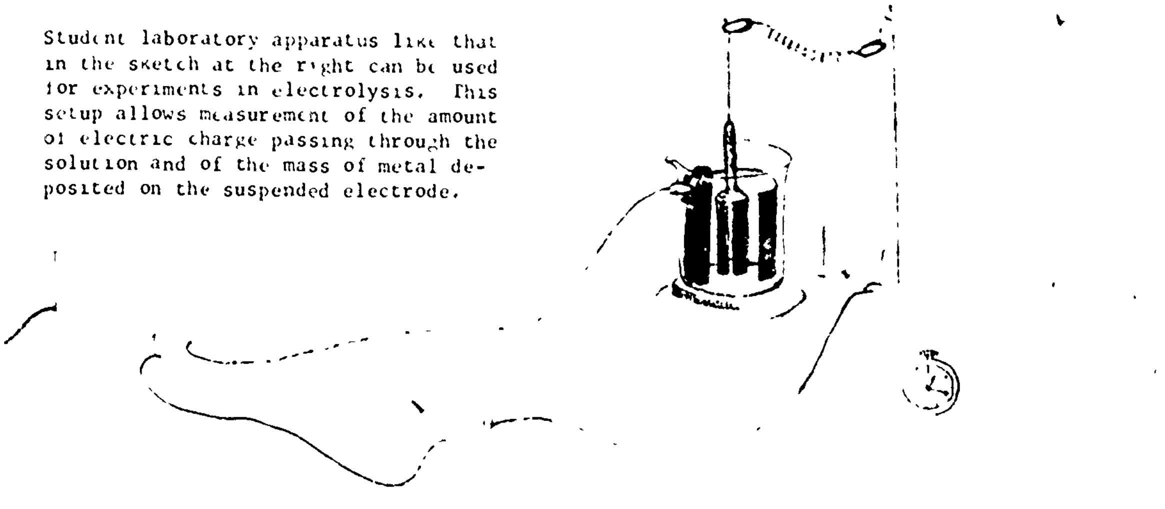
Humphry Davy (1778-1829) was the son of a farmer. In his youth he worked as an assistant to a physician but was discharged because of his liking for explosive chemical experiments. He became a chemist, discovered nitrous oxide (laughing gas), later used as an anaesthetic, and developed a safety lamp for miners. His work in electrochemistry and his discovery of several elements made him world-famous; he was knighted in 1812. In 1813 Sir Humphry Davy hired a young man, Michael Faraday, as his assistant and took him along on an extensive trip through France and Italy. It became evident to Davy that young Faraday was a man of scientific genius. Davy is said to have been envious, at first, of Faraday's great gifts. He later said that he believed his greatest discovery was Faraday.

Q12 Why was the first electrolysis of water such a surprising phenomenon?

Q13 Some equally striking results of electrolysis followed. What were they?

Electrolysis

Student laboratory apparatus like that in the sketch at the right can be used for experiments in electrolysis. This setup allows measurement of the amount of electric charge passing through the solution and of the mass of metal deposited on the suspended electrode.

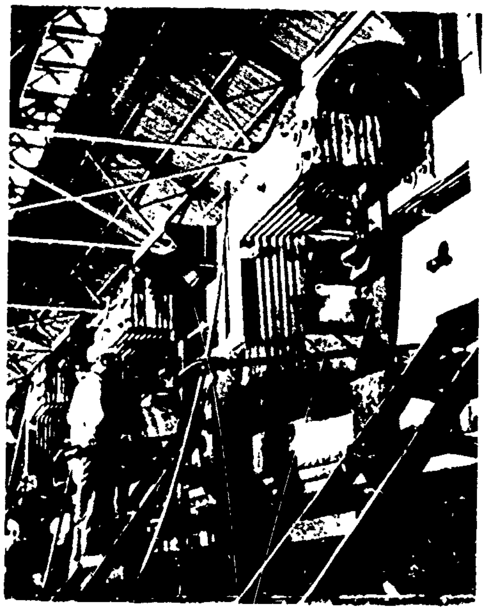


c

a

The separation of elements by electrolysis is important in industry, particularly in the production of aluminum. These photographs show the vast scale of a plant where aluminum is separated out of aluminum ore in electrolytic tanks.

a) A row of tanks where aluminum is separated out of aluminum ore.
b) A closer view of the front of some tanks, showing the thick copper straps that carry the current.
c) A huge vat of molten aluminum that has been siphoned out of the tanks is poured into molds.



b

17 8 *Electricity and matter: quantitative studies.* Davy's work on electrolysis was mainly qualitative. But quantitative questions were also asked. How much chemical change can be produced by a given amount of electricity? If solutions of *different* chemical compounds are electrolyzed with a given amount of current, how do the amounts of chemical change produced compare? Will doubling the amount of electricity double the chemical effects?

Answers to these questions were supplied by Michael Faraday, who discovered two fundamental laws of electrolysis. He studied the electrolysis of a solution of copper sulfate, a blue salt, in water. He made an electrolytic cell by immersing two bars of copper in the solution and attaching them to the terminals of a battery. The electric current that flowed through the resulting circuit caused copper from the solution to be deposited on the cathode and oxygen to be liberated at the anode. Faraday determined the amount of copper deposited by weighing the anode before the electrolysis started and again after a known amount of current had passed through the solution. He measured the current with an ammeter. Faraday found that the mass of copper deposited depends on two things: on the magnitude (say, in amperes) of the current (I), and on the length of time (t) that the current was maintained. In fact, the mass of copper deposited was directly *proportional* to both the current and the time. When either was doubled, the mass of copper deposited was doubled. When both were doubled, four times as much copper was deposited. Similar results were found in experiments on the electrolysis of many different substances.

Faraday's results may be described by stating that the amount of chemical change produced in electrolysis is proportional to the product: $I \cdot t$. Now, the current (in amperes) is the quantity of charge (in coulombs) which moves through the electrolytic cell per unit time (in seconds). The product $I \cdot t$ therefore gives the *total charge* that has moved through the cell during the given experiment. We then have Faraday's first law of electrolysis:

> The mass of electrolytically liberated chemicals is proportional to the amount of charge which has passed through the electrolytic cell.

Next Faraday measured the amounts of different elements liberated from chemical compounds by given amounts of electric charge, that is, by different values of the product $I \cdot t$. He found that the amount of an element produced by a given amount of electricity depends on the atomic mass of the element and on the valence of the element. His second law of electrolysis states:

> If A is the atomic mass of an element, and if v is its valence, a certain amount of electric charge, 96,540 coulombs, produces A/v grams of the element.

This amount of electric charge, 96,540 coulombs, is called one faraday.

Table 17.4 gives examples of Faraday's second law of electrolysis.

Table 17.4. Masses of elements produced from compounds by 96,540 coulombs of electric charge.

Element	Atomic Mass	Valence	Mass of Element Produced (grams)
Hydrogen	1.008	1	1.008
Chlorine	35.45	1	35.45
Oxygen	16.00	2	8.00
Copper	63.54	2	31.77
Zinc	65.37	2	32.69
Aluminum	26.98	3	8.99

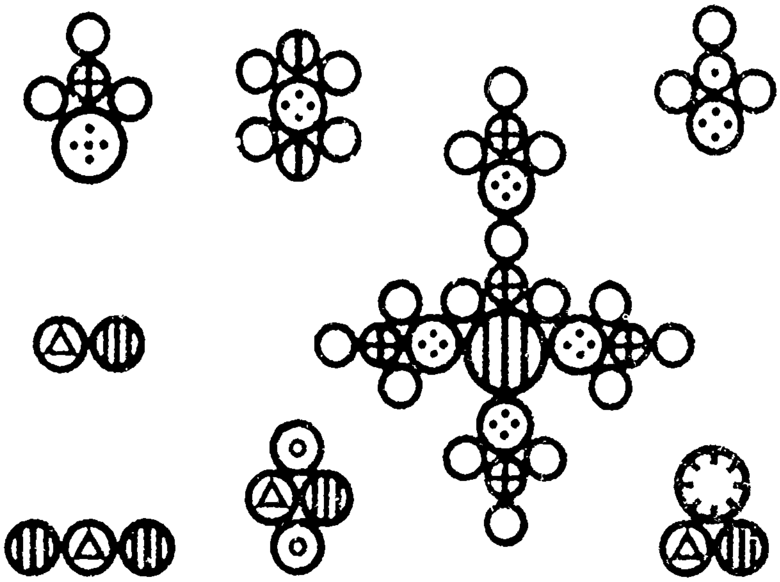
The mass of the element produced is seen to be equal to the atomic mass divided by the valence. This quantity, A/v, is a measure of the amount of one element that combines with another element. For example, the ratio of the amounts of oxygen and hydrogen liberated by 96,540 coulombs of electric charge is $\frac{8.00}{1.008} = 7.94$. But this is just the ratio of the mass of oxygen to the mass of hydrogen in water.

Faraday's second law of electrolysis has an important implication. A given amount of electric charge is somehow closely connected with the atomic mass and valence of an element. The mass and valence are characteristic of the atoms of the element. Perhaps, then, a certain amount of electricity is somehow connected with an atom of the element. The implication is that electricity may also be atomic in nature. This possibility was considered by Faraday, who wrote:

> ...if we adopt the atomic theory or phraseology, then the atom of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them. But I must confess that I am jealous of the term atom; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

In Chapter 18 you will read about the details of the research that established the atomic nature of electricity. This research was of great and fundamental importance, and helped make possible the exploration of the structure of the atom.

[illegible] The amount of an element deposited in electrolysis depends on three factors. What are they?



Dalton's visualization of the composition of various compounds

17.1 The chemical compound zinc oxide (molecular formula ZnO) contains equal numbers of atoms of zinc and oxygen. Using values of atomic masses from the modern version of the periodic table, find the percentage by mass of zinc in zinc oxide. What is the percentage of oxygen in zinc oxide?

17.2 The chemical compound zinc chloride (molecular formula $ZnCl_2$) contains two atoms of chlorine for each atom of zinc. Using values of atomic masses from the modern version of the periodic table, find the percentage by mass of zinc in zinc chloride.

17.3 From the decomposition of a 5.00-gram sample of ammonia gas into its component elements, nitrogen and hydrogen, 4.11 grams of nitrogen were obtained. The molecular formula of ammonia is NH . Find the mass of a nitrogen atom relative to that of a hydrogen atom. Compare your result with the one you would get by using the values of the atomic masses in the modern version of the periodic table. If your result is different from the latter result, how do you account for the difference?

17.4 From the information in Problem 17.3, calculate how much nitrogen and hydrogen are needed to make 1.2 kg of ammonia.

17.5 _If_ the molecular formula of ammonia were NH_2, and you used the result of the experiment of Problem 17.3, what value would you get for the ratio of the mass of a nitrogen atom relative to that of a hydrogen atom?

17.6 A sample of nitric oxide gas, weighing 1.00 g, after separation into its components, is found to have contained 0.47 g of nitrogen. Taking the atomic mass of oxygen to be 16.00, find the corresponding numbers that express the atomic mass of nitrogen relative to oxygen on the respective assumptions that the molecular formula of nitric oxide is (a) NO; (b) NO_2; (c) N_2O.

17.7 Early data yielded 8/9.2 for the mass ratio of nitrogen and oxygen atoms, and 1/7 for the mass ratio of hydrogen and oxygen atoms. Show that these results lead to a value of 6 for the relative atomic mass of nitrogen, provided that the value 1 is assigned to hydrogen.

17.8 Given the molecular formulae HCl, NaCl, $CaCl_2$, $AlCl_3$, $SnCl_4$, PCl_5, find possible valence numbers of sodium, calcium, aluminum, tin and phosphorus.

17.9 a) Examine the modern periodic table of elements and cite all reversals of order of increasing atomic mass.

b) Restate the periodic law in your own words, not forgetting about these reversals.

17.10 In recent editions of the _Handbook of Chemistry and Physics_ there are printed in or below one of the periodic tables the valence numbers of the elements. Neglect the negative valence numbers and plot (to element 65) a graph of maximum valences observed vs. atomic mass. What periodicity is found? Is there any physical or chemical significance to this periodicity? Does there have to be any?

17.11 Look up the data in the _Handbook of Chemistry and Physics_, then plot some other physical characteristic against the atomic masses of the elements from hydrogen to barium in the periodic table. Comment on the periodicity (melting point, boiling point, etc.).

17.12 According to Table 17.4, when 96,500 coulombs of charge pass through a water solution, 1.008 g of hydrogen and how much of oxygen will be released? How much hydrogen and how much oxygen will be produced when a current of 3 amperes is passed through water for 60 minutes (3600 seconds)?

17.13 If a current of 0.5 amperes is passed through molten zinc chloride in an electrolytic apparatus, what mass of zinc will be deposited in

a) 5 minutes (300 seconds),
b) 30 minutes;
c) 120 minutes?

17.14 a) For 20 minutes (1200 seconds) a current of 2.0 amperes is passed through molten zinc chloride in an electrolytic apparatus. What mass of chlorine will be released at the anode?

b) If the current had been passed through molten zinc iodide rather than molten zinc chloride what mass of iodine would have been released at the anode?

c) Would the quantity of zinc deposited in part (b) have been different from what it was in part (a)? Why?

17.15 How is Faraday's speculation about an 'atom of electricity" related to atomicity in the chemical elements?

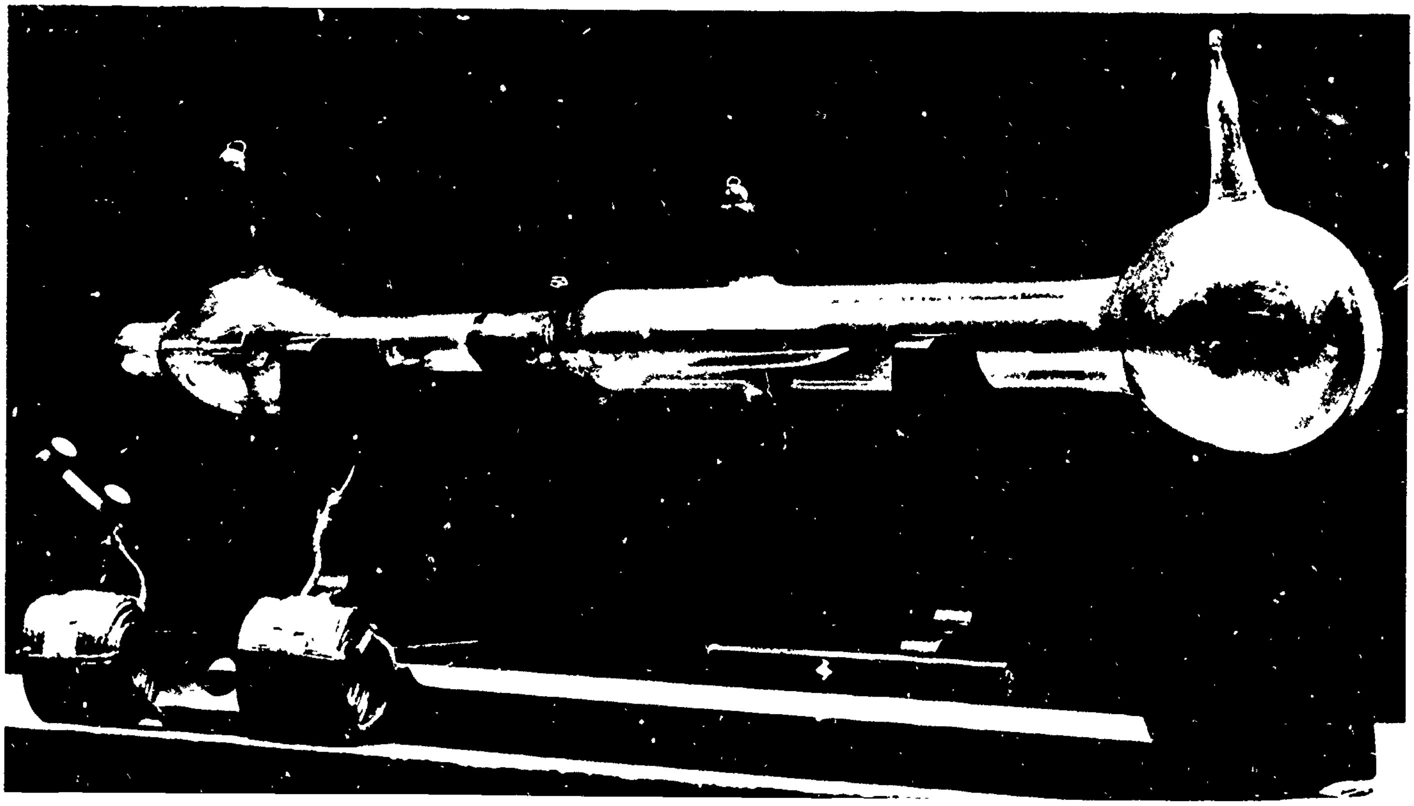
17.16 The idea of chemical elements composed of identical atoms makes it easier to correlate the phenomena discussed in this chapter. Could the phenomena be explained without using the idea of atoms? Are chemical phenomena, which usually involve a fairly large quantity of material (in terms of the number of "atoms" involved), sufficient evidence for belief in the atomic character of materials?

17.17 A sociologist recently wrote a book about the place of man in modern society called Multivalent Man. In what sense might he have used the term "multivalent?"

17.18 Compare the atomic theory of the Greeks, as described in the prologue to this chapter, with the atomic theories described in Unit 3. (You will probably need to consult reference books for more details of the theory. The best reference is probably Lucretius, On the Nature of Things.)

Chapter 18 Electrons and Quanta

The tube used by J.J. Thomson to determine the charge to mass ratio of electrons.



18.1 The problem of atomic structure: pieces of atoms. The development of chemistry in the nineteenth century raised the general question: are atoms really indivisible, or do they consist of still smaller particles? We can see the way in which this question arose by thinking a little more about the periodic table. Mendeleev had arranged the elements in the order of increasing atomic mass. But the atomic masses of the elements cannot explain the periodic features of Mendeleev's table. Why, for example, do the third, eleventh, nineteenth, thirty-seventh, fifty-fifth and eighty-seventh elements, with quite different atomic masses, have similar chemical properties? Why are these properties somewhat different from those of the fourth twelfth, twentieth, thirty-eighth, fifty-sixth and eighty-eighth elements in the list, but greatly different from the properties of the second, tenth, eighteenth, thirty-sixth, fifty-fourth and eighty-sixth elements? The differences in atomic mass were not enough to account, by themselves, for the differences in the properties of the elements. Other reasons had to be sought.

These elements burn when exposed to air; they decompose water, often explosively.

These elements combine slowly with air and water.

These elements rarely combine with anything.

The periodicity of the properties of the elements led to speculation about the possibility that atoms might have structure, that they might be made up of smaller pieces. The gradual changes of properties from group to group might suggest that some unit of atomic structure is added, in successive elements, until a certain portion of the structure is completed. The completed condition might occur in a noble gas. In atoms of the next heavier element, a new portion of the structure may be started, and so on. The methods and techniques of classical chemistry could not supply experimental evidence for such structure. In the nineteenth century, however, discoveries and new techniques in physics opened the way to the proof that atoms do, indeed, consist of smaller pieces. Evidence piled up which showed that the atoms of different elements differ in the number and arrangement of these pieces, or building blocks.

In this chapter, we shall discuss the discovery of one kind of piece which atoms contain: the electron. We shall see how experiments with light and electrons led to a revolutionary idea—that light energy is transmitted in discrete amounts. In Chapter 19, we shall describe the discovery of another part of the atom, the nucleus. Then we shall show how Niels Bohr combined these pieces to create a workable model of the atom. The story starts with the discovery of cathode rays.

18.2 Cathode rays. In 1855 a German physicist, Heinrich Geissler, invented a vacuum pump which could remove enough gas from a strong glass tube to reduce the pressure to 0.01 percent of normal air pressure. His friend, Julius Plücker, connected one of Geissler's evacuated tubes to a battery. He was surprised to find that at the very low gas pressure that could be obtained with Geissler's pump, electricity flowed through the tube. Plucker used apparatus similar to that shown in Fig. 18.1. He sealed a wire into each end of a strong glass tube. Inside the tube, each wire ended in a metal plate, called an electrode. Outside the tube, each wire ran to a source of high voltage. (The negative plate is called the cathode, and the positive plate is called the anode.) A meter indicated the current in the tube.

Geissler (1814-1879) made the first major improvement in vacuum pumps after Guericke invented the air pump two centuries earlier.

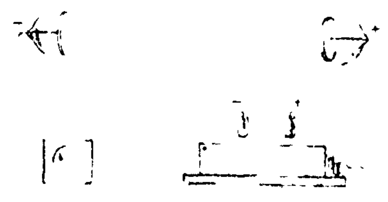


Fig. 18.1 Cathode ray apparatus.

Plucker and his student, Johann Hittorf, noticed that when an electric current passes through a tube at low gas pressure, the tube itself glows with a pale green color. Plucker described these effects in a paper published in 1858. He wrote:

> ...a pale green light...appeared to form a thin coating immediately upon the surface of the glass bulb.... the idea forcibly presented itself that it was a fluorescence in the glass itself. Nevertheless the light in question is in the inside of the tube; but it is situated so closely to its sides as to follow exactly [the shape of the tubes], and thus to give the impression of belonging to the glass itself.

Substances which glow when exposed to light are called fluorescent. Fluorescent lights are essentially Geissler tubes with an inner coating of fluorescent powder.

Several other scientists observed these effects, but two decades passed before anyone undertook a thorough study of the glowing tubes. By 1875, Sir William Crookes had designed new tubes for studying the glow produced when an electric current passes through an evacuated tube. When he used a bent tube, as in Fig. 18.2, the most intense green glow appeared on the part of the tube which was directly opposite the cathode. This suggested that the green glow was produced by something which comes out of the cathode and travels straight down the tube until it hits the glass. Another physicist, Eugen Goldstein, who was studying the effects of passing an electric current through a gas at low pressure, named whatever was coming from the cathode, cathode rays.

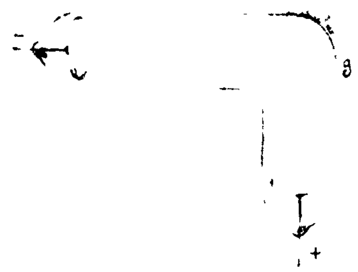


Fig. 18.2 Bent Geissler tube. The most intense green glow appeared at g.

To study the nature of the rays, Crookes did some ingenious experiments. He reasoned that if the cathode rays could be stopped before they reached the end of the tube, the intense green glow should disappear. He therefore introduced a barrier in the form of a Maltese cross, as in Fig. 18.3. Instead of the intense green glow, a shadow of the cross appeared at the end of the tube. The cathode seemed to act like a candle which produces light; the cross acted like a barrier blocking the light. Because the shadow, cross and cathode were lined up, Crookes concluded that the cathode rays, like light rays, travel in straight lines. Next, Crookes moved a magnet near the tube, and the shadow moved. Thus he found that magnetic fields deflected the paths of cathode rays. In the course of many experiments, Crookes found the following properties of cathode rays:

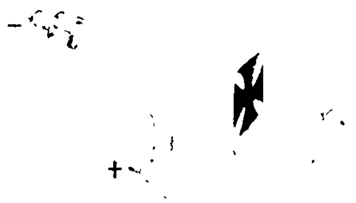


Fig. 18.3 Crookes' tube.

a) cathodes of many different materials produce rays with the same properties;
b) in the absence of a magnetic field, the rays travel in straight lines perpendicular to the surface that emits them;
c) a magnetic field deflects the path of the cathode rays;
d) the rays can produce chemical reactions similar to the reactions produced by light: for example, certain silver salts change color when hit by the rays.

Crookes suspected, but did not succeed in showing that
e) charged objects deflect the path of cathode rays.

J. J. Thomson observed this in 1897.

Physicists were fascinated by the cathode rays and worked hard to understand their nature. Some thought that the rays must be a form of light, because they have so many of the properties of light: they travel in straight lines, produce chemical changes and fluorescent glows just as light does. According to Maxwell's theory of electricity and magnetism (Unit 4) light consists of electromagnetic waves. So the cathode rays might be electromagnetic waves of frequency higher or lower than that of visible light.

Magnetic fields, however, do not bend light; they do bend the path of cathode rays. In Unit 4, we found that magnets exert forces on currents, that is, on moving electric charges. Since a magnet deflects cathode rays in the same way that it deflects negative charges, some physicists believed that cathode rays consisted of negatively charged particles.

The controversy over the wave or particle nature of cathode rays continued for 25 years. Finally, in 1897, J. J. Thomson made a series of experiments which convinced physicists that the cathode rays are negatively charged particles.

It was known that the paths of charged particles are affected by both magnetic and electric fields. By assuming

18 2

that the cathode rays were negatively charged particles, Thomson could predict what should happen to the cathode rays when they passed through such fields. For example, the deflection of the path of the cathode rays by a magnetic field could be just balanced by an electric field with the right direction and magnitude. The predictions were verified and Thomson could conclude that the cathode rays did indeed act like charged particles. He was then able to calculate, from the experimental data, the ratio of the charge of a particle to its mass. This ratio is denoted by q/m where q is the charge and m is the mass of the particle. For those who are interested in the details of Thomson's experiment and calculations, they are given on page 41.

Sir Joseph John Thomson (1856-1940), one of the greatest British physicists, attended Owens College in Manchester, England (home of John Dalton) and then Cambridge University. Throughout his career, he was interested in atomic structure. We shall read about his work often during the rest of the course. He worked on the conduction of electricity through gases, on the relation between electricity and matter and on atomic models. His greatest single contribution was the discovery of the electron. He was the head of the famous Cavendish Laboratory at Cambridge University, where one of his students was Ernest Rutherford—about whom you will hear a great deal later in this unit and in Unit 6.

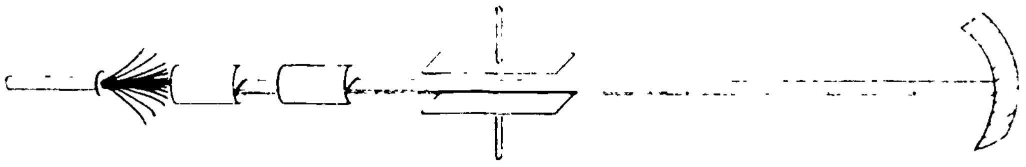
Thomson found that the rays from cathodes made of <u>different</u> materials all had the <u>same</u> value of q/m, namely 1.76×10^{11} coulombs per kilogram. This value was about 1800 times larger than the values of q/m for hydrogen ions measured in electrolysis experiments, 9.6×10^{7} coulombs per kilogram. Thomson concluded from these results that either the charge of the cathode ray particles was much larger than that of the hydrogen ion, or the mass of the cathode ray particles was much smaller than the mass of the hydrogen ion.

Thomson's negatively charged particles were later called <u>electrons</u>. Thomson also made measurements of the charge on the negatively charged particles with methods other than those involving deflection by electric and magnetic fields. Although these experiments were inaccurate, they were good enough to indicate that the charge of a cathode ray particle was not much different from that of the hydrogen ion in electrolysis. Thomson was therefore able to conclude that the cathode ray particles have much smaller mass than hydrogen ions.

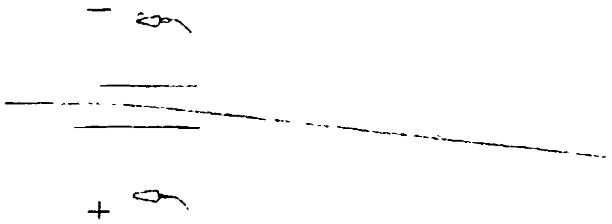
The cathode ray particles, or electrons, were found to have two important properties: (1) they were emitted by a wide variety of cathode materials, and (2) they were much smaller in mass than the hydrogen atom, which has the smallest known mass. Thomson therefore concluded that the cathode ray particles form a part of all kinds of matter. He suggested that the atom is not the ultimate limit to the subdivision of matter, and that the electron is one of the bricks of which atoms are built up, perhaps even the fundamental building block of atoms.

Thomson's q/m Experiment

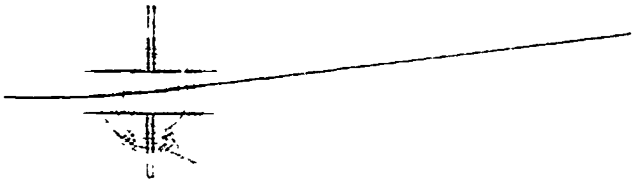
J. J. Thomson measured the ratio of charge to mass for cathode-ray particles by means of the evacuated tube in the photograph on page 36. A high voltage between two electrodes in one end of the tube produced cathode rays. The rays that passed through both slotted cylinders formed a nearly parallel beam. The beam produced a spot of light on a fluorescent coating inside the large end of the tube.



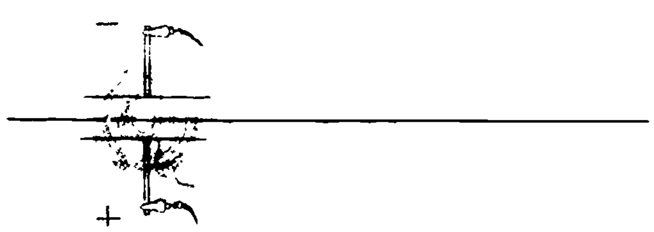
The beam could be deflected by an electric field produced between two plates in the mid-section of the tube.



The beam could also be deflected by a magnetic field produced between a pair of wire coils placed around the mid-section of the tube.



When only the magnetic field B was turned on, the particles in the beam of charge q and speed v would experience a force Bqv; because the force is always perpendicular to the velocity, the beam would be deflected into a nearly circular arc of radius R in the nearly uniform field. If the particles in the beam have mass m, they must be experiencing a centripetal force mv^2/R. Since the centripetal force is the magnetic force, $Bqv = mv^2R$. Rearranging terms: $q/m = v/BR$.
B can be calculated from the geometry of the coils and the current in them. R can be found geometrically from the displacement of the beam spot on the end of the tube. To determine v, Thomson applied the electric field and the magnetic field at the same time. By arranging the directions and strengths of the fields appropriately, the electric field can be made to exert a downward force Eq on the beam particles exactly equal to the upward force Bqv due to the magnetic field.



If the magnitudes of the electric and magnetic forces are equal, then $Eq = Bqv$. Solving for v: $v = E/B$. E can be calculated from the separation of the two plates and the voltage between them, so the speed of the particles can be determined. So all the terms on the right of the equation for q/m are known and q/m can be found.

18 2

In the article in which he announced his discovery, Thomson speculated on the ways in which the particles could be arranged in atoms of different elements in order to account for the periodicity of the chemical properties of the elements. Although, as we shall see, he did not say the last word about this problem, he did say the first word about it.

What was the most convincing evidence that cathode rays were not electromagnetic radiation?

Why was q/m for electrons 1800 times larger than q/m for hydrogen ions?

What were two main reasons that Thomson believed electrons to be "building blocks" from which all atoms are made?

18 3 The measurement of the charge of the electron: Millikan's experiment. After the ratio of charge to the mass (q/m) of the electron had been determined, physicists tried to measure the value of the charge q separately. If the charge could be determined, the mass of the electron could be found from the known value of q/m. In the years between 1909 and 1916 an American physicist, Robert A. Millikan, succeeded in measuring the charge of the electron. This quantity is one of the fundamental constants of physics because of its importance in atomic and nuclear physics as well as in electricity and electromagnetism.

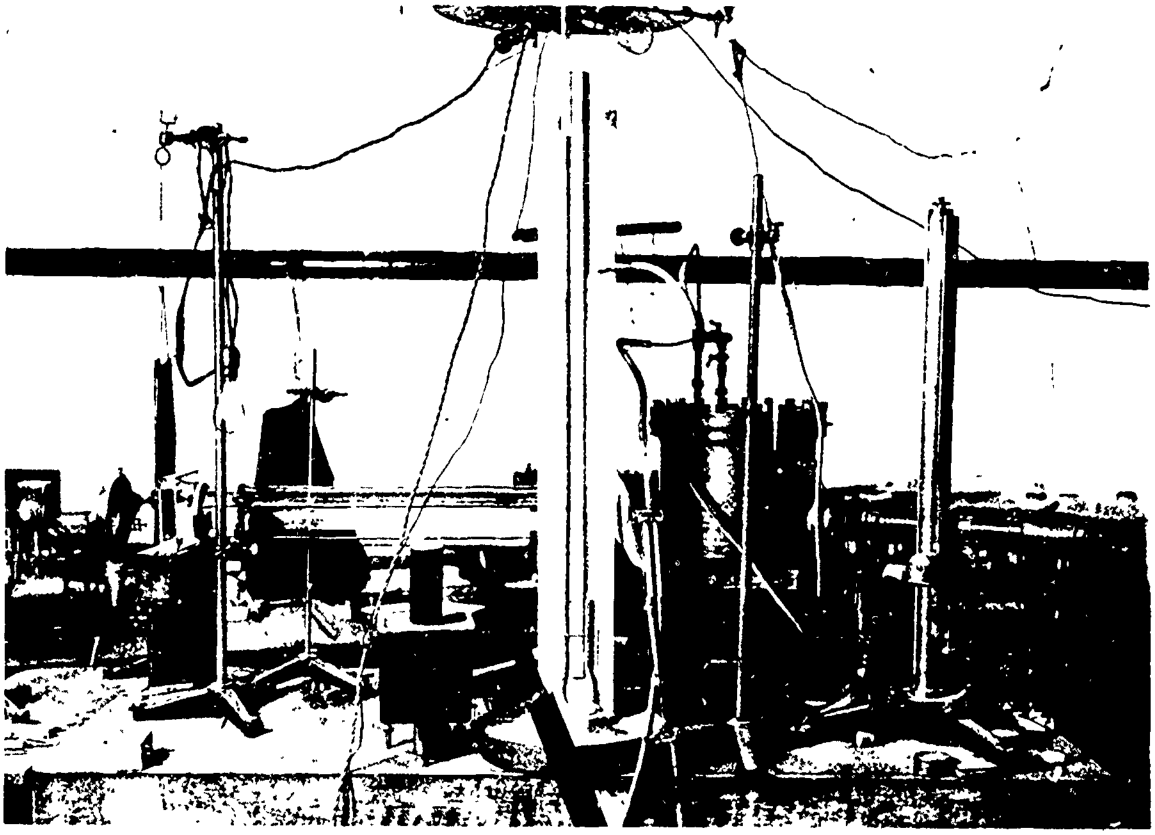
Millikan's "oil-drop experiment" is described on page 43. He found that the electric charge that an oil drop picks up is always a simple multiple of a certain minimum value. For example, the charge may have the value 4.8×10^{-19} coulombs, or 1.6×10^{-19} coulombs, or 6.4×10^{-19} coulombs, or 1.6×10^{-18} coulombs. But it never has a charge of, say, 2.4×10^{-19} coulombs, and it never has a value smaller than 1.6×10^{-19} coulombs. In other words, electric charges always come in multiples of 1.6×10^{-19} coulombs. Millikan took this minimum charge to be the charge of a single electron.

From now on we denote the magnitude of the charge of the electron by q_e:

$q_e = 1.6 \times 10^{-19}$ coul.

Charges of atomic and molecular ions are measured in units of the electron charge q_e. For example, when a chemist refers to a "doubly charged oxygen ion," he means that the charge of the ion is $2q_e = 3.2 \times 10^{-19}$ coulombs.

Note that Millikan's experiments did not prove that no smaller charges than q_e can exist. All we can say is that no experiment has yet proved the existence of smaller charges. Since Millikan's work, physicists have been convinced that electric charges always come in multiples of q_e.



Millikan's Oil-Drop Experiment

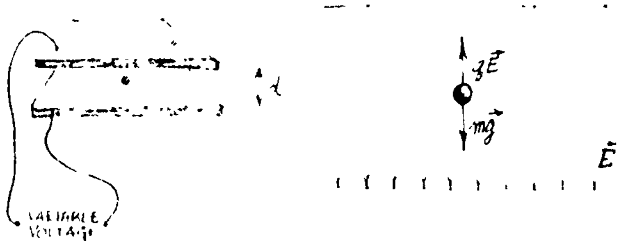


Fig. 18.5

In principle Millikan's experiment is simple; it is sketched in Fig. 18.5. When oil is sprayed into a chamber, the minute droplets formed are found to be electrically charged. The charge on a droplet can be measured by means of an electric field in the chamber. Consider a small oil drop of mass m carrying an electric charge q. It is situated between two horizontal plates separated by a distance d and at an electrical potential difference V. There will be a uniform electric field $\vec{E}$ between the plates, of strength V/d. This field can be adjusted so that the electrical force $q\vec{E}$ exerted upward on the drop's charge will balance the force $m\vec{g}$ exerted downward by gravity. Equating the magnitudes of these forces gives:

$$F_{el} = F_{grav},$$

$$qE = mg,$$

$$\text{or} \qquad q = mg/E.$$

The mass of the drop can, in principle, be determined from its radius and the density of the oil from which it was made. Millikan had to measure these quantities by an indirect method, but it is now possible to do the experiment with small manufactured polystyrene spheres whose mass is accurately known, so that some of the complications of the original experiment can be avoided. Millikan's own set-up is seen in the photograph above. A student version of Millikan's apparatus is shown in the photograph at the right.

In 1964, an American physicist, Murray Gell-Mann, suggested that particles with charge equal to 1/3 or 2/3 of q_e might exist. He named these particles "quarks"—the word comes from James Joyce's novel Finnegan's Wake. Quarks are now being looked for in cosmic-ray and bubble-chamber experiments.

18 3

In everyday life, the electric charges one meets are so large that one can think of a current as being continuous—just as one usually thinks of the flow of water in a river as continuous rather than as a flow of individual molecules. A current of one ampere, for example, is equivalent to the flow of $6.25 \cdot 10^{18}$ electrons per second. The "static" electric charge one accumulates by shuffling over a rug on a dry day consists of approximately $10^{1[illegible]}$ electron charges.

Since the work of Millikan, a wide variety of other experiments involving many different fields within physics have all pointed to the same basic unit of charge as being fundamental in the structure and behavior of atoms. For example, it has been shown directly that cathode ray particles carry this basic unit of charge—that they are, in other words, electrons.

By combining Millikan's value for the electron charge q_e with Thomson's value for the ratio of charge to mass (q_e/m), we can calculate the mass of a single electron (see margin). The result is that the mass of the electron is about 10^{-30} kilograms. The charge-to-mass ratio of a hydrogen ion is 1836 times smaller than the charge-to-mass ratio of an electron. It is reasonable to consider that an electron and a hydrogen ion have equal and opposite electric charge, since they form a neutral hydrogen atom when they combine. We may therefore conclude that the mass of the hydrogen ion is 1836 times as great as the mass of the electron.

Oil drops pick up different amounts of electric charge. How did Millikan know that the lowest charge he found was actually just one electron charge?

18.4 The photoelectric effect. The photoelectric effect was discovered in 1887 by the German physicist Heinrich Hertz. Hertz was testing Maxwell's theory of electromagnetic waves (Unit 4). He noticed that a metallic surface can emit electric charges when light of very short wave length falls on it. Because light and electricity are both involved, the name photoelectric effect was given to this new phenomenon. When the electricity produced was passed through electric and magnetic fields, its direction was changed in the same ways as the path of cathode rays. It was therefore deduced that the electricity consists of negatively charged particles. In 1898, J. J. Thomson measured the value of the ratio q/m for these particles with the same method that he used for the cathode ray particles. He got the same value for the particles ejected in the photoelectric effect as he did for the cathode ray particles. By means of these experiments (and others) the photoelectric particles were shown to have the same properties as electrons. They are often referred to as photoelectrons to indicate their source. Later work showed that all substances, solids, liquids and gases, undergo the photoelectric effect under appropriate conditions. It is, however, convenient to study the effect with metallic surfaces.

The "electric eye" used, for example, for opening a door automatically, is based on the photoelectric effect. When a solid object interrupts a beam of light shining from one side of the door to the other, an electric current is changed; this change switches on a motor that operates the door. The photoelectric effect is also used in projectors for sound motion pictures.

The photoelectric effect has been studied in great detail and has had an important place in the development of atomic physics. The effect could not be explained in terms of the classical physics we have studied so far. New ideas had to be introduced to account for the experimental results. In particular, a revolutionary concept had to be introduced—that of quanta—and a new branch of physics—quantum theory—had to be developed, at least in part because of the photoelectric effect. Modern atomic theory is actually the quantum theory of matter and radiation. The study of the photoelectric effect is, therefore, an important step on the way to the understanding of the atom.

Two types of measurements can be made which yield useful information about the photoelectric effect: (1) measurements of the photoelectric current (the number of electrons emitted per unit time); (2) measurements of the kinetic energies with which the electrons are emitted.

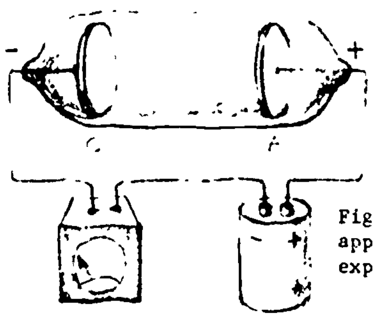


Fig. 18.6a Schematic diagram of apparatus for photoelectric experiments.

The electron current can be studied with an apparatus like that sketched in Fig. 18.6. Two metal plates, C and A, are sealed inside a well-evacuated quartz tube. (Quartz is transparent to ultraviolet light as well as visible light.) The two plates are connected to a source of potential difference. When light strikes plate C, electrons are emitted. If the potential of plate A is positive relative to plate C, the emitted electrons will accelerate to plate A. (Some electrons will reach plate A even if it isn't positive relative to C.) The resulting current is indicated by the meter.

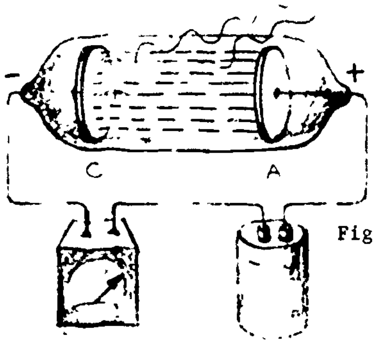


Fig. 18.6b

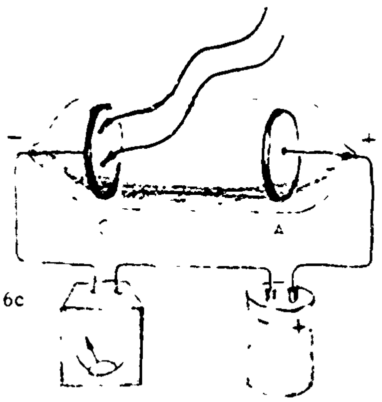


Fig. 18.6c

Any metal used as the plate C shows a photoelectric effect, but only if the light has a frequency greater than a certain value. This value of the frequency is called the threshold frequency. Different metals have different threshold frequencies. If the incident light has a frequency lower than the threshold frequency, no electrons are emitted no matter how great the intensity of the light is or how long the light is left on.

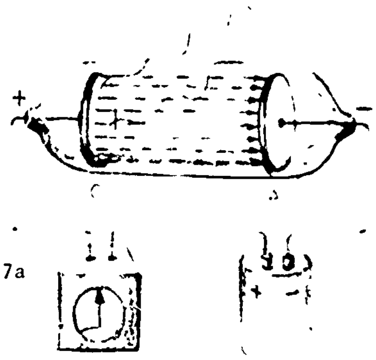


Fig. 18.7a

The kinetic energies of the electrons can be measured in a slightly modified version of the apparatus of Fig. 18.6. The battery is reversed so that the plate A repels the electrons. The voltage can be varied from zero to a value just large enough to keep any electrons from reaching the plate A. A sketch of the modified apparatus is shown in Fig. 18.7.

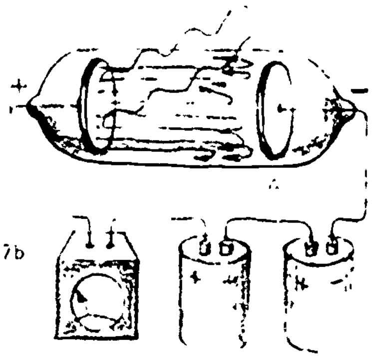


Fig. 18.7b

When the voltage across the plates is zero, the meter indicates a current, showing that the electrons emerge from the metallic surface with kinetic energy. As the voltage is increased the electron current decreases until a certain voltage is reached at which the current becomes zero. This voltage, which is called the stopping voltage, is a measure of the maximum kinetic energy of the photoelectrons. If the stopping voltage is denoted by V_{stop}, the maximum kinetic energy is given by the relation:

$$KE_{max} = \frac{1}{2}mv^2_{max} = V_{stop}\, q_e .$$

The results may be stated more precisely. (We shall number the important experimental results to make it more convenient to discuss their theoretical interpretation later.)

(1) A substance shows a photoelectric effect only if the incident radiation has a frequency above a certain value called the threshold frequency.

(2) If light of a given frequency *can* liberate electrons from a surface, the current is proportional to the intensity of the light.

(3) If light of a given frequency can liberate electrons, the emission of the electrons is *immediate*. The time interval between the incidence of the light on the metallic surface and the appearance of electrons is not more than $3 \cdot 10^{-9}$ sec. This is true even for the lowest light intensities used.

(4) The maximum kinetic energy of the photoelectrons increases linearly with the frequency of the light which causes their emission, and is independent of the intensity of the incident light. The way in which the maximum kinetic energy of the electrons varies with the frequency of the light is shown in Fig. 18.8. The symbols $(f_0)_1$, $(f_0)_2$ and $(f_0)_3$ stand for the different threshold frequencies of three different substances. For each substance, the experiments fall on a straight line. All the lines have the same slope.

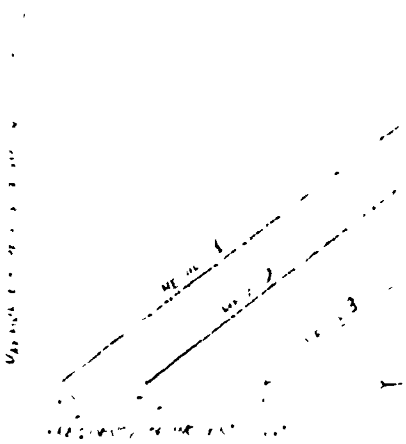


Fig. 18.8 Photoelectric effect: maximum kinetic energy of the electrons as a function of the frequency of the incident light; different metals yield lines that are parallel, but have different threshold frequencies.

What is most surprising about the results is that photoelectrons are emitted at light frequencies *barely above* the threshold frequency, no matter how low the intensity of the light. Yet, at light frequencies just a *bit below* the threshold frequency, no electrons are emitted *no matter how high the intensity of the light*.

The experimental results could not be explained on the basis of the classical electromagnetic theory of light. There was no way in which a very low-intensity train of light waves spread out over a large number of atoms could, in a very short time interval, concentrate enough energy on one electron to knock the electron out of the metal. In some experiments, the light intensity was so low that, according to the classical theory, it should take several hundred seconds for an electron to accumulate enough energy from the light to be emitted. But experimental result (3) shows that electrons are emitted about a billionth of a second after the light strikes the surface.

Furthermore, the classical wave theory was unable to account for the existence of a threshold frequency. There seemed to be no reason why a sufficiently intense beam of

18.4

low-frequency radiation would not be able to produce photoelectricity, if low-intensity radiation of higher frequency could produce it. Finally, the classical theory was unable to account for the fact that the maximum kinetic energy of the photoelectrons increases linearly with the frequency of the light but is independent of the intensity. Thus, the photoelectric effect posed a challenge which the classical wave theory of light could not meet.

Light falling on a certain metal surface causes electrons to be emitted. What happens as the intensity of the light is decreased?

What happens as the frequency of the light is decreased?

18.5 Einstein's theory of the photoelectric effect: quanta. The explanation of the photoelectric effect was the major work cited in the award to Albert Einstein of the Nobel Prize in physics for the year 1921. Einstein's theory, proposed in 1905, played a major role in the development of atomic physics. The theory was based on a daring proposal. Not only were many of the experimental details unknown in 1905, but the key point of Einstein's explanation was contrary to the classical ideas of the time.

See the articles "Einstein" and "Einstein and some Civilized Discontents" in Project Physics Reader 5.

Einstein assumed that the energy of light is not distributed evenly over the whole expanding wave front (as is assumed in the classical theory) but rather is concentrated into discrete small regions. Further, the amount of energy in each of these regions is not just any amount, but is a definite amount of energy which is proportional to the frequency f of the wave. The proportionality factor is a constant, denoted by h and called Planck's constant, for reasons which will be discussed later. Thus, on this model, the light energy comes in pieces, each of amount hf. The amount of radiant energy in each piece is called a *quantum* of energy; it represents the smallest quantity of energy of light of that frequency. The quantum of light energy was later called a *photon*.

$h = 6.6 \times 10^{-34}$ joule-sec

There is no explanation clearer or more direct than Einstein's. We quote from his first paper (1905) on this subject, changing only the notation used there to make it coincide with usual current practice (including our own notation):

> ...According to the idea that the incident light consists of quanta with energy hf, the ejection of cathode rays by light can be understood in the following way. Energy quanta penetrate the surface layer of the

> body, and their energy is converted, at least in part, into kinetic energy of electrons. The simplest picture is that a light quantum gives up all its energy to a single electron; we shall assume that this happens. The possibility is not to be excluded, however, that electrons receive their energy only in part from the light quantum. An electron provided with kinetic energy inside the body may have lost part of its kinetic energy by the time it reaches the surface. In addition it is to be assumed that each electron, in leaving the body, has to do an amount of work W (which is characteristic of the body). The electrons ejected directly from the surface and at right angles to it will have the greatest velocities perpendicular to the surface. The kinetic energy of such an electron is
>
> $$KE_{max} = hf - W$$
>
> If the body is charged to a positive potential V_{stop} just large enough to keep the body from losing electric charge, we must have
>
> $$KE_{max} = hf - W = V_{stop}\, q_e$$
>
> where q_e is the magnitude of the electronic charge. ...
>
> If the derived formula is correct, V_{stop}, when plotted as a function of the frequency of the incident light, should yield a straight line whose slope should be independent of the nature of the substance illuminated.

We can now compare Einstein's photoelectric equation with the experimental results to test whether or not the theory accounts for the results. According to the equation, the kinetic energy is greater than zero only when the frequency f is high enough so that hf is greater than W. Hence, the equation says that an electron can be emitted only when the frequency of the incident light is greater than a certain value.

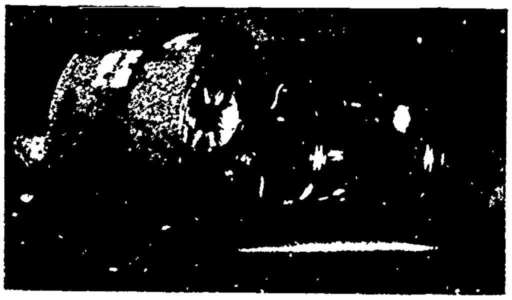
How Einstein's theory explains the photoelectric effect:

(1) no photoelectric emission below threshold frequency. Reason: low-frequency photons don't have enough energy.

Next, according to Einstein's photon model, it is an individual photon that ejects an electron. The intensity of the light is proportional to the number of the photons, and the number of electrons ejected is proportional to the number of photons. Hence the number of electrons ejected is proportional to the intensity of the incident light.

(2) current $\propto$ light intensity. Reason: one photon ejects one electron.

Student apparatus for photoelectric experiments often includes a vacuum phototube like the one at the right (actual size). The collecting wire is at the center of a cylindrical photosensitive surface. The frequency of the light entering the tube is controlled by placing colored filters between the tube and a light source.



Albert Einstein (1879-1955) was born in the city of Ulm, in Germany. He received his early education in Germany and Switzerland. Like Newton he showed no particular intellectual promise as a youngster. After graduation from the Polytechnic School, Einstein (in 1901) went to work in the Swiss Patent Office in Berne. This job gave Einstein a salary to live on and an opportunity to use his spare time in thinking about physics. In 1905 he published three papers of epoch-making importance. One dealt with quantum theory and included his theory of the photoelectric effect. Another treated the problem of molecular motions and sizes, and worked out a mathematical analysis of the phenomenon of "Brownian motion." Einstein's analysis and experimental work by Jean Perrin, a French physicist, made a strong argument for the molecular motions assumed in the kinetic theory. Einstein's third 1905 paper discusses the theory of special relativity which revolutionized modern thought about the nature of space, time and physical theory.

In 1915, Einstein published his paper on the theory of general relativity, in which he provided a new theory of gravitation which included Newton's theory as a special case.

When Hitler and the Nazis came to power in Germany, in 1933, Einstein came to the United States and became a member of the Institute for Advanced Studies at Princeton. He spent the rest of his working life seeking a unified theory which would include gravitation and electromagnetics. At the beginning of World War II, Einstein wrote a letter to President Franklin D. Roosevelt warning of the war potential of an "atomic bomb," on which the Germans had begun to work. After World War II, Einstein worked for a world agreement to end the threat of atomic warfare.

According to Einstein's model the light energy is concentrated in the quanta (or photons). Hence, no time is needed for collecting light energy; the quanta transfer their energy immediately to the photoelectrons, which appear after the very short time required for them to escape from the surface.

(3) immediate emission. Reason: a single photon provides the energy concentrated in one place.

Finally, according to the photoelectric equation, the greater the frequency of the incident light, the greater is the maximum kinetic energy of the ejected electrons. According to the photon model, the photon energy is directly proportional to the light frequency. The minimum energy needed to eject an electron is that required to supply the energy of escape from the metal surface—which explains why light of frequency less than f_o cannot eject any electrons. The difference in the energy of the absorbed photon and the energy lost by the electron in passing through the surface is the kinetic energy of the escaping electron.

(4) KE_{max} increases linearly with frequency above f_o. Reason: the work needed to remove the electron is $W = hf_o$; any energy left over from the original photon is now available for kinetic energy of the electron.

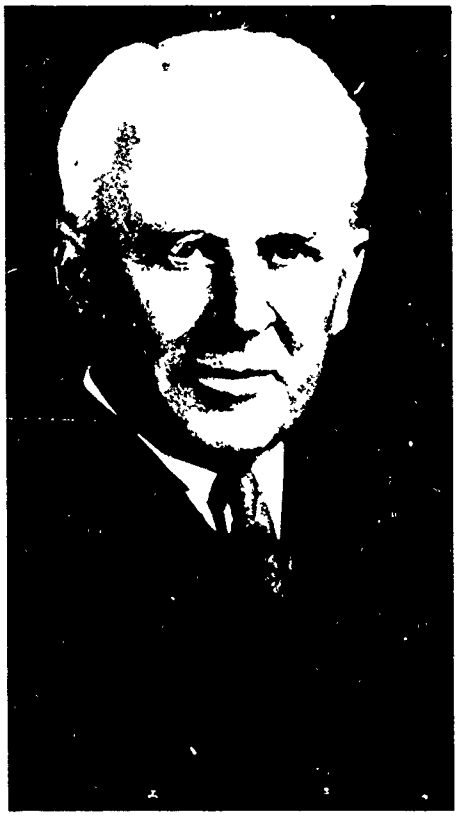
Thus, Einstein's photoelectric equation agrees qualitatively with the experimental results. There remained two quantitative tests: (1) does the maximum energy vary linearly with the light frequency? (2) is the proportionality factor h the same for all substances? The quantitative test of the theory required some ten years. There were experimental difficulties connected with preparing metal surfaces which were free of impurities (for example, a layer of oxidized metal). It was not until 1916 that it was established that there is indeed a straight-line relationship between the frequency of the light and the maximum kinetic energy of the electrons. to the point where the experimental points on the graph fit a straight line obviously better than any other line. (See the figure on the next page.) Having achieved that degree of accuracy, Millikan could then show that the straight lines obtained for different metals all had the same slope, even though the threshold frequencies were different. The value of h could be obtained from Millikan's measurements; it agreed very well with a value obtained by means of another, independent method. So Einstein's theory was verified quantitatively.

See "Space Travel: Problems of Physics and Engineering" in <u>Project Physics Reader 5</u>.

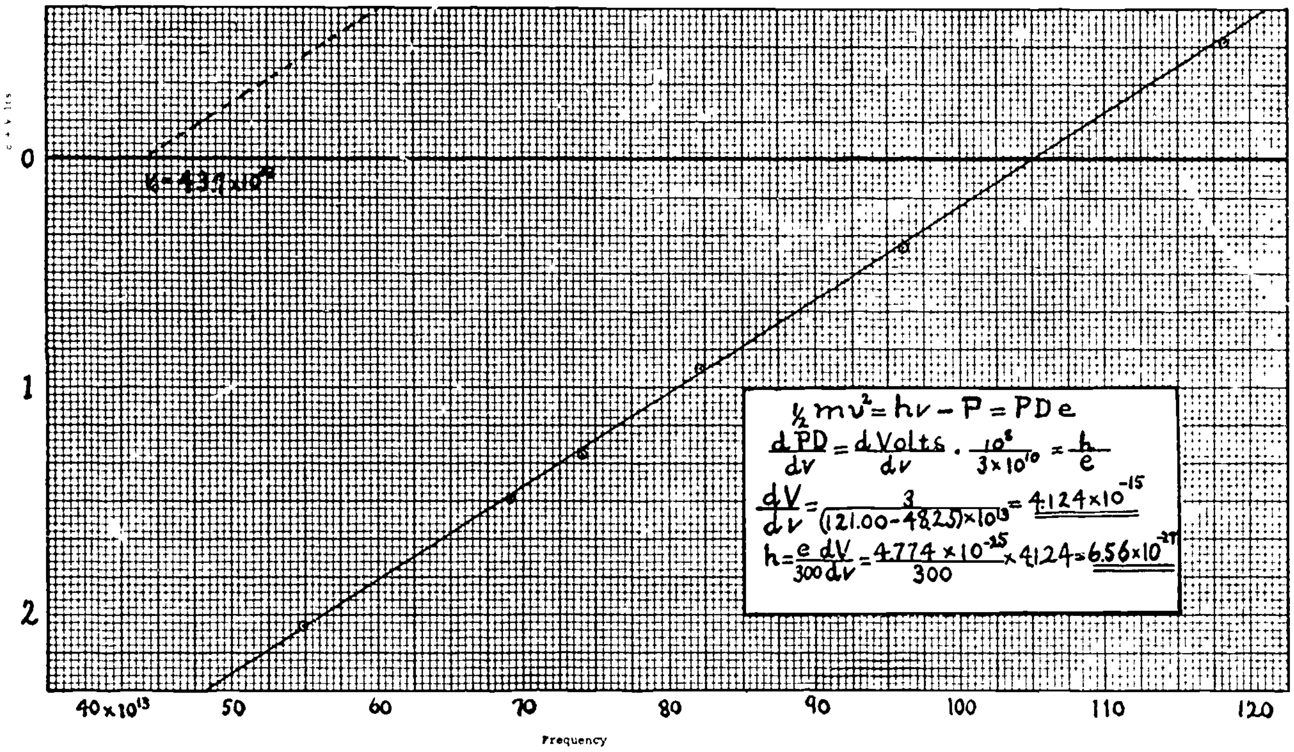
The equation $KE_{max} = hf - W$ led to two Nobel prizes: one to Einstein, who derived it theoretically, and one to Millikan, who verified it experimentally.

Historically, the first suggestion of a quantum aspect of electromagnetic radiation came from studies of the heat radiated by solids rather than from the photoelectric effect. The concept of <u>quanta of energy</u> hf was introduced by Max Planck, a German physicist, in 1900, five years before Einstein's theory. The constant h is known as <u>Planck's constant</u>. Planck was trying to account for the way in which

Robert Andrews Millikan (1868-1953), an American physicist, attended Oberlin College, where his interest in physics was only mild. After his graduation he became more interested in physics, taught at Oberlin while taking his master's degree, and then obtained his doctor's degree from Columbia University in 1895. After post-doctoral work in Germany he went to the University of Chicago, where he became a professor of physics in 1910. His work on the determination of the electronic charge took from 1906 to 1913. He was awarded the Nobel Prize in physics in 1923 for this research and for the very careful experiments which resulted in the verification of the Einstein photoelectric equation. In 1921, Millikan moved to the California Institute of Technology, eventually becoming its president.



Some of Millikan's data, which verified Einstein's photoelectric equation, are plotted below. The straight-line relationship between frequency and potential is evident and the calculated value of h (in the inset) differs from the best modern values by only one percent. To obtain his data Millikan designed an apparatus in which the metal photoelectric surface was cut clean while in a vacuum. A knife inside the evacuated volume was manipulated by an electromagnet outside the vacuum to make the cuts. This rather intricate arrangement was required to achieve an uncontaminated metal surface.



(Millikan's own symbols are shown here; they are different from the ones used in the text. Can you figure out the meaning of his symbols and units from the information given?)

the heat energy radiated by a hot body depends on the frequency of the radiation. Classical physics (nineteenth-century thermodynamics and electromagnetism) could not account for the experimental facts. Planck found that the facts could only be interpreted in terms of quanta. Einstein's theory of the photoelectric effect was actually an extension and application of Planck's quantum theory of thermal radiation. Both the experiments on thermal radiation and the theory are much more difficult to describe than are the experiments and the theory of the photoelectric effect. That is why we have chosen to introduce the new (and difficult) concept of quanta of energy by means of the photoelectric effect.

Planck's application of his theory to the experimental data available in 1900 yielded a value of his constant h. The value of h obtained by Millikan in his experiments agreed very well with Planck's value and had greater precision. Additional, independent methods of determining Planck's constant have been devised; the values obtained with all different methods are in excellent agreement.

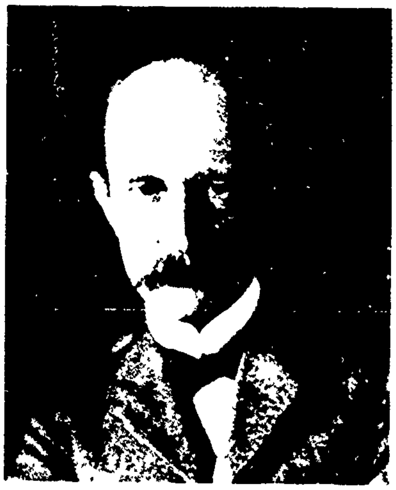
The photoelectric effect presented physicists with a difficult problem. According to the classical wave theory, light consists of electromagnetic waves extending continuously throughout space. This theory was highly successful in explaining optical phenomena (reflection, refraction, polarization, interference) but could not account for the photoelectric effect. Einstein's theory, in which the existence of discrete bundles of light energy was postulated, accounted for the photoelectric effect; it could not account for the other properties of light. The result was that there were two models whose basic concepts were mutually contradictory. Each model had its successes and failures. The problem was: what, if anything, could be done about the contradictions between the two models? We shall see later that the problem and its treatment have a central position in modern physics.

Einstein's idea of a quantum of light had a definite relation to the wave model of light. What was it?

Why doesn't the electron have as much energy as the quantum of light which ejects it?

What does a "stopping voltage" of 2.0 volts indicate?

18.6 X rays. In 1895, another discovery was made which, like the photoelectric effect, did not fit in with accepted ideas about electromagnetic waves and needed quanta for its ex-



Max Planck (1858-1947), a German physicist, was the originator of the quantum theory, one of the two great revolutionary physical theories of the 20th century. (The other is Einstein's relativity theory.) Planck won the Nobel Prize in 1918 for his quantum theory. He tried hard to make this theory fit in with the classical physics of Newton and Maxwell, but never succeeded. Einstein extended the idea of quanta much further than Planck himself did.

Surprisingly, Planck was skeptical of Einstein's photoelectric theory when it was first introduced and once said, "If in some of his speculations—as for example in his hypothesis of the light quanta—he was overshooting the target, this should hardly be counted against him. Without taking certain risks one would not be able to advance even in the most exact of the sciences." In spite of this early disagreement Planck and Einstein were friends and had the greatest respect for each other's scientific achievements.

planation. The discovery was that of x rays by the German physicist, Wilhelm Rontgen. The original discovery, its consequences for atomic physics, and the uses of x rays are all dramatic and important. We shall, therefore, discuss x rays in some detail.

Wilhelm Konrad Röntgen
(1845-1923)

On November 8, 1895, Röntgen was experimenting with cathode rays, as were many physicists all over the world. According to a biographer,

> He had covered the all-glass pear-shaped tube with pieces of black cardboard, and had darkened the room in order to test the opacity of the black paper cover. Suddenly, about a yard from the tube, he saw a weak light that shimmered on a little bench he knew was nearby. Highly excited, Rontgen lit a match and, to his great surprise, discovered that the source of the mysterious light was a little barium platinocyanide screen lying on the bench.

Barium platinocyanide, a mineral, is one of the many chemicals known to <u>fluoresce</u>, that is, to emit visible light when illuminated with ultraviolet light. No source of ultraviolet light was present in Röntgen's experiment. Cathode rays had not been observed to travel more than a few centimeters in air. Hence, neither ultraviolet light nor the cathode rays themselves could have caused the fluorescence. Röntgen, therefore, deduced that the fluorescence he had observed was due to rays of a new kind, which he named x rays, that is rays of an unknown nature. During the next seven weeks he made a series of experiments to determine the properties of this new radiation. He reported his results on Dec. 28 1895 to the Würtzberg Physical Medical Society in a paper whose title, translated, is "On a New Kind of Rays."

Röntgen's paper described nearly all of the properties of x rays that are known even now. It included an account of the method of production of the rays and proof that they originated in the glass wall of the tube where the cathode rays strike. Rontgen showed that the rays travel in straight lines from their place of origin and that they darken a photographic plate. He reported in detail the ability of the x rays to penetrate various substances—paper, wood, aluminum, platinum and lead. Their penetrating power was greater through light materials (paper, wood, flesh) than through dense materials (platinum, lead, bone). He described photographs showing "the shadows of bones of the hand, of a set of weights in a small box, and of a piece of metal whose inhomogeneity becomes apparent with x rays.' He gave a clear description of the shadows cast by the bones of the hand on the fluorescent screen. Röntgen also reported that the x rays

The discovery of x rays was narrowly missed by several physicists. Hertz and Lenard (another well-known German physicist) failed to distinguish the cathode rays—perhaps because they didn't happen to have a piece of paper covered with barium platinocyanide lying around to set them on the track. An English physicist, Frederick Smith, found that photographic plates kept in a box near a cathode-ray tube were liable to be fogged—he told his assistant to keep them in another place!

Opposite: One of the earliest x-ray photographs made in the United States. It was made by Michael Pupin of Columbia University in 1896. The man x rayed had been hit by a shotgun blast.


Michael I.
Columbia U

were not deflected by a magnetic field, and showed no reflection, refraction or interference effects in ordinary optical apparatus.

One of the most important properties of x rays was discovered by J. J. Thomson a month or two after the rays themselves had become known. He found that when the rays pass through a gas they make it a conductor of electricity. He attributed this effect to "a kind of electrolysis, the molecule being split up, or nearly split up by the Röntgen rays." The x rays, in passing through the gas, knock electrons loose from some of the atoms of the gas. The atoms that lose these electrons become positively charged. They are called ions because they resemble the positive ions in electrolysis, and the gas is said to be ionized.

X rays were often referred to as Röntgen rays after their discoverer.

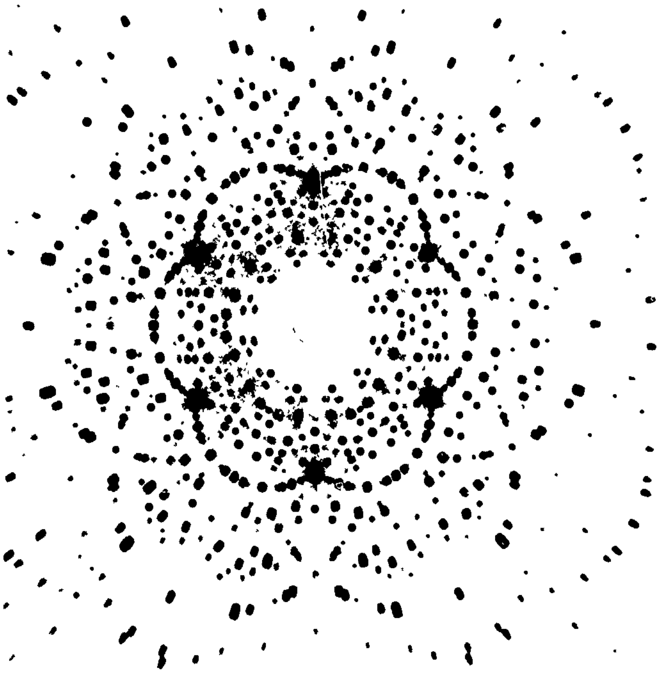
Röntgen and Thomson found, independently, that the ionization of air produced by x rays discharges electrified bodies. The rate of discharge was shown to depend on the intensity of the rays. This property was therefore used as a quantitative means of measuring the intensity of an x-ray beam. As a result, careful quantitative measurements of the properties and effects of x rays could be made.

One of the problems that aroused interest during the years following the discovery of x rays was that of the nature of the rays. They did not act like charged particles—electrons for example—because they were not deflected by a magnetic field (or by an electric field). They therefore had to be either neutral particles or electromagnetic waves. It was difficult to choose between these two possibilities. On the one hand, no neutral particles of atomic size (or smaller) were known which had the penetrating power of x rays. The existence of neutral particles with high penetrating power would be extremely hard to prove in any case, because there was no way of getting at them. On the other hand, if the x rays were electromagnetic waves, they would have to have extremely short wavelengths: only in this case, according to theory, could they have high penetrating power and show no refraction or interference effects with optical apparatus.

Such a particle—the neutron—was discovered in 1932. You will see in Chapter 23 (Unit 6) how hard it was to identify. But the neutron has nothing to do with x rays.

The spacing between atoms in a crystal is very small. It was thought, therefore, that if x rays were waves, they would show diffraction effects when transmitted through crystals. In 1912, experiments on the diffraction of x rays by crystals showed that x rays do, indeed, act like electromagnetic radiations of very short wavelength—like ultra ultraviolet light. These experiments are too complicated to discuss here but they were convincing to physicists, and the problem of the nature of x rays seemed to be solved.

X rays were also found to have quantum properties. They cause the emission of electrons from metals. These electrons have greater kinetic energies than those produced by ultraviolet light. The ionization of gases by x rays is also an example of the photoelectric effect; in this case the electrons are freed from molecules. Thus, x rays also require quantum theory for the explanation of their behavior. The problem of the apparent wave and particle properties of light was aggravated by the discovery that x rays also showed wave and particle properties.

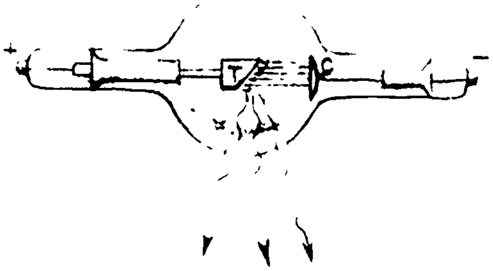


X-ray diffraction patterns from a metal crystal.

Rontgen's discovery excited intense interest throughout the entire scientific world. His experiments were repeated, and extended, in many laboratories in both Europe and America. The scientific journals, during the year 1896, were filled with letters and articles describing new experiments or confirming the results of earlier experiments. This widespread experimentation was made possible by the fact that, during the years before Rontgen's discovery, the passage of electricity through gases had been a popular topic for study by physicists. Hence many physics laboratories had cathode-ray tubes and could produce x rays easily. Intense interest in x rays was generated by the spectacular use of these rays in medicine. Within three months of Rontgen's discovery, x rays were being put to practical use in a hospital in Vienna in connection with surgical operations. The use of this new aid to surgery spread rapidly. Since Röntgen's time, x rays have revolutionized certain phases of medical practice, especially the diagnosis of some diseases and the treatment of cancer. In other fields of applied science, both physical and biological, uses have been found for x rays which are nearly as important as their use in medicine. Among these are the study of the crystal structure of materials; "industrial diagnosis," such as the search for possible defects in the materials of engineering; the analysis of such different substances as coal and corn; the study of old paintings; the detection of artificial gems; the study of the structure of rubber; and many others.

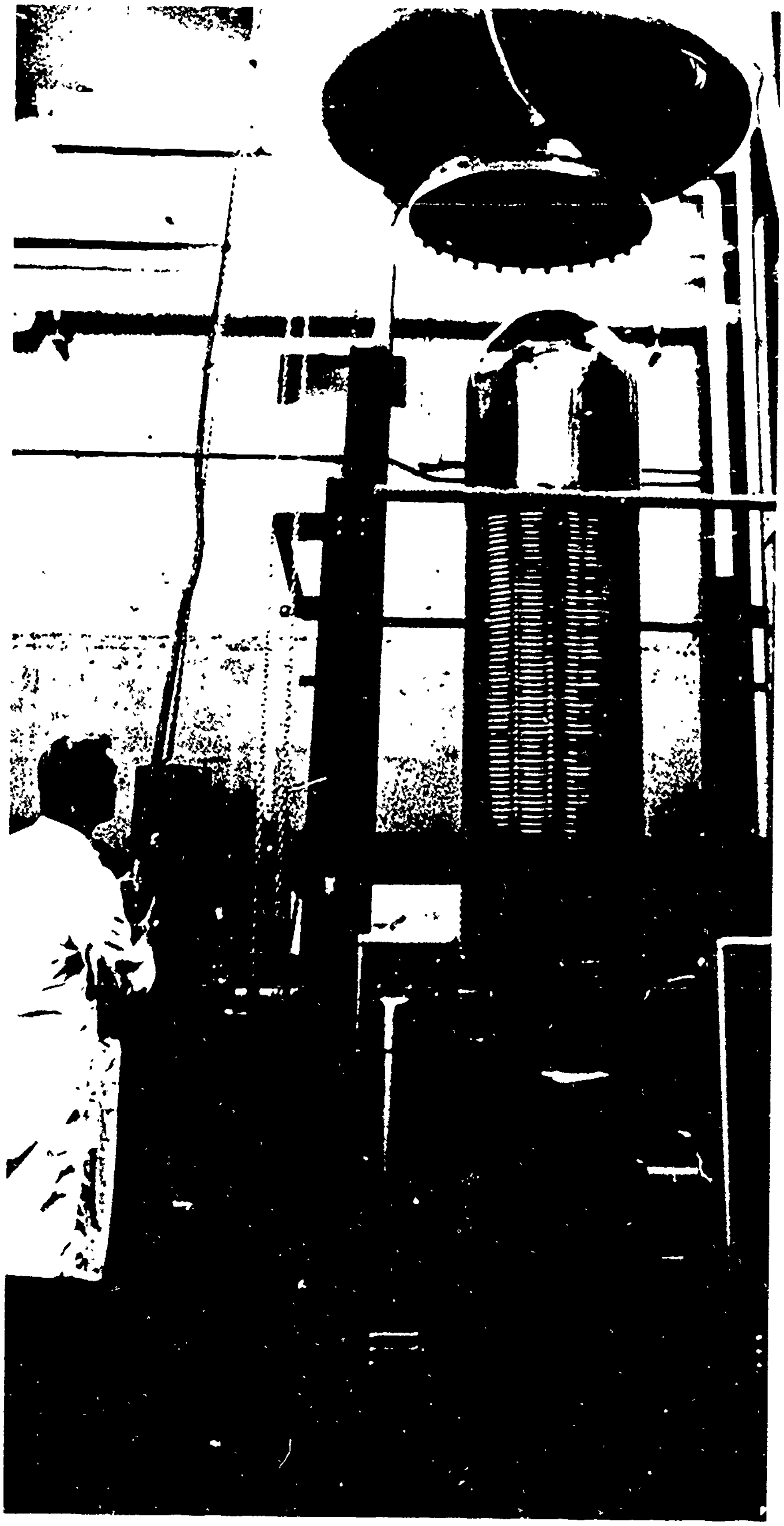
An English physicist, Sir Arthur Schuster, wrote that for some time after the discovery of x rays, his laboratory at Manchester was crowded with medical men bringing patients who were believed to have needles in various parts of their bodies.

X rays are commonly produced by directing a beam of high energy electrons onto a metal target. As the electrons are deflected and stopped, x rays of various energies are produced. The maximum energy a single x ray can have is the total kinetic energy of an incident electron. So the greater the voltage across which the electron beam is accelerated, the more energetic—and penetrating—are the x rays. One type of x ray tube is shown in the sketch below, where a stream of electrons is emitted from C and accelerated across a high voltage to a tungsten target T.

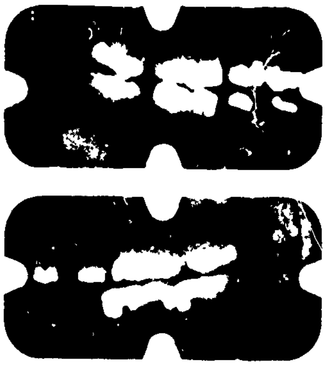


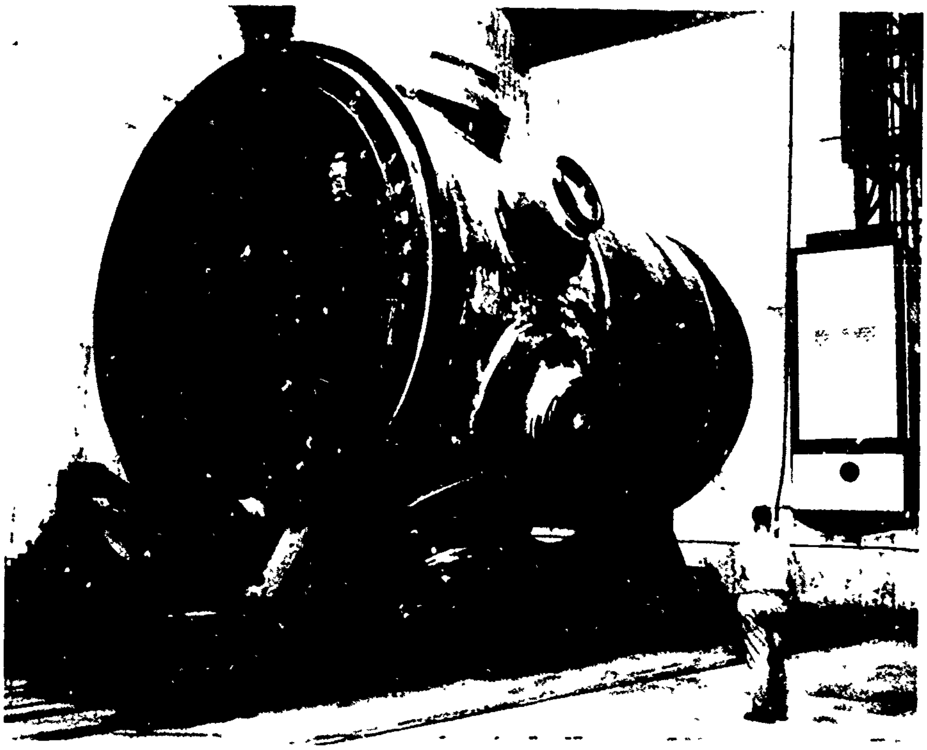
In the photograph at the right is a high voltage machine which is used to produce x rays for research. This van de Graaf type of generator (named after the American physicist who invented it), although not very different in principle from the electrostatic generators of the 1700's, can produce n electric potential difference of ,000,000 volts.

Such a high voltage is possible because of a container, seen in the photograph about to be lowered over the generator, which will be filled with a nonconducting gas under high pressure. (Ordinarily, the strong electric fields around the charged generator would ionize the air and charge would leak off.)



Above left is a rose, photographed with x rays produced by an accelerator-voltage of 30,000 volts. At left is the head of a dogfish shark; its blood vessels have been injected with a fluid that absorbs x rays. Below, x rays are being used to inspect the welds of a 400-ton tank for a nuclear reactor. At the right is the familiar use of x rays in dentistry and the resulting records. Because x rays are injurious to tissues, a great deal of caution is required in using them. For example, the shortest possible pulse is used, lead shielding is provided for the body, and the technician retreats behind a wall of lead and lead glass.





X rays were the first "ionizing" radiation discovered. What does "ionizing" mean?

What were three properties of x rays that led to the conclusion that x rays were electromagnetic waves?

Q12 What was the evidence that x rays had a very short wavelength?

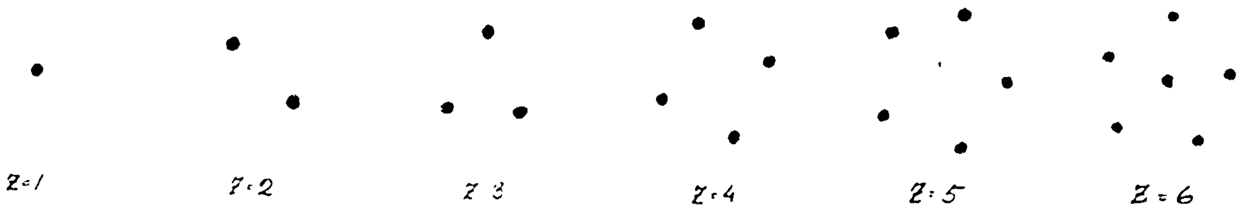
18.7 **Electrons, quanta and the atom.** By the beginning of the twentieth century enough chemical and physical information was available so that many physicists devised models of atoms. It was known that electrons could be obtained from many different substances and in different ways. But, in whatever way the electrons were obtained, they were always found to have the same properties. This suggested the notion that electrons are constituents of all atoms. But electrons are negatively charged, while samples of an element are ordinarily neutral and the atoms making up such samples are also presumably neutral. Hence the presence of electrons in an atom would require the presence also of an equal amount of positive charge.

The determination of the values of q/m for the electron and for charged hydrogen atoms (ions, in electrolysis experiments) indicated, as mentioned in Sec. 18.2, that hydrogen atoms are nearly two thousand times more massive than electrons. Experiments (which will be discussed in some detail in Chapter 22) showed that electrons constitute only a very small part of the atomic mass in atoms more massive than those of hydrogen. Consequently any model of an atom must take into account the following information: (a) an electrically neutral atom contains equal amounts of positive and negative charge; (b) the negative charge is associated with only a small part of the mass of the atom. Any atomic model should answer two questions: (1) how many electrons are there in an atom, and (2) how are the electrons and the positive charges arranged in an atom?

During the first ten years of the twentieth century several atomic models were proposed, but none was satisfactory. The early models were all based upon classical physics, that is, upon the physics of Newton and Maxwell. No one knew how to invent a model based upon the theory of Planck which incorporated the quantization of energy. There was also need for more experimental knowledge. Nevertheless this state of affairs didn't keep physicists from trying: even a partly wrong model might suggest experiments that might, in turn, provide clues to a better model. Until 1911 the most popular model was one proposed by J. J. Thomson in 1904.

Thomson suggested that an atom consisted of a sphere of positive electricity in which was distributed an equal amount of negative charge in the form of electrons. Under this assumption, the atom was like a pudding of positive electricity with the negative electricity scattered in it like raisins. The positive "fluid" was assumed to act on the negative charges, holding them in the atom by means of electric forces only. Thomson did not specify how the positive "fluid" was held together. The radius of the atom was taken to be of the order of 10^{-8} cm on the basis of information from the kinetic theory of gases and other considerations. With this model Thomson was able to calculate certain properties of atoms. For example, he could calculate whether it would be possible for a certain number of electrons to remain in equilibrium, that is, to stay inside the atom without flying apart. Thomson found that certain arrangements of electrons would be stable. Thus, Thomson's model was consistent with the existence of stable atoms. Thomson's theory also suggested that chemical properties might be associated with particular groupings of electrons. A systematic repetition of chemical properties might then occur among groups of elements. But it was not possible to deduce the structure of particular elements and no detailed comparison with the actual periodic table could be made.

See "The 'Thomson' Atom" in Project Physics Reader 5.



Some stable arrangements of electrons in Thomson atoms. The atomic number Z is interpreted as the number of electrons.

In Chapter 19 we shall discuss some additional experimental information that provided valuable clues to the structure of atoms. We shall also see how one of the greatest physicists of our time, Niels Bohr, was able to combine the experimental evidence with the concept of quanta into an exciting theory of atomic structure. Although Bohr's theory was eventually replaced, it provided the clues that led to the presently accepted theory of the atom—the quantum mechanical theory.

Q13 Why was most of the mass of an atom believed to be associated with positive electric charge?

18.1 In Thomson's experiment (Fig. 18.4) on the ratio of charge to mass of cathode ray particles, the following might have been typical values for B, V and d: with a magnetic field B alone the deflection of the beam indicated a radius of curvature of the beam within the field of 0.114 meters for B = 1.0×10^{-3} tesla. With the same magnetic field, the addition of an electric field in the same region (V = 200 volts, plate separation d = 0.01 meter) made the beam come straight through.

a) Find the speed of the cathode ray particles in the beam.

b) Find q/m for the cathode ray particles.

The MKSA unit of B is $\frac{N}{\text{amp-m}}$ and is now called the tesla (after the electrical engineer, Nikola Tesla). Measured in this unit the earth's magnetic field is about 0.00005 T and that of a good electromagnet about 1.0t.

18.2 Given the value for the charge on the electron, show that a current of one ampere is equivalent to the movement of 6.25×10^{18} electrons per second past a given point.

18.3 In the apparatus of Fig. 18.7, an electron is turned back before reaching plate A and eventually arrives at plate C from which it was ejected. It arrives with some kinetic energy. How does this final energy of the electron compare with the energy it had as it left the cathode?

18.4 It is found that at light frequencies below the critical frequency no photoelectrons are emitted. What happens to the light energy?

18.5 For most metals, the work function W is about 10^{-19} joules. To what frequency does this correspond? In what region of the spectrum is this frequency?

Planck's constant has the value $h = 6.6 \times 10^{-34}$ joule-sec.

18.6 What is the energy of a light photon which has a wavelength of 5×10^{-7} m? 5×10^{-8} m?

18.7 The minimum or threshold frequency for emission of photoelectrons for copper is 1.1×10^{15} cycles/sec. When ultraviolet light of frequency 1.5×10^{15} cycles/sec shines on a copper surface, what is the maximum energy of the photoelectrons emitted, in joules? In electron volts?

18.8 What is the lowest-frequency light that will cause the emission of photoelectrons from a surface for which the work function is 2.0 eV, that is, a surface such that at least 2.0 eV of energy are needed to eject an electron from it?

18.9 Monochromatic light of wavelength 5000 Å falls on a metal cathode to produce photoelectrons. The light intensity at the surface of the metal is 10^2 joules/m^2 per sec.

a) How many photons fall on 1 m^2 in one sec?

b) If the diameter of an atom is 1 Å, how many photons fall on one atom in one second on the average?

c) How often would one photon fall on one atom on the average?

d) How many photons fall on one atom in 10^{-10} sec on the average?

e) Suppose the cathode is a square 0.05 m on a side. How many electrons are released per second, assuming every photon releases a photoelectron? How big a current would this be in amperes?

18.10 Roughly how many photons of visible light are given off per second by a 1-watt flashlight? (Only about 5 per cent of the electric energy input to a tungsten-filament bulb is given off as visible light.)

Hint: first find the energy, in joules, of an average photon of visible light.

18.11 The highest frequency, f_{max}, of the x rays produced by an x-ray machine is given by the relation

$$hf_{max} = q_e V,$$

where h is Planck's constant and V is the potential difference at which the machine operates. If V is 50,000 volts, what is f_{max}?

18.12 The equation giving the maximum energy of the x rays in the preceding problem looks like one of the equations in Einstein's theory of the photoelectric effect. How would you account for this similarity?

18.13 What potential difference must be applied across an x-ray tube for it to emit x rays with a minimum wavelength of 10^{-11} m? What is the energy of these x rays in joules? In electron volts?

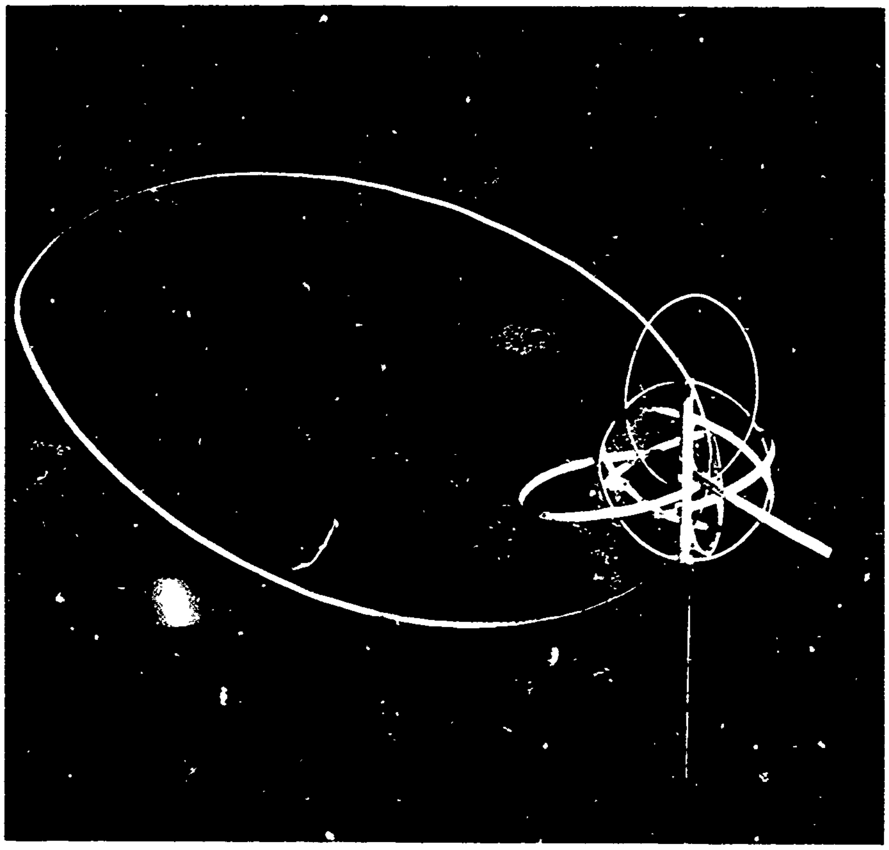
18.14 A glossary is a collection of terms limited to a special field of knowledge. Make a glossary of terms that appeared for the first time in this course in Chapter 18. Make an informative statement about each concept.

18.15 In his Opticks, Newton proposed a set of hypotheses about light which, taken together, constitute a fairly complete model of light. The hypotheses were stated as questions. Three of the hypotheses are given below:

> Are not all hypotheses erroneous, in which light is supposed to consist in pression or motion waves ...? [Quest. 28]
>
> Are not the rays of light very small bodies emitted from shining substances? [Quest. 29]
>
> Are not gross bodies and light convertible into one another, and may not bodies receive much of their activity from the particles of light which enter their composition? [Quest. 30]

a) Was Einstein's interpretation of the photoelectric effect anticipated by Newton? How are the models similar? How different?
b) Why would Newton's model be insufficient to explain the photoelectric effect? What predictions can we make with Einstein's model that we can't with Newton's?

Chapter 19 The Rutherford-Bohr Model of the Atom



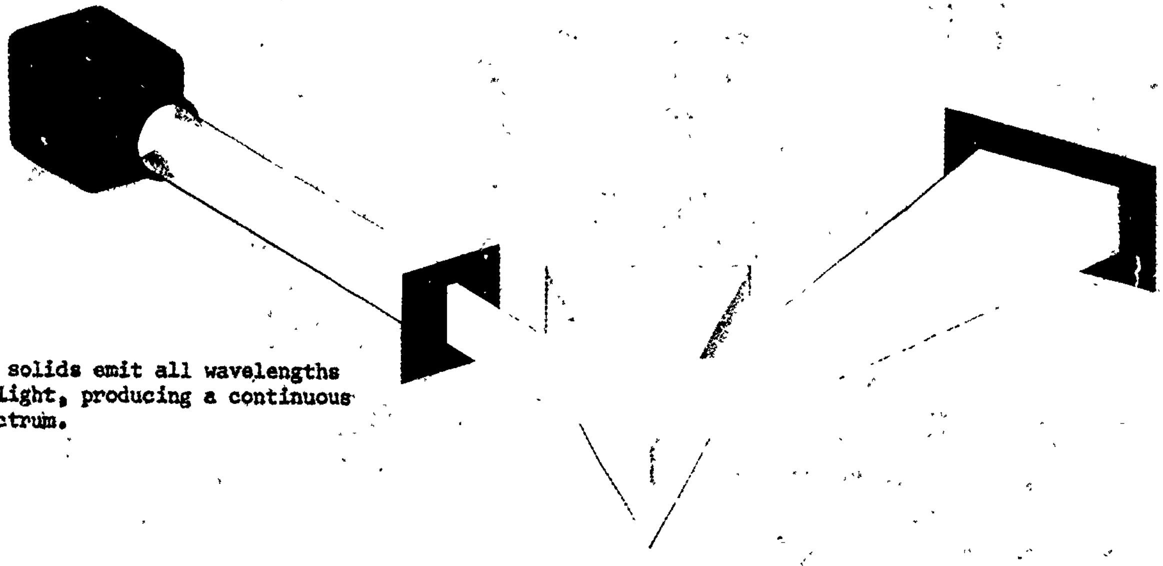
Sculpture representing the Bohr model of a sodium atom.

19.1 Spectra of gases. One of the first real clues to our understanding of atomic structure was provided by the study of the emission and absorption of light by samples of the elements. This study, carried on for many years, resulted in a clear statement of certain basic questions that had to be answered by any theory of atomic structure, that is, by any atomic model. The results of this study are so important to our story that we shall review the history of their development in some detail.

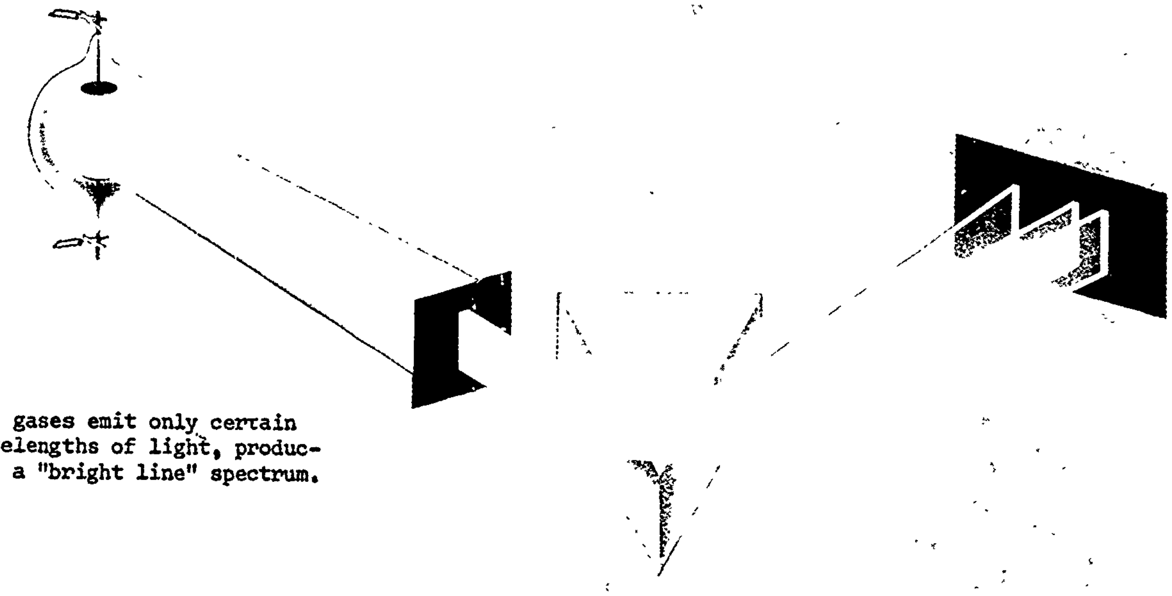
It had long been known that light is emitted by gases or vapors when they are excited in any one of several ways: by heating the gas to a high temperature, as when some volatile substance is put into a flame; by an electric discharge, as when the gas is between the terminals of an electric arc or spark; by a continuous electric current in a gas at low pressure, as in the familiar "neon sign."

The pioneer experiments on light emitted by various excited gases were made in 1752 by the Scottish physicist Thomas Melvill. He put one substance after another in a flame; and "having placed a pasteboard with a circular hole in it between my eye and the flame..., I examined the constitution of these different lights with a prism." Melvill found the spectrum of light from a hot gas to be different from the continuum of rainbow colors in the spectrum of a glowing solid or liquid. Melvill's spectrum consisted, not of an unbroken stretch of color continuously graded from violet to red, but of individual circular spots, each having the color of that part of the spectrum in which it was located, and with dark gaps (missing colors) between the spots. Later, when more general use was made of a narrow slit through which to pass the light, the spectrum of a gas was seen as a set of lines (Fig. 19.1); the lines are colored images of the slit. Thus the spectrum of light from a gas came to be called a line emission spectrum. From our general theory of light and of the separation of light into its component colors by a prism, we may infer that light from a gas is a mixture of only a few definite colors or narrow wavelength regions of light.

Melvill also noted that the colors and locations of the bright spots were different when different substances were put in the flame. For example, with ordinary table salt in the flame, the predominant color was "bright yellow" (now known to be characteristic of the element sodium). In fact, the line emission spectrum is markedly different for each chemically different gas. Each chemical element has its own characteristic set of wavelengths (Fig. 19.1). In



Hot solids emit all wavelengths of light, producing a continuous spectrum.



Hot gases emit only certain wavelengths of light, producing a "bright line" spectrum.

Cool gases absorb only certain wavelengths of light, producing a "dark line" spectrum.

looking at a gaseous source without the aid of a prism or a grating, the eye synthesizes the separate colors and perceives the mixture as reddish for glowing neon, pale blue for nitrogen, yellow for sodium vapor, and so on.

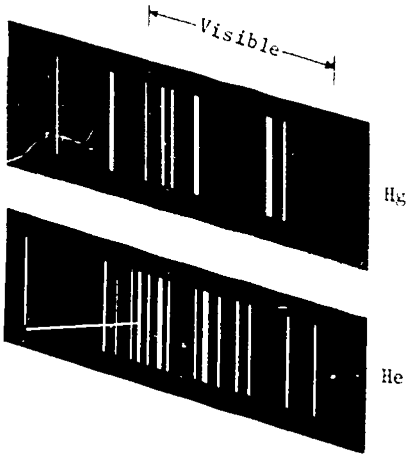


Fig. 19.1 Parts of the line emission spectra of mercury (Hg) and helium (He), redrawn from photographic records.

Some gases have relatively simple spectra. Thus sodium vapor shows two bright yellow lines in the visible part of the spectrum. Modern measurements give 5889.953 Å and 5895.923 Å for their wavelengths. Only a good spectrometer can separate them clearly, and we usually speak of them as a sodium "doublet" at about 5890 Å. Some gases or vapors, on the other hand, have exceedingly complex spectra. Iron vapor, for example, has some 6000 bright lines in the visible range alone.

In 1823 the British astronomer John Herschel suggested that each gas could be identified from its unique line spectrum. Here was the beginning of what is known as <u>spectrum analysis</u>. By the early 1860's the physicist Gustav R. Kirchhoff and the chemist Robert W. Bunsen, in Germany, had jointly discovered two new elements (rubidium and cesium) by noting previously unreported emission lines in the spectrum of the vapor of a mineral water. This was the first of a series of such discoveries: it started the development of a technique making possible the speedy chemical analysis of small samples by spectroscopy.

In 1802 the English scientist William Wollaston saw in the spectrum of sunlight something that had been overlooked before. Wollaston noticed a set of seven sharp, irregularly spaced <u>dark</u> lines across the continuous solar spectrum. He did not understand why they were there, and did not carry the investigation further. A dozen years later, Fraunhofer, the inventor of the grating spectrometer, used better instruments and detected many hundred such dark lines. To the most prominent dark lines, Fraunhofer assigned the letters A, B, C...

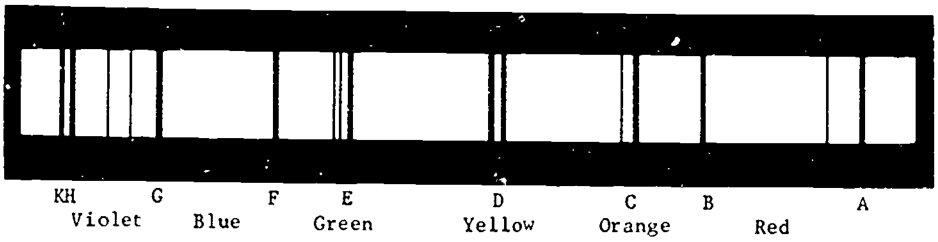


Fig. 19.2 The Fraunhofer dark lines in the visible part of the solar spectrum; only a few of the most prominent lines are represented.

In the spectra of several other bright stars, he found similar dark lines, many of them, although not all, being in the same positions as those in the solar spectrum.

19 1

The key observations toward a better understanding of both the dark-line and the bright-line spectra of gases were made by Kirchhoff in 1859. By that time it was known that the two prominent yellow lines in the emission spectrum of heated sodium vapor had the same wavelengths as two prominent dark lines in the solar spectrum to which Fraunhofer had assigned the letter D. It was also known that the light emitted by a glowing solid forms a perfectly continuous spectrum that shows no dark lines. Kirchhoff now demonstrated that if the light from a glowing solid, as on page 66, is allowed first to pass through sodium vapor having a temperature lower than that of the solid emitter and is then dispersed by a prism, the spectrum exhibits two prominent dark lines at the same place in the spectrum as the D-lines of the sun's spectrum. When this experiment was repeated with other gases placed between the glowing solid and the prism, each was found to produce its own characteristic set of dark lines. Evidently each gas in some way absorbs light of certain wavelengths from the passing "white" light; hence such a pattern of dark lines is called a line absorption spectrum, to differentiate it from the bright-line emission spectrum which the same gas would send out at a higher temperature. Most interesting of all, Kirchhoff showed that the wavelength corresponding to each absorption line is equal to the wavelength of a bright line in the emission spectrum of the same gas. The conclusion is that a gas can absorb only light of those wavelengths which, when excited, it can emit (Fig. 19.4). But not every emission line is represented in the absorption spectrum.

SG 19.1

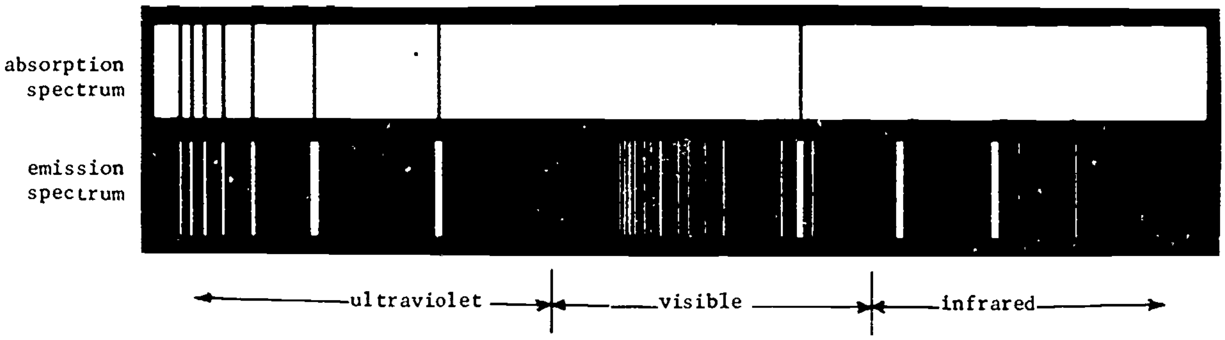


Fig. 19.4 Comparison of the line absorption and emission spectra of sodium vapor.

Q1 What can you infer about light which gives a bright line spectrum?

Q2 How can such light be produced?

Q3 What can you infer about light which gives a dark line spectrum?

Q4 How can such light be produced?

19.2 Regularities in the hydrogen spectrum. The spectrum of hydrogen is especially interesting for historical and theoretical reasons. In the visible and near ultraviolet regions, the emission spectrum consists of a series of lines whose positions are indicated in Fig. 19.5. In 1885, a Swiss school teacher, Johann Jakob Balmer, found a simple formula —an empirical relation—which gave the wavelengths of the lines known at the time. The formula is:

$$\lambda = b\left[\frac{n^2}{n^2 - 2^2}\right].$$

Johann Jakob Balmer (1825-1898), a teacher at a girls' school in Switzerland, came to study wavelengths of spectra listed in tables through his interest in mathematical puzzles and numerology.

Here b is a constant which Balmer determined empirically and found to be equal to 3645.6 Å, and n is a whole number, different for each line. Specifically, n must be 3 for the first (red) line of the hydrogen emission spectrum (named H_α); n = 4 for the second (green) line (H_β); n = 5 for the third (blue) line (H_γ); and n = 6 for the fourth (violet) line (H_δ). Table 19.1 shows the excellent agreement (within 0.02 %) between the values Balmer computed from his empirical formula and previously measured values.

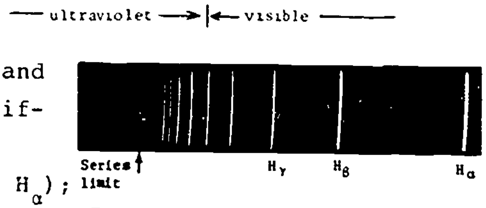


Fig. 19.5 The Balmer lines of hydrogen; redrawn from a photograph made with a film sensitive to ultraviolet light as well as to visible light.

In his paper of 1885, Balmer also speculated on the possibility that there might be additional series of hitherto unsuspected lines in the hydrogen spectrum, and that their wavelengths could be found by replacing the 2^2 in the denominator of his equation by other numbers such as 1^2, 3^2, 4^2, and so on. This suggestion, which stimulated many workers to search for such additional spectral series, also turned out to be fruitful. The formula was found to need still another modification (which we shall discuss shortly) before it would correctly describe the new series.

To use modern notation, we first rewrite Balmer's formula in a more suggestive form:

$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right].$$

Table 19.1 Data on hydrogen spectrum (as given in Balmer's paper).

		Wavelength λ (Å)		
Name of Line	n	From Balmer's formula	By Ångstrom's measurement	Difference
H_α	3	6562.08	6562.10	+0.02
H_β	4	4860.8	4860.74	-0.06
H_γ	5	4340	4340.1	+0.1
H_δ	6	4101.3	4101.2	-0.1

In this equation, which can be derived from the first one, R_H is a constant, equal to 4/b. It is called the Rydberg constant for hydrogen in honor of the Swedish spectroscopist J. R. Rydberg who, following Balmer, made great progress in the search for various spectral series. The lines described by Balmer's formula are said to form a series, called the Balmer series.

If we can now follow Balmer's speculative suggestion of replacing 2^2 by other numbers, we obtain the possibilities:

$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n^2}\right]; \qquad \frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n^2}\right]; \qquad \frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n^2}\right],$$

and so on. All these possible series of lines can be summarized in one formula:

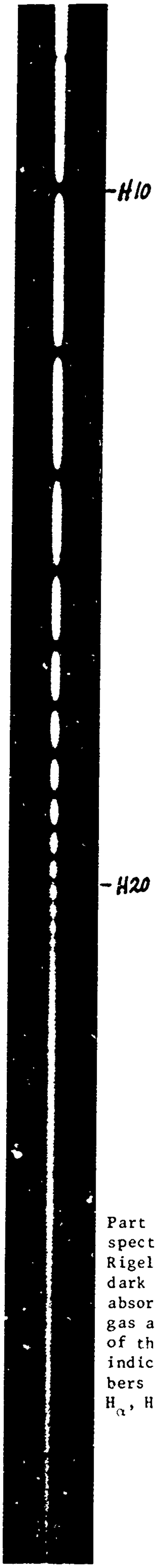
$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right],$$

where n_f is an integer that is fixed for any one series for which wavelengths are to be found (for example, it is 2 for the Balmer series). The letter n_i denotes integers that take on the values $n_f + 1$, $n_f + 2$, $n_f + 3$,... for the successive individual lines in a given series (thus, for the first two lines of the Balmer series, n_i is 3 and 4, respectively). The Rydberg constant R_H should have the same value for all of these hydrogen series.

So far, our discussion has been merely speculation. No series, no single line fitting the formula in the general formula, need exist (except for the Balmer series, where $n_f = 2$). But when we look for these hypothetical lines—we find that they do exist.

In 1908, F. Paschen in Germany found two hydrogen lines in the infrared whose wavelengths were correctly given by setting $n_f = 3$ and $n_i = 4$ and 5 in the general formula, and many other lines in this Paschen series have since been identified. With improvements of experimental apparatus and techniques, new regions of the spectrum could be explored, and then to the Balmer and Paschen series others gradually were added. In Table 19.2 the name of each series is that of its discoverer.

Balmer had also expressed the hope that his formula might indicate a pattern for finding series relationships in the spectra of other gases. This suggestion bore fruit even sooner than the one concerning additional series for hydrogen. Rydberg and others now made good headway in finding



Part of the ultraviolet spectrum of the star Rigel (β Orion). The dark bands are due to absorption by hydrogen gas and match the lines of the Balmer series as indicated by the H numbers (where H_1 would be H_α, H_2 would be H_β etc.).

series formulas for various gases. While Balmer's formula did not serve directly in the description of spectra of gases other than hydrogen, it inspired formulas of similar mathematical form that were useful in expressing order in portions of a good many complex spectra. The Rydberg constant R_H also reappeared in such empirical formulas.

Table 19.2 Series of lines in the hydrogen spectrum.

Name of series	Date of Discovery	Values in Eq. (19.3)	Region of spectrum
Lyman	1906-1914	$n_f = 1,\ n_i = 2, 3, 4, \ldots$	ultraviolet
Balmer	1885	$n_f = 2,\ n_i = 3, 4, 5, \ldots$	ultraviolet-visible
Paschen	1908	$n_f = 3,\ n_i = 4, 5, 6, \ldots$	infrared
Brackett	1922	$n_f = 4,\ n_i = 5, 6, 7, \ldots$	infrared
Pfund	1924	$n_f = 5,\ n_i = 6, 7, 8, \ldots$	infrared

SG 19 2
SG 19 3
SG 19 4

Physicists tried to account for spectra in terms of atomic models. But the great number and variety of spectral lines, even from the simplest atom, hydrogen, made it difficult to do so. Nevertheless, physicists did eventually succeed in understanding the origin of spectra. In this chapter and the next one, we shall get some idea of how this was done.

Q5 What evidence did Balmer have that there were other series of lines in the hydrogen spectrum with terms 3^2, 4^2, etc.?

Q6 Often discoveries result from careful theories (like Newton's) or a good intuitive grasp of phenomena (like Faraday's). What led Balmer to his relation for spectra?

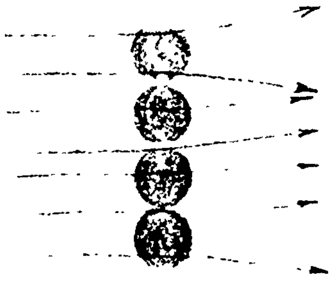
19.3 Rutherford's nuclear model of the atom.

A new basis for atomic models was provided during the period 1909 to 1911 by Ernest Rutherford (1871-1937), a New Zealander who had already shown a rare ability as an experimentalist at McGill University, Montreal, Canada. He had been invited in 1907 to Manchester University in England, where he headed a productive research laboratory. Rutherford was specially interested in the rays emitted by radioactive substances, in particular in α (alpha) rays. As we shall see in Chapter 20, α rays consist of positively charged particles. These particles are positively charged helium atoms with masses about 7500 times larger than the electron mass. Some radioactive substances emit α particles at a great enough rate and with enough energy so that the particles can be used as

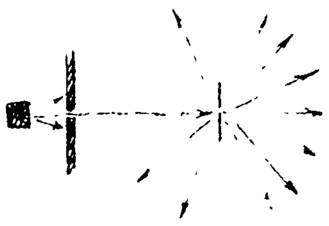
SG 19 5

projectiles to bombard samples of elements. The experiments that Rutherford and his colleagues did with α particles are an example of a highly important kind of experiment in atomic and nuclear physics—the scattering experiment.

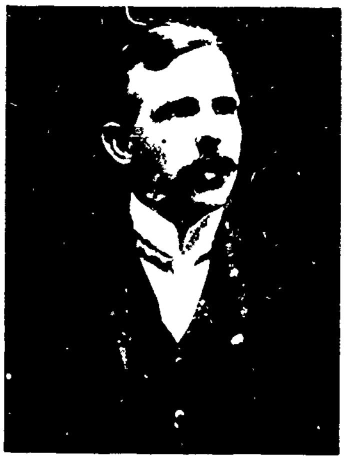
In a scattering experiment, a narrow, parallel beam of projectiles or bullets (α particles, electrons, x rays) is aimed at a target that is usually a very thin foil or film of some material. As the beam strikes the target, some of the projectiles are deflected, or scattered, from their original direction. The scattering is the result of the interaction between the particles or rays in the beam and the atoms of the material. A careful study of the projectiles after they have been scattered can yield information about the projectiles, the atoms, or both—or the interaction between them. Thus if we know the mass, energy and direction of the projectiles, and see what happens to them in a scattering experiment, we can deduce properties of the atoms that scattered the projectiles.



Rutherford noticed that when a beam of α particles passed through a thin metal foil, the beam spread out. He thought that some of the particles were scattered out of the beam by colliding with atoms in the foil. The scattering of α particles can be described in terms of the electrostatic forces between the positively charged α particles and the charges that make up atoms. Since atoms contain both positive and negative charges, an α particle is subjected to both repulsive and attractive forces as it passes through matter. The magnitude and direction of these forces depend on how near the particle happens to approach to the centers of the atoms past which it moves. When a particular atomic model is postulated, the extent of the scattering can be calculated quantitatively and compared with experiment. In the case of the Thomson atom, calculation showed that the probability that an α particle would be scattered through an angle of more than a few degrees is negligibly small.



One of Rutherford's assistants, H. Geiger, found that the number of particles scattered through large angles, 10° or more, was much greater than the number predicted on the basis of the Thomson model. In fact, one out of about every 8000 α particles was scattered through an angle greater than 90°. This result meant that a significant number of α particles bounced back from the foil. This result was unexpected. Some years later, Rutherford wrote:



Ernest Rutherford was born, grew up, and received most of his education in New Zealand. At age 24 he went to Cambridge, England to work at the Cavendish Laboratory under J.J. Thomson. From there he went to McGill University in Canada, then home to be married and back to England again, now to Manchester University. At these universities, and later at the Cavendish Laboratory where he succeeded J.J. Thomson as director, Rutherford performed important experiments on radioactivity, the nuclear nature of the atom, and the structure of the nucleus. Rutherford introduced the names "alpha," "beta" and "gamma" rays, "protons," and "half-life." For his scientific work, Rutherford was knighted and received a Nobel Prize.

In the photograph above, Rutherford holds the apparatus in which he arranged for α particles to bombard nitrogen nuclei—not to study scattering, but to detect actual disintegration of the nitrogen nuclei! (See Sect. 23.3 in Unit 6 Text.)

19 3

> ...I had observed the scattering of α-particles, and Dr. Geiger in my laboratory had examined it in detail. He found, in thin pieces of heavy metal, that the scattering was usually small, of the order of one degree. One day Geiger came to me and said, "Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?" Now I had thought that, too, so I said, "Why not let him see if any α-particles can be scattered through a large angle?" I may tell you in confidence that I did not believe that they would be, since we knew that the α-particle was a very fast, massive particle, with a great deal of [kinetic] energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings, the chance of an α-particle's being scattered backward was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, 'We have been able to get some of the α-particles coming backward...." It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backward must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive centre, carrying a charge.

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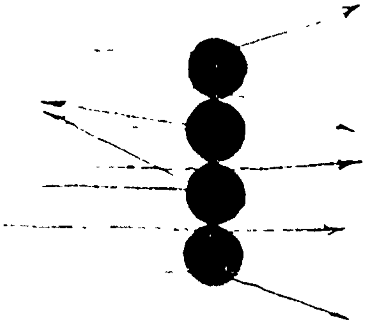


These experiments and Rutherford's idea marked the origin of the modern concept of the nuclear atom. Let us look at the experiments more closely to see why Rutherford concluded that the atom must have its mass and positive charge concentrated at the center, thus forming a nucleus about which the electrons are clustered.

A possible explanation of the observed scattering is that there exist in the foil concentrations of mass and charge—positively charged nuclei—much more dense than Thomson's atoms. An α particle heading directly toward one of them is stopped and turned back, as a ball would bounce back from a rock but not from a cloud of dust particles. Figure 19.6 is based on one of Rutherford's diagrams in his paper of 1911, which may be said to have laid the foundation for the modern theory of atomic structure. It shows two α particles A and A'. The α particle A is heading directly toward a nucleus N. Because of the electrical repulsive force between the two, A is slowed to a stop at some distance r from N, and then moves directly back. A' is another α particle that is not headed directly toward the nucleus N; it swerves away from N along a path which calculation showed must be an hyperbola. The deflection of A' from its original path is indicated by the angle φ.

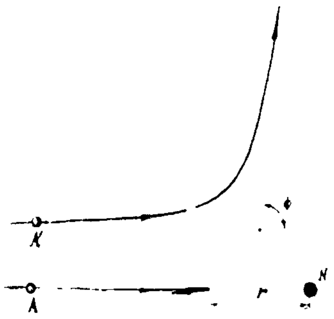


Fig. 19.6 Paths of two α particles A and A' approaching a nucleus N. (Based on Rutherford, Philosophical Magazine, vol. 21 (1911), p. 669.)

19.3

Rutherford considered the effects of important factors on the α particles—their initial speed v_α, the foil thickness t, and the quantity of charge Q on each nucleus. According to the theory most of the α particles should be scattered through small angles, but a significant number should be scattered through large angles.

Geiger and Marsden undertook tests of these predictions with the apparatus shown schematically in Fig. 19.8. The lead box B contains a radioactive substance (radon) which emits α particles. The particles emerging from the small hole in the box are deflected through various angles φ in passing through the thin metal foil F. The number of particles deflected through each angle φ is found by letting the particles strike a small zinc sulfide screen S. Each α particle that strikes the screen produces a scintillation (a momentary pinpoint of fluorescence). These scintillations can be observed and counted by looking through the microscope M; S and M can be moved together along the arc of a circle up to φ = 150°. In later experiments, the number of α particles at any angle φ was counted more conveniently by replacing S and M by a counter (Fig. 19.9) invented by Geiger. The Geiger counter, in its more recent versions, is now a standard laboratory item.

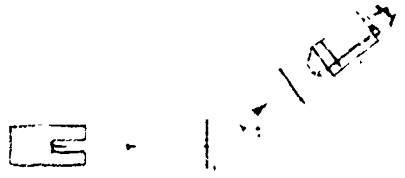


Fig. 19.8 Scintillation method for verifying Rutherford's theoretical predictions for α particle scattering. The whole apparatus is placed in an evacuated chamber so that the α particles will not be slowed down by collisions with air molecules.

Geiger and Marsden found that the number of α particles counted depended on the scattering angle, the speed of the particles, and on the thickness of the foil of scattering material in just the ways that Rutherford had predicted.

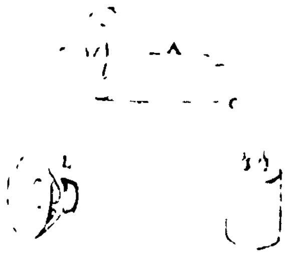


Fig. 19.9 A Geiger counter (1928). It consists of a metal cylinder C containing a gas and a thin axial wire A that is insulated from the cylinder. A potential difference slightly less than that needed to produce a discharge through the gas is maintained between the wire (anode A) and cylinder (cathode C). When an α particle enters through the thin mica window W, it frees a few electrons from the gas molecules, leaving the latter positively charged. The electrons are accelerated toward the anode, freeing more electrons along the way by collisions with gas molecules. The avalanche of electrons constitutes a sudden surge of current which may be amplified to produce a click in the loudspeaker (L).

Why should α particles be scattered by atoms?

What was the basic difference between the Rutherford and the Thomson models of the atom?

19.4 Nuclear charge and size. At the time Rutherford made his predictions about the effect of the speed of the α particle and the thickness of foil on the angle of scattering, there was no way independently to measure the charge Q on each nucleus. However, some of Rutherford's predictions were confirmed by scattering experiments and, as often happens when part of a theory is confirmed, it is reasonable to proceed temporarily as if the whole of that theory were justified. Thus it was assumed that the scattering of α particles through a given angle is proportional to the square of the nuclear charge. With this relation in mind, Q could be estimated. Experimental data were obtained for the scattering of different elements. Among them were carbon, aluminum and gold. Therefore, on the basis of this assumption the following nuclear charges were obtained: for carbon $6q_e$ for aluminum 13 or $15q_e$ and for gold 78 or $79q_e$. Similar tentative values were found for other elements.

The magnitude of the positive charge of the nucleus was an important piece of information about the atom. If the nucleus has a positive charge of $6\ q_e$, 13 or $14\ q_e$, etc., the number of electrons surrounding the nucleus must be 6 for carbon, 13 or 14 for aluminum, etc., since the atom as a whole is electrically neutral. It was soon noticed that the values found for the nuclear charge were close to the atomic number Z, the place number of the element in the periodic table. The data seemed to indicate that each nucleus has a positive charge Q numerically equal to Zq_e. But the results of experiments on the scattering of α particles were not precise enough to permit this conclusion to be made with certainty.

The suggestion that the number of positive charges on the nucleus and also the number of electrons around the nucleus are equal to the atomic number Z made the picture of the nuclear atom clearer. The hydrogen atom ($Z = 1$) has, in its neutral state, one electron outside the nucleus; a helium atom ($Z = 2$) has in its neutral state two electrons outside the nucleus; a uranium atom ($Z = 92$) has 92 electrons. This simple scheme was made more plausible when additional experiments showed that it was possible to produce singly ionized hydrogen atoms, H^+, and doubly ionized helium atoms, He^{++}, but not H^{++} or He^{+++}, evidently because a hydrogen atom has only one electron to lose, and a helium atom only two. The concept of the nuclear atom provided new insight into the periodic table of the elements: it suggested that the periodic table is really a listing of the elements according to the number of electrons around the nucleus or according to the number of positive units of charge in the nucleus.

Additional evidence for this suggestion was provided by research with x rays during the years 1910 to 1913. It was found that the elements have characteristic x-ray spectra as well as optical spectra. The x-ray spectra show separate lines against a continuous background. A young English physicist, H. G. J. Moseley (1887-1915), found that the frequencies of certain lines in the x-ray spectra of the elements vary in a strikingly simple way with the nuclear charge Z. The combination of the experimental results with the Bohr theory of atomic structure made it possible to assign an accurate value to the nuclear charge of an element. As a result, Moseley established with complete certainty that the place number of an element in the periodic table is the same as the value of the positive charge of the nucleus (in multiples of the unit electric charge) and the same as the number of electrons outside the nucleus. These results made it possible to remove some of the discrepancies in Mendeleev's periodic table and to relate the table in a definite way to the Bohr theory.

H.G.J. Moseley (1887-1915) was a co-worker with Rutherford at Manchester. Bohr characterized him as a man of extraordinary energy and gifts for purposeful experimentation. J.J. Thomson said he made one of the most brilliant discoveries ever made by so young a man. At the start of World War I he volunteered for army service, was sent to the Dardanelles and was killed during the unsuccessful attack at Gallipoli. Rutherford wrote that "it is a national tragedy that our military organization at the start was so inelastic as to be unable, with few exceptions, to utilize the offers of services for scientific men except as combatants on the firing line." In his will Moseley left all his apparatus and private wealth to the Royal Society to promote scientific research.

As an important result of these scattering experiments the size of the nucleus may be estimated. Suppose an α particle is moving directly toward a nucleus (A, Fig. 19.6). Its kinetic energy on approach is transformed into electrical potential energy. It slows down and eventually stops. The distance of closest approach may be computed from the original kinetic energy of the α particle and the charges of α particle and nucleus. It turns out to be approximately 3×10^{-14}m. If the α particle is not to penetrate the nucleus, this distance must be at least as great as the sum of the radii of α particle and nucleus; then the radius of the nucleus could not be larger than about 10^{-14}m, only about 1/1000 of the radius of an atom. Thus if we consider volumes, which are proportional to cubes of radii, it is clear that the atom is mostly empty space. This must be so to explain the ease with which α particles or electrons penetrate thousands of layers of atoms in metal foils or in gases.

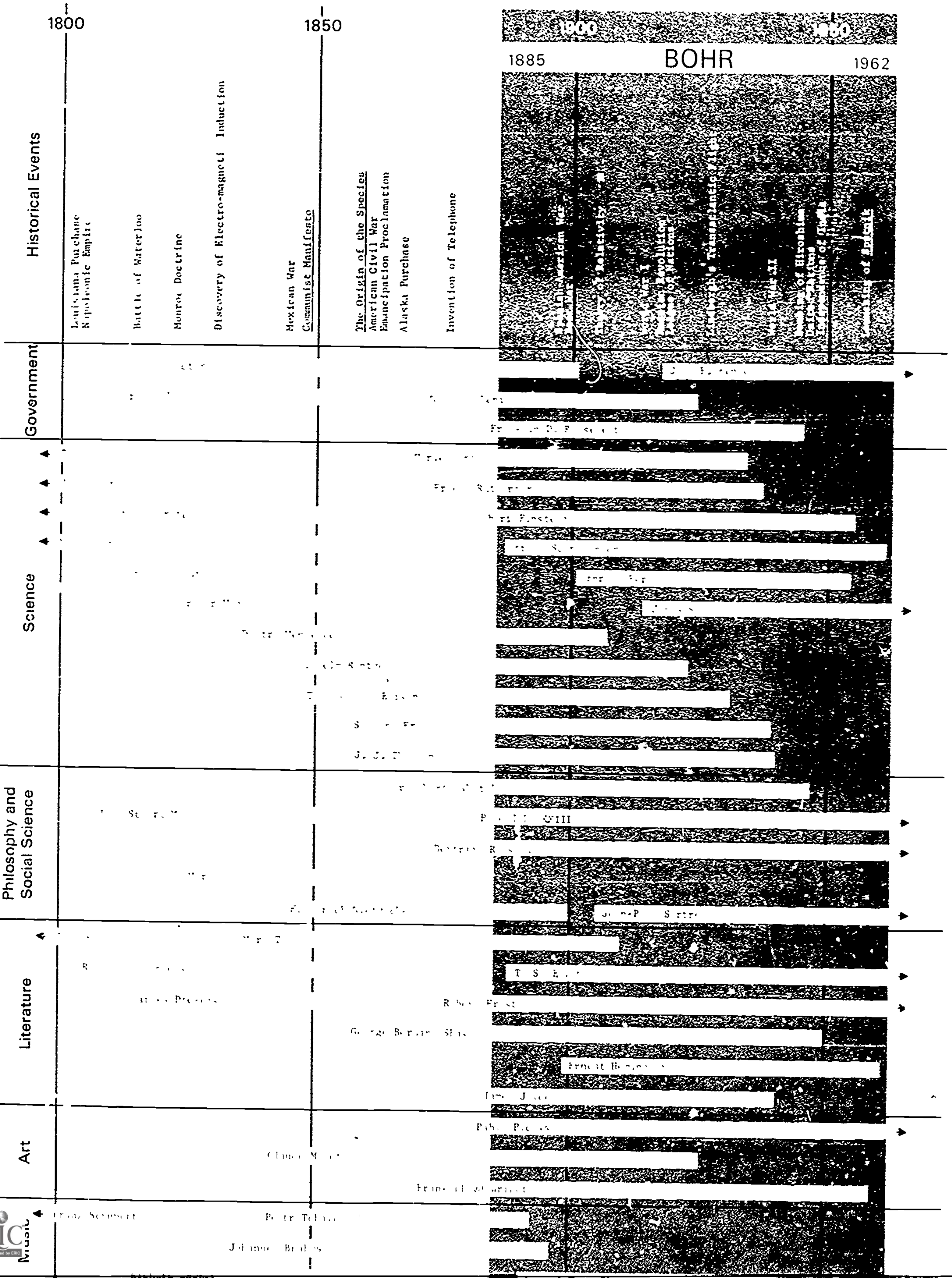
The dot drawn in the middle to represent the nucleus is about 100 times too large. Popular diagrams of atoms often greatly exaggerate the size of the nucleus, to suggest the greater mass.

SG 19 8

Successful as this model of the nuclear atom was in explaining scattering phenomena, it raised many new questions: What is the arrangement of electrons about the nucleus? What keeps the negative electron from falling into a positive nucleus by electrical attraction? How is the nucleus made up? What keeps it from exploding on account of the repulsion of its positive charges? Rutherford realized the problems raised by these questions and the failure of his model to answer them. Additional assumptions were needed to complete the model—to find answers to the additional questions posed about the details of atomic structure The remainder of this chapter will deal with the theory proposed by Niels Bohr, a young Danish physicist who joined Rutherford's group just as the nuclear model was being announced.

Q9 What is the "atomic number" of an element, according to the Rutherford model of the atom?

Q10 What is the greatest electric charge an ion of lithium (the next heaviest element after helium) could have?


1800
1850
1900
1950
1885
BOHR
1962
Historical Events
Louisiana Purchase
Napoleonic Empire
Battle of Waterloo
Monroe Doctrine
Discovery of Electro-magnetic Induction
Mexican War
Communist Manifesto
The Origin of the Species
American Civil War
Emancipation Proclamation
Alaska Purchase
Invention of Telephone
Spanish-American War
Theory of Relativity
World War I
Russian Revolution
League of Nations
Lindbergh's Transatlantic Flight
World War II
Bombing of Hiroshima
United Nations
Launching of Sputnik
Government
Franklin D. Roosevelt
Science
Albert Einstein
Philosophy and Social Science
Pius XII
Bertrand Russell
Jean-Paul Sartre
Literature
T. S. Eliot
Robert Frost
George Bernard Shaw
Ernest Hemingway
James Joyce
Art
Pablo Picasso
Claude Monet
Frank Lloyd Wright
Music
Franz Schubert
Peter Tchaikovsky
Johannes Brahms

19 5 *The Bohr theory: the postulates.* If an atom consists of a positively charged nucleus surrounded by a number of negatively charged electrons, what keeps the electrons from falling into the nucleus—from being pulled in by the Coulomb force of attraction? One possible answer to this question is that an atom may be like a planetary system with the electrons revolving in orbits about the nucleus. Instead of the gravitational force, the Coulomb attractive force between the nucleus and an electron would supply a centripetal force that would tend to keep the electron in an orbit. Although this idea seems to start us on the road to a theory of atomic structure, a serious problem arises concerning the stability of a planetary atom. According to Maxwell's theory of electromagnetism, a charged particle radiates energy when it is accelerated. Now, an electron moving in an orbit around a nucleus is constantly being accelerated by the centripetal force mv^2/r. The electron, therefore, should lose energy by emitting radiation. A detailed analysis of the motion of the electron (which we can't do here because of the mathematical difficulty) shows that the electron should be drawn closer to the nucleus. Within a very short time, the electron should actually be pulled into the nucleus. According to classical physics—mechanics and electromagnetics—a planetary atom would not be stable for more than a small fraction of a second.

The idea of a planetary atom was sufficiently attractive that physicists continued to look for a theory that would include a stable planetary structure and predict discrete line spectra for the elements. Bohr succeeded in constructing such a theory in 1913. This theory, although it had to be radically modified later, showed how to attack atomic problems by using quantum theory. In fact, Bohr showed that only by using quantum theory would the problem of atomic structure be attacked with any hope of success. Bohr used the quantum ideas of Planck and Einstein that electromagnetic energy is absorbed or emitted as discrete quanta; and that each quantum has a magnitude equal to Planck's constant h multiplied by the frequency of the radiation.

Bohr introduced two postulates designed to account for the existence of stable electron orbits and of the discrete emission spectra. These postulates may be stated as follows.

(1) An atomic system possesses a number of states in which no emission of radiation takes place, even if the particles (electrons and nucleus) are in motion relative to each other. These states are called *stationary states* of the atom.

(2) Any emission or absorption of radiation, either as visible light or other electromagnetic radiation, will correspond to a transition between two stationary states. The radiation emitted or absorbed in a transition has a frequency f determined by the relation

$$hf = E_i - E_f ,$$

where h is Planck's constant and E_i and E_f are the energies of the atom in the initial and final stationary states, respectively.

These postulates are a combination of some ideas taken over from classical physics together with others in direct contradiction to classical physics. For example, Bohr assumed that when an atom is in one of its stationary states, the motions of the electrons are in accord with the laws of mechanics. A stationary state may be characterized by its energy, or by the orbits of the electrons. Thus, in the simple case of the hydrogen atom, with a single electron revolving about the nucleus, a stationary state corresponds to the electron moving in a particular orbit and having a certain energy. Bohr avoided the difficulty of the electron emitting radiation while moving in its orbit by postulating that it does not emit radiation when it is in a particular orbit. This postulate implies that classical, Maxwellian electromagnetics does not apply to the motion of electrons in atoms. The emission of radiation was to be associated with a jump from a state with one energy (or orbit) to another state with a different energy (or orbit). Bohr did not attempt to explain why the atom should be stable in a given stationary state.

SG 19.9

The first postulate has in view the general stability of the atom, while the second has (chiefly) in view the existence of spectra with sharp lines. The use of quantum theory enters in the second postulate, and is expressed in the equation $hf = E_i - E_f$. Bohr also used the quantum concept in defining the stationary states of the atom. The states are highly important in atomic theory so we shall look at their definition carefully. For simplicity we consider the hydrogen atom, with a single electron revolving around the nucleus. The positive charge of the nucleus is given by Zq_e with $Z = 1$. We also assume, following Bohr, that the possible orbits of the electron are circles. The condition that the centripetal force is equal to the attractive Coulomb force is:

$$\frac{mv^2}{r} = k\,\frac{q_e^{\,2}}{r^2} .$$

In this formula, m is the mass of the electron; v is the speed; r is the radius of the circular orbit, that is, the distance of the electron from the nucleus; the nucleus is assumed to be stationary. The symbol k stands for a constant which depends on the units used; q_e is the magnitude of the electronic charge.

The values of r and v which satisfy the centripetal force equation characterize the possible electron orbits. We can write the equation in a slightly different form by multiplying both sides by r and dividing both sides by v; the result is:

$$mvr = k \frac{q_e^2}{v} .$$

The quantity on the left side of this equation, which is the product of the momentum of the electron and the radius of the orbit, can also be used to characterize the orbits. This quantity is often used in problems of circular motion, and it is called the *angular momentum*:

$$\text{angular momentum} = mvr.$$

According to classical mechanics, the radius of the orbit could have any value and the angular momentum could also have any value. But we have seen that under classical mechanics there would be no stable orbits in the hydrogen atom. Since Bohr's first postulate implies that only certain orbits are permitted, Bohr needed a rule for *which* orbits were possible. The criterion he chose was that only those orbits are permitted for which the angular momenta have certain discrete values. These values are defined by the relation:

$$mvr = n \frac{h}{2\pi} ,$$

where h is Planck's constant, and n is a positive integer; that is, n = 1, 2, 3, 4, ... When the possible values of the angular momentum are restricted in this way, the angular momentum is said to be *quantized*. The integer n which appears in the formula, is called the *quantum number*. For each value of n there is a stationary state.

With his two postulates and his choice of the permitted stationary states, Bohr was able to calculate additional properties of the stationary states: the radius of each permitted orbit, the speed of the electron in the orbits, and the total energy of the electron in the orbit; this energy is the energy of the stationary state.

The results that Bohr obtained may be summarized in three

[illegible]

[illegible] Zeeman [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

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[illegible]

[illegible]

[illegible]

[illegible] L. Bragg (Gr Brit)—analysis [illegible] crystal structure by X-rays

[illegible] No award

[illegible] Charles Glover Barkla (Gr Brit)—discovery [illegible] X-ray [illegible] the elements

[illegible] Max Planck (Ger)—discovery of energy [illegible]

[illegible] Johannes Stark (Ger)—discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields.

[illegible] Charles Edouard Guillaume (Switz)—discovery of anomalies in nickel steel alloys

[illegible] Albert Einstein (Ger)—for services to theoretical physics and especially for his discovery of the law of the photoelectric effect.

[illegible] Niels Bohr (Den)—atomic structure and radiation

[illegible] Robert Andrews Millikan (US)—elementary charge of electricity and photoelectric effect.

[illegible] Karl Manne Siegbahn (Swed)—X-ray spectroscopy

[illegible] James Franck and Gustav Hertz (Ger)—laws governing the impact of an electron upon an atom.

[illegible] Jean Baptiste Perrin (Fr)—discontinuous structure of matter and especially for his discovery of sedimentation equilibrium

[illegible] Arthur Compton (US)—discovery of effect named after him. C. T. R. Wilson (Gr Brit)—method of making paths of electrically charged particles visible by condensation of vapor.

[illegible] Owen Willans Richardson (Gr Brit)—thermionic phenomena and discovery of effect named after him.

[illegible] Louis Victor de Broglie (Fr)—discovery of wave nature of electrons

[illegible] Sir Chandrasekhara V. Raman (Ind)—scattering of light and effect named after him

[illegible] No award

[illegible] Werner Heisenberg (Ger)—quantum mechanics leading to discovery of allotropic forms of hydrogen

[illegible] Erwin Schrödinger (Ger) and P. A. M. Dirac (Gr Brit)—new productive forms of atomic theory

[illegible] No award

[illegible] James Chadwick (Gr Brit)—discovery of the neutron

[illegible] Victor Franz Hess (Aus)—cosmic radiation. Carl David Anderson (US)—discovery of the positron

Nobel Prize winners in Physics.

19 5

simple formulas. The radius of an orbit with quantum number n is given by the expression:

$$r_n = n^2 r_1,$$

where r_1 is the radius of the first orbit (the orbit for $n = 1$), and has the value 5.29×10^{-9} cm or 5.29×10^{-11} m.

The speed of the electron in the orbit with quantum number n is:

$$v_n = \frac{1}{n} v_1,$$

where v_1 is the speed of the electron in the first orbit, and has the value 2.2×10^8 cm/sec or 2.2×10^6 m/sec.

The energy of the electron in the orbit with quantum number n is:

$$E_n = \frac{1}{n^2} E_1,$$

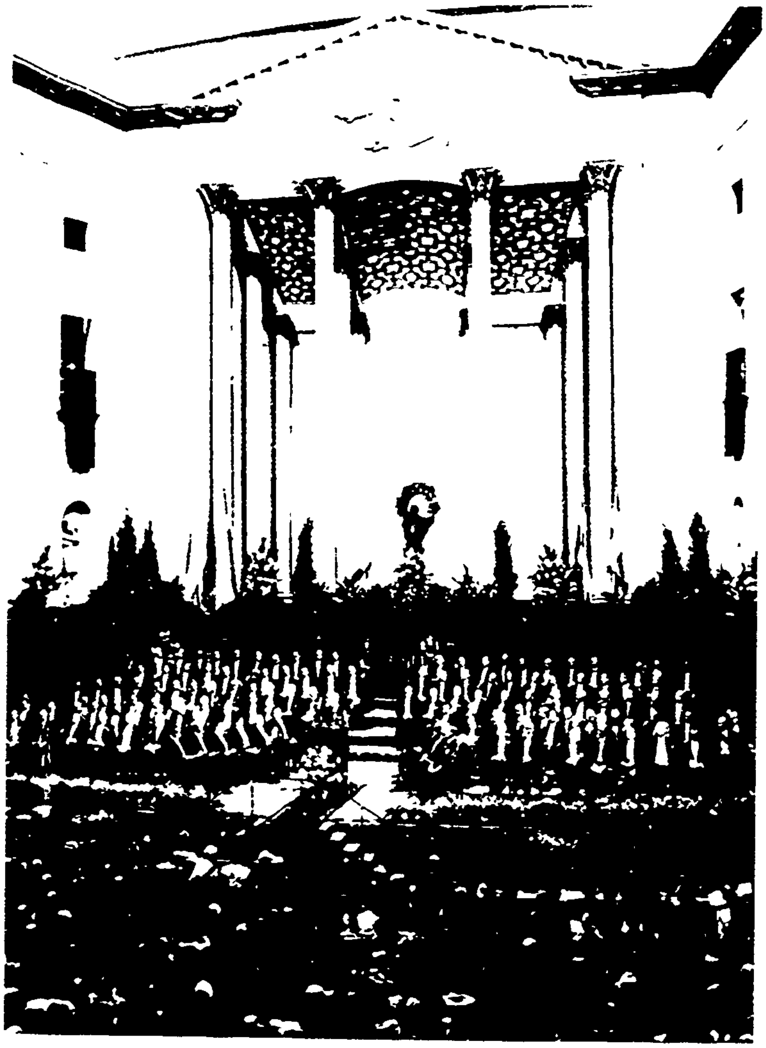
where E_1 is the energy of the electron in the first orbit, and has the value -13.6 electron volts or -21.76×10^{-19} joule.

It may seem strange to you that the energy is written with a negative value. Recall that, since it is only changes in energy that can be measured, the zero level for energy can be defined in any way that is convenient. It is customary to define the potential energy of an electron in the field of a nucleus so that it is zero at a very large (or infinite) distance from the nucleus. An energy of zero implies, then, that the electron is just free from the nucleus. Positive values of energy imply that the electron is free of the nucleus and has kinetic energy besides. Negative values of energy imply that the electron is bound to the atom; the more negative, the less the total energy. The lowest energy possible for an electron in a hydrogen atom is -13.6 eV, for which $n = 1$. This is called the "ground" state.

According to the formula for r_n, the first Bohr orbit has the smallest radius, with $n = 1$. Higher values of n correspond to orbits that have larger radii. Although the higher orbits are spaced increasingly far apart, the force field of the nucleus falls off rapidly, so the work required to move out to the next orbit actually becomes smaller. Therefore the jumps from one energy level to the next become smaller and smaller at higher energies.

What was the main evidence that an atom could exist only in certain energy states?

What reason did Bohr give for the atom existing only in certain energy states?



The Nobel Prize

Alfred Bernhard Nobel (1833-1896), a Swedish chemist, was the inventor of dynamite. As a result of his studies of explosives, Nobel found that when nitroglycerine (an extremely unstable chemical) was absorbed in an inert substance it could be used safely as an explosive. This combination is dynamite. He also invented other explosives (blasting gelatin and ballistite) and detonators. Nobel was primarily interested in the peaceful uses of explosives, such as mining, road building and tunnel blasting, and he amassed a large fortune from the manufacture of explosives for these applications. Nobel abhorred war and was conscience-stricken by the military uses to which his explosives were put. At his death, he left a fund of some $315 million to honor important accomplishments in science, literature and international understanding. Prizes were established to be awarded each year to persons who have made notable contributions in the fields of physics, chemistry, medicine or physiology, literature and peace. The first Nobel Prizes were awarded in 1901. Since then, men and women from about 30 countries have received prizes. The Nobel Prize is generally considered the most prestigious prize in science.

19 6 The Bohr theory: the spectral series of hydrogen. Bohr could now use his model to derive the Balmer formula by applying his second postulate: the radiation emitted or absorbed in a transition has a frequency f determined by the relation

$$hf = E_i - E_f .$$

If n_f is the quantum number of the final state and n_i is the quantum number of the initial state, then according to the E_n formula we have

$$E_f = \frac{E_1}{n_f^2} \qquad \text{and} \qquad E_i = \frac{E_1}{n_i^2} .$$

The frequency of radiation emitted or absorbed when the atom goes from the initial state to the final state is therefore determined by the equation

$$hf = \frac{E_1}{n_i^2} - \frac{E_1}{n_f^2} .$$

Balmer's original formula (p. 70) was written in terms of wavelength instead of frequency. The relation between frequency and wavelength was given in Unit 4: the frequency is equal to the speed of the wave divided by its wavelength,

$$f = \frac{c}{\lambda}$$

If we substitute c/λ for f in the equation above, and then divide both sides by the constant hc (Planck's constant times the speed of light), we obtain the equation:

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right] .$$

According to Bohr's model, then, this equation gives the wavelength λ of the radiation that will be emitted or absorbed when the state of a hydrogen atom changes from n_i to n_f. How does this formula compare with Balmer's formula? The Balmer formula was given on page 70:

$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n_i^2}\right] .$$

We see at once that the equation derived from the Bohr model is exactly the same as Balmer's formula if:

$$n_f = 2 \qquad \text{and} \qquad R_H = -\frac{E_1}{hc} .$$

1937	Clifton J. Davisson (US) and George P Thomson (Gr Brit)—experimental diffraction of electrons by crystals
1938	Enrico Fermi (Ital)—new radioactive elements produced by neutron irradiation and nuclear reactions by slow neutrons
1939	Ernest O Lawrence (US)—cyclotron and its use in regard to artificial radio active elements.
1940	No award
1941	No award
1942	No award
1943	Otto Stern (Ger)—molecular ray method nd magnetic moment of the Proton.
1944	Isidor Isaac Rabi (US)—resonance method for magnetic properties of atomic nuclei
1945	Wolfgang Pauli (Aus)—exclusion or Pauli principle.
1946	P W Bridgman (US)—high pressure physics
1947	Sir Edward V Appleton (Gr Brit)—physics of the upper atmosphere and discovery of so called Appleton layers.
1948	Patrick M S Blackett, (Gr Brit)—development of Wilson cloud chamber and discoveries in nuclear physics and cosmic rays
1949	Hideki Yukawa (Japan)—prediction of mesons and theory of nuclear forces.
1950	Cecil Frank Powell (Gr Brit)—photographic method of studying nuclear processes and discoveries regarding mesons
1951	Sir John D. Cockcroft and Ernest T S Walton (Gr Brit)—transmutation of atomic nuclei by artificially accelerated atomic particles.
1952	Felix Bloch (Switz) and Edward M Purcell (US)—nuclear magnetic precision measurements
1953	Frits Zernike (Neth)—phase-contrast microscope
1954	Max Born (Ger)—statistical interpretation of wave functions, and Walter Bothe (Ger)—coincidence method for nuclear reactions and cosmic rays.
1955	Willis E. Lamb (US)—fine structure of hydrogen spectrum, and Polykarp Kusch (US)—precision determinations of magnetic moment of electron
1956	William Shockley, John Bardeen and Walter Houser Brattain (US)—researches on semiconductors and their discovery of the transistor effects
1957	Chen Ning Yang and Tsung Dao Lee (Chin)—investigation of laws of parity, leading to discoveries regarding the elementary particles.
1958	Pavel A Cerenkov, Il ya M. Frank and Igor E Tamm (USSR)—discovery and interpretation of the Cerenkov effect
1959	Emilio G. Segre and Owen Chamberlain (US)—discovery of the antiproton
1960	Donald A Glaser (US)—invention of bubble chamber
1961	Robert Hofstadter (US)—electron scattering in atomic nuclei Rudolf Ludwig Mossbauer (Ger)—resonance absorption of γ-radiation and discovery of effect which bears his name
1962	Lev D. Landau (USSR)—theories for condensed matter, especially liquid helium
1963	Eugene P Wigner (US)—theory of the atomic nucleus and elementary particles Marie Goeppert Mayer (US) and J. Hans D Jensen (Ger)—nuclear shell structure.
1964	Charles Townes (US), Alexander Prokhorov and Nikolay Basov (USSR)—development of maser
1965	S. Tomonaga (Japan), Julian Schwinger and Richard Feynman (US)—quantum electrodynamics and elementary particles
1966	Alfred Kastler (Fr)—new optical methods for studying properties of atom.
1967	Hans Bethe (US)—nuclear physics and theory of energy production in the sun

Nobel Prize winners in Physics.

All the lines in the Balmer series simply correspond to transitions from various initial states (various values of n_i) to the same final state, $n_f = 2$. Similarly, lines of the Lyman series correspond to transitions from various initial states to the final state $n_f = 1$; the lines of the Paschen series correspond to transitions from various initial states to the final state $n_f = 3$, etc. (see Table 19.2). The general scheme of possible transitions is shown in Fig. 19.10.

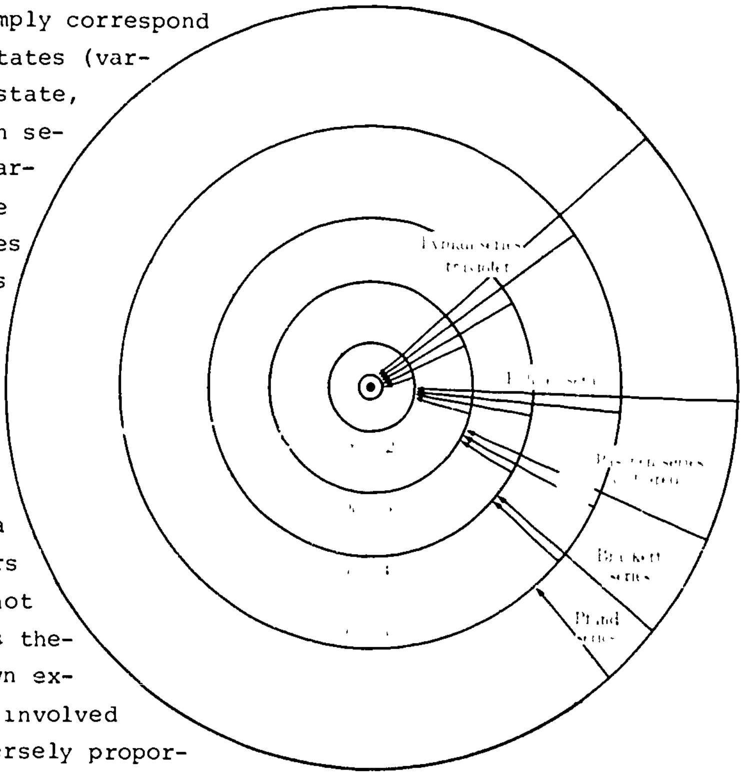


Fig. 19.10 Possible transitions of an electron in the Bohr model of the hydrogen atom.

The Bohr formula, for hydrogen, agrees exactly with the Balmer formula as far as the dependence on the numbers n_f and n_i is concerned. But this is not surprising, since Bohr constructed his theory in such a way as to match the known experimental results. Any theory which involved stationary states whose energy is inversely proportional to the square of a quantum number n would do as well as this. Of course any such theory would have to rely in some way on the idea that radiation is quantized and that the electron has stationary states in the atom. Not only did Bohr's model lead to correct dependence on n_f and n_i, but more remarkably, the value of the constant came out right. The Rydberg constant R_H, which had previously been just an experimentally determined constant, was now shown to depend on the mass and charge of the electron, on Planck's constant and on the speed of light.

When the Bohr theory was proposed, in 1913, only the Balmer and Paschen series for hydrogen were known. The theory suggested that additional series should exist. The experimental search for these series yielded the Lyman series in the ultraviolet portion of the spectrum (1916), the Brackett series (1922), and the Pfund series (1924). In each series the measured frequencies of the lines were found to be those predicted by the theory. Thus, the theory not only correlated known information about the spectrum of hydrogen, but also predicted hitherto unknown series of lines in the spectrum.

The scheme shown in Fig. 19.10 is useful, but it also has the danger of being too specific. For instance, it leads us to visualize the emission of radiation in terms of "jumps" of electrons between orbits. But we cannot actually detect an electron moving in an orbit, nor can we see an electron "jump" from one orbit to another. A second way of presenting the results of Bohr's theory was suggested, which yields the same facts but does not commit us too closely to a picture of orbits. This new scheme is shown in Fig. 19.11. It focusses attention on the possible energy states, which are all given by the formula, $E_n = \frac{1}{n} E_1$. In terms of this <u>mathematical model</u>, the atom is normally unexcited, its <u>energy</u> then being E_1, or $-22 \cdot 10^{-19}$ joules. Absorption of energy can place the atoms in an excited state, with a larger energy. The excited atom is then ready to emit light with a consequent reduction in energy. But the energy absorbed or emitted must always shift the energy of the atom to one of the values specified by the E_n formula. We may thus, if we wish, represent the hydrogen atom by means of the energy-level diagram shown on the left.

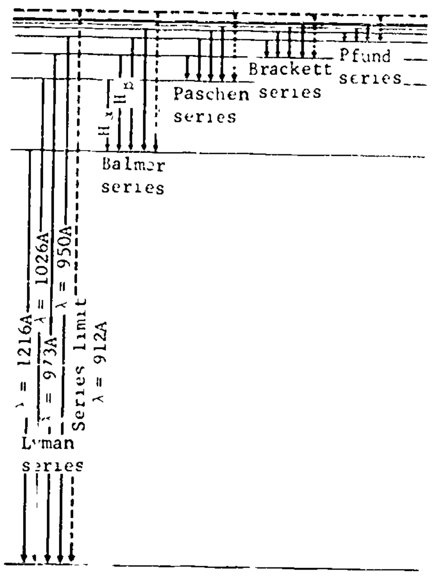


Fig. 19.11 Energy-level diagram for the hydrogen atom. The energy units are 10^{-19} joules.

Q13 Balmer had predicted accurately the other spectral series in hydrogen thirty years before Bohr did. Why is Bohr's prediction considered more important?

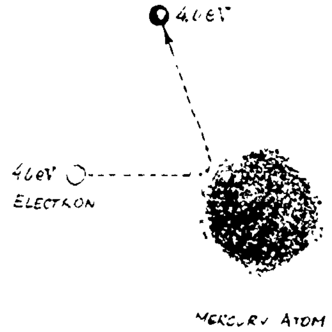
19.7 <u>Stationary states of atoms: the Franck-Hertz experiment.</u>

The success of the Bohr theory in accounting for the spectrum of hydrogen raised the question: can experiments show directly that atoms have only certain discrete energy states? In other words, are there really gaps between the energies that an atom can have? A famous experiment in 1914, by the German Physicists James Frank and Gustav Hertz, showed the existence of these discrete energy states.

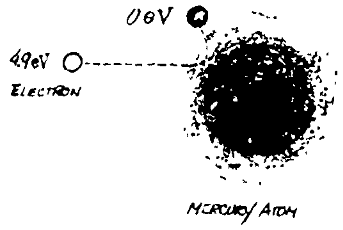
James Franck (1882-1946) and Gustav Hertz (1887-) won a Nobel Prize for their work in 1925. In the 1930's they both were dismissed from their university posts because they were of Jewish descent. Franck fled to the United States and worked on the atomic bomb during World War II. He tried to have the bomb's power demonstrated before an international group in a test instead of in the destruction of Japanese cities. Hertz chose to remain in Germany. He survived in one of the concentration camps that were liberated by Russian forces in 1945.

Franck and Hertz bombarded atoms with electrons (from an electron gun) and were able to measure the energy lost by electrons in collisions with atoms. They could also determine the energy gained by atoms in these collisions. Their work was very ingenious, but it is too complex to describe and interpret in detail in this course. We shall therefore give here a somewhat oversimplified account of their experiments.

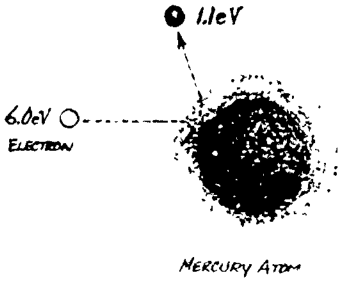
In their first experiment, Franck and Hertz bombarded mercury atoms in mercury vapor contained in a chamber at very low pressure. Their experimental procedure was equivalent to measuring the kinetic energy of electrons leaving the electron gun and the kinetic energy of electrons that had passed through the mercury vapor. The only way electrons could lose energy was in collisions with mercury atoms. Franck and Hertz found that when the kinetic energy of the electrons leaving the electron gun was very small, for example, about 1 eV, the electrons that passed through the mercury vapor had almost exactly the same energy as they had on leaving the gun. This result could be explained in the following way. A mercury atom is several hundred thousand times more massive than an electron. At low electron energies the electron just bounces off a mercury atom, much as a golf ball thrown at a bowling ball would bounce off it. A collision of this kind is called an "elastic" collision. In an elastic collision, the mercury atom (bowling ball) takes up only an extremely small part of the kinetic energy of the electron (golf ball). The electron loses practically none of its kinetic energy.



When the energy of the bombarding electrons was raised to 5 eV, there was a dramatic change in the experimental results. An electron that collided with a mercury atom lost almost exactly 4.9 electron-volts of energy. When the electron energy was increased to about 6 electron-volts, an electron still lost 4.9 electron-volts of energy in a collision with a mercury atom. The electron had just 1.1 eV of energy after passing through the mercury vapor. These results indicated that a mercury atom cannot accept less than 4.9 eV of energy; and that when it is offered somewhat more, for example, 5 or 6 eV, it still can accept only 4.9 eV. This energy cannot go into kinetic energy of the mercury atom because of the relatively enormous mass of the atom as compared with that of an electron. Hence, Franck and Hertz concluded that the 4.9 eV of energy is added to the internal energy of the mercury atom—that the mercury atom has a permitted or stationary state with energy 4.9 eV greater than that of the lowest energy state. They also concluded that there is no state with an energy in between.



What happens to this 4.9 eV of additional internal energy? According to the Bohr theory, if the mercury atom has a state with energy 4.9 eV greater than that of the lowest state, this amount of energy should be emitted in the form of electromagnetic radiation when the atom returns to its lowest state. Franck and Hertz looked for this radiation with a spectroscope, and found it. They observed a spectrum line at a wavelength of 2535 Å, a line that was known in the emission spectrum of mercury. The wavelength corresponds to a frequency f that is equivalent to an energy, hf, of 4.9 eV.



19.7
This result showed that the mercury atoms had indeed gained 4.9 eV of energy in their collisions with the electrons.

Later experiments showed that mercury atoms could also gain other, sharply defined amounts of energy when bombarded with electrons, for example, 6.7 eV and 10.4 eV. In each case radiation was emitted that corresponded to lines in the spectrum of mercury. Experiments have also been made on many other elements besides mercury; in each case analogous results were obtained. The electrons always lost energy, and the atoms always gained energy in sharply defined amounts. Each type of atom studied was found to have discrete energy states. The amounts of energy gained by the atoms in collisions with electrons could always be correlated with spectrum lines. The existence of discrete "permitted" or "stationary" states of atoms predicted by the Bohr theory of atomic spectra was thus verified by direct experiment. This verification was considered to provide strong confirmation of the validity of the Bohr theory.

• How much kinetic energy will an electron have after a collision with a mercury atom if its kinetic energy before collision is (a) 4.0 eV? (b) 5.0 eV? (c) 7.0 eV?

19.8 The periodic table of the elements. In the Rutherford-Bohr model, the atoms of the different elements differ in the charge and mass of the nucleus, and in the number and arrangement of the electrons about the nucleus. As for the arrangement of the electrons, Bohr came to picture the electronic orbits as on the next page, though not as a series of concentric rings in one plane but as tracing out patterns in three dimensions. For example, the orbits of the two electrons of He in the normal state are indicated as circles in planes inclined at about 60° with respect to each other. In addition to circular orbits, elliptical ones with the nucleus at one focus are also possible.

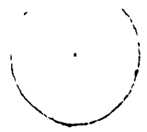
Bohr found a way of correlating his model with the periodic table of the elements and the periodic law. He suggested that the chemical and physical properties of an element depend on how the electrons are arranged around the nucleus. He also indicated how this might come about. He regarded the electrons in an atom as grouped into shells. Each shell can contain not more than a certain number of electrons. The chemical properties are related to how nearly full or empty a shell is. For example, full shells are associated with chemical stability, and in the inert gases the electron shells are completely filled.

To relate the Bohr model of atoms with their chemical properties we may begin with the observation that the elements hydrogen (Z = 1) and lithium (Z = 3) are somewhat alike chemically. Both have valences of 1. Both enter into compounds of analogous types, for example hydrogen chloride, HCl, and lithium chloride, $LiCl$. Furthermore, there are some similarities in their spectra. All this suggests that the lithium atom resembles the hydrogen atom in some important respects. Bohr conjectured that two of the three electrons of the lithium atom are relatively close to the nucleus, in orbits like those pertinent to the helium atom, while the third is in a circular or elliptical orbit outside the inner system. Since this inner system consists of a nucleus of charge (+) $3q_e$ and two electrons each of charge (-) q_e, its <u>net</u> charge is (+) q_e. Thus the lithium atom may be roughly pictured as having a central core of charge (+) q_e, around which one electron revolves, somewhat as for a hydrogen atom.

Helium (Z = 2) is a chemically inert element, belonging to the family of noble gases. So far no one has been able to form compounds from it. These properties indicated that the helium atom is highly stable, having both of its electrons closely bound to the nucleus. It seemed sensible to regard both electrons as moving in the same innermost <u>shell</u> around the nucleus when the atom is unexcited. Moreover, because of the stability and the chemical inertness of the helium atom, we may reasonably assume that this shell cannot accommodate more than two electrons. This shell is called the <u>K-shell</u>. The single electron of hydrogen is also said to be in the K-shell when the atom is unexcited. For lithium, two electrons are in the K-shell, filling it to capacity, and the third electron starts a new one, called the L-shell. To this single outlying and loosely bound electron must be ascribed the strong chemical affinity of lithium for oxygen, chlorine and many other elements.

Sodium (Z = 11) is the next element in the periodic table that has chemical properties similar to those of hydrogen and lithium, and this suggests that the sodium atom also is hydrogen-like in having a central core about which on electron revolves. Moreover, just as lithium follows helium in the periodic table, so does sodium follow another noble gas, neon (Z = 10). For the neon atom, we may assume that 2 of its 10 electrons are in the first (K) shell, and that the remaining 8 electrons are in the second (L) shell. Because of the great chemical inertness and stability of neon, these 8 electrons may be expected to fill the L-shell to capacity.

The sketches below are based on diagrams Bohr used in his university lectures.



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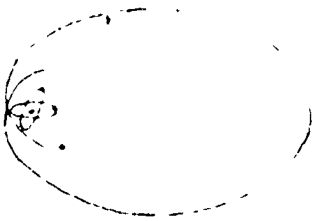

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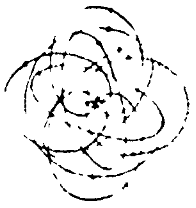

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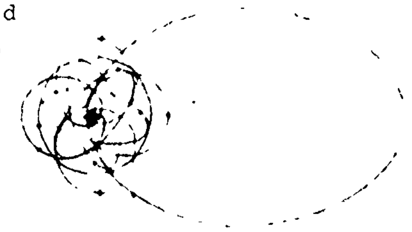

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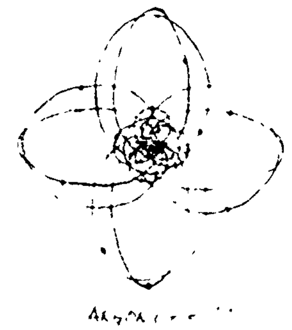

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These two pages will be easier to study if you refer to the table of the elements and the periodic table in Chapter 18.

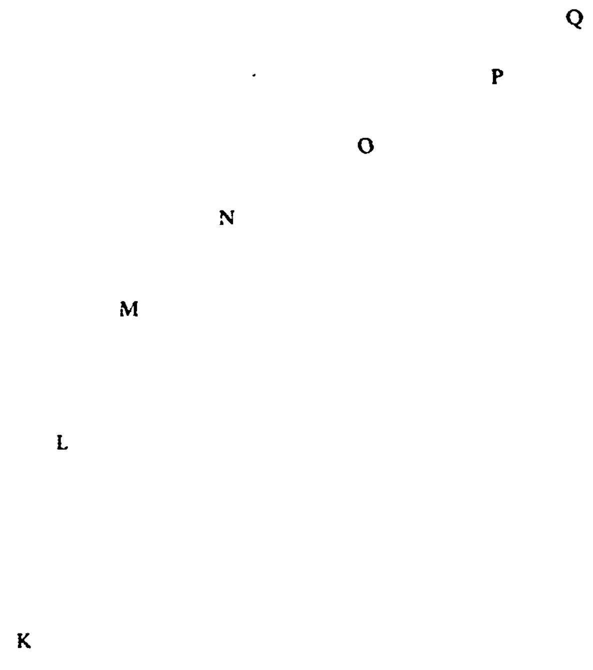
For sodium, then, the eleventh electron must be in a third shell, which is called the M-shell. Passing on to potassium (Z = 19), the next alkali metal in the periodic table, we again have the picture of an inner core and a single electron outside it. The core consists of a nucleus with charge (+) $19q_e$ and 2, 8, and 8 electrons occupying the K-, L-, and M-shells, respectively. The 19th electron revolves around the core in a fourth shell, called the N-shell. The atom of the noble gas, argon with Z = 18 just before potassium in the periodic table, again represents a distribution of electrons in a tight and stable pattern, with 2 in the K-, 8 in the L-, and 8 in the M-shell.

These qualitative considerations have led us to a consistent picture of electrons in groups, or shells, around the nucleus. The arrangement of electrons in the noble gases can be taken to be particularly stable, and each time we encounter a new alkali metal in Group I of the periodic table, a new shell is started with a single electron around a core which resembles the pattern for the preceding noble gas. We may expect that this outlying electron will easily come loose under the attraction of neighboring atoms, and this corresponds with the facts. The elements lithium, sodium and potassium belong to the group of alkali metals. In compounds or in solution (as in electrolysis) they may be considered to be in the form of ions such as Li^+, Na^+ and K^+, each with one positive net charge $(+)q_e$. In the atoms of these elements, the outer electron is relatively free to move about. This property has been used as the basis of a theory of electrical conductivity. According to this theory, a good conductor has many "free" electrons which can form a current under appropriate conditions. A poor conductor has relatively few "free" electrons. The alkali metals are all good conductors. Elements whose electron shells are filled are very poor conductors because they have no "free" electrons.

Turning now to Group II of the periodic table, we would expect those elements that follow immediately after the alkali metals to have atoms with two outlying electrons. For example, beryllium (Z = 4) should have 2 electrons in the K-shell, thus filling it, and 2 in the L-shell. If the atoms of all these elements have two outlying electrons, they should be chemically similar, as indeed they are. Thus, calcium and magnesium, which belong to this group, should easily form ions such as Ca^{++} and Mg^{++}, each with two positive charges, $(+)2q_e$, and this is also found to be true.

As a final example, consider those elements that immediately precede the noble gases in the periodic table. For example, fluorine atoms (Z = 9) should have 2 electrons filling the K-shell but only 7 electrons in the L-shell, which is one less than enough to fill it. If a fluorine atom should capture an additional electron, it should become an ion F^- with one negative charge. The L-shell would then be filled, as it is for neutral neon (Z = 10), and thus we would expect the F^- ion to be stable. This prediction is in accord with observation. Indeed, all the elements immediately preceding the inert gases in the periodic table tend to form stable singly charged negative ions in solution. In the solid state, we would expect these elements to be lacking in free electrons, and all of them are in fact poor conductors of electricity.

Altogether there are seven main shells, K, L, M, ... Q, and further analysis shows that all but the first are divided into subshells. Thus the first shell K is one shell without substructure, the second shell L consists of two subshells, and so on. The first subshell in any shell can always hold up to 2 electrons, the second up to 6, the third up to 10, the fourth up to 14, and so on. Electrons that are in different subsections of the same shell in general differ very little in energy as compared with electrons that are in different shells. For all the elements up to and including argon (Z = 18), the buildup of electrons proceeds quite simply. Thus the argon atom has 2 electrons in the K-shell, 8 in the L-shell, then 2 in the first M-subshell and 6 in the second M-subshell. But after argon, there may be electrons in an outer shell before an inner one is filled. This complicates the scheme somewhat but still allows it to be consistent. The arrangement of the electrons in any unexcited atom is always the one that provides greatest stability for the whole atom. According to this model, chemical phenomena generally involve only the outermost electrons of the atoms.



Relative energy levels of electron states in atoms. Each circle represents a state which can be occupied by 2 electrons.

SG 19.14
SG 19.15

19.8

Bohr carried through a complete analysis along these lines and, in 1921, proposed the form of the periodic table shown in Fig. 19.12. This table was the result of physical theory and offered a fundamental physical basis for understanding chemistry. This was another triumph of the Bohr theory.

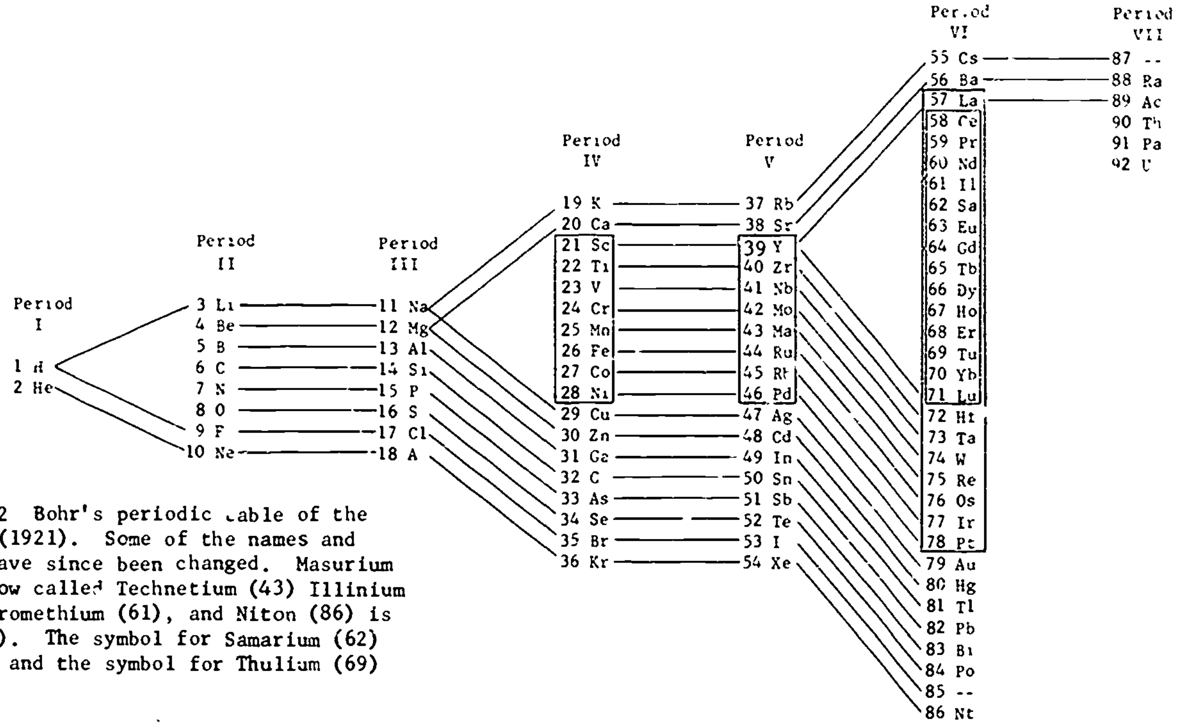


Fig. 19.12 Bohr's periodic table of the elements (1921). Some of the names and symbols have since been changed. Masurium (43) is now called Technetium (43) Illinium (61) is Promethium (61), and Niton (86) is Radon (86). The symbol for Samarium (62) is now Sm and the symbol for Thulium (69) is Tm.

Q15 Why do the next heavier elements after the noble gases easily become positively charged?

19.9 The failure of the Bohr theory and the state of atomic theory in the early 1920's. In spite of the successes achieved with the Bohr theory in the years between 1913 and 1924, serious problems arose for which the theory proved inadequate. Although the Bohr theory accounted for the spectra of atoms with a single electron in the outermost shell, serious discrepancies between theory and experiment appeared in the spectra of atoms with two electrons in the outermost shell. Indeed the theory could not account in any satisfactory way for the spectra of elements whose atoms have more than one electron in the outermost shell. It was also found experimentally that when a sample of an element is in an electric or magnetic field, its emission spectrum shows additional lines. For example, in a magnetic field each line is split into several lines. The Bohr theory could not account in a quantitative way for the observed splitting. Further, the theory supplied no method for predicting the relative intensities of spectral lines. These intensities depend on the numbers of atoms in a sample that undergo transitions among

Niels Bohr (1885-1962) was born in Copenhagen, Denmark and was educated there, receiving his doctor's degree in physics in 1911. In 1912 he was at work in Rutherford's laboratory in Manchester, England, which was a center of research on radioactivity and atomic structure. Here he developed his theory of atomic structure and atomic spectra. Bohr played an important part in the development of quantum mechanics, in the advancement of nuclear physics, and in the study of the philosophical aspects of modern physics. In his later years he devoted much time to promoting the peaceful uses of atomic and nuclear physics.

the stationary state Physicists wanted to be able to calculate the probability of a transition from one stationary state to another. They could not make such calculations with the Bohr theory.

By the early 1920's it had become clear that the Bohr theory, despite its great successes, had deficiencies and outright failures. It was understood that the theory would have to be revised, or replaced by a new one. The successes of the Bohr theory showed that a better theory of atomic structure would have to account for the existence of stationary states—discrete atomic levels—and would, therefore, have to be based on quantum concepts. Besides the inability to predict certain properties at all, the Bohr theory had two additional shortcomings: it predicted some results that disagreed with experiment; and it predicted others that could not be tested in any known way. Of the former kind were predictions about the spectra of elements with two or three electrons in the outermost electron shells. Of the latter kind were predictions of the details of electron orbits. Details of this latter type could not be observed directly, nor could they be related to any observable properties of atoms such as the lines in the emission spectrum. Planetary theory has very different implications when applied to a planet revolving around the sun, and when applied to an electron in an atom. The precise position of a planet is important, especially if we want to do experiments such as photographing the surface of the moon or of Mars from a satellite. But the calculation of the position of an electron in an orbit is neither useful nor interesting because it has no relation to any experiment physicists have been able to devise. It thus became evident that, in using the Bohr theory, physicists were asking some questions which could not be answered experimentally.

See "The Sea-Captain's Box" in Project Physics Reader 5.

In March 1913, Bohr wrote to Rutherford enclosing a draft of his first paper on the quantum theory of atomic constitution. On March 20, 1913, Rutherford replied in a letter, the first part of which we quote,

"Dear Dr. Bohr:

I have received your paper safely and read it with great interest, but I want to look it over again carefully when I have more leisure. Your ideas as to the mode of origin of spectra in hydrogen are very ingenious and seem to work out well; but the mixture of Planck's ideas with the old mechanics makes it very difficult to form a physical idea of what is the basis of it. There appears to me one grave difficulty in your hypothesis, which I have no doubt you fully realize, namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other. It seems to me that you would have to assume that the electron knows beforehand where it is going to stop...."

In the early 1920's, physicists began to think seriously about what could be wrong with the basic ideas of the theory. One fact that stood out was that the theory started with a mixture of classical and quantum ideas. An atom was assumed to act in accordance with the laws of classical physics up to the point where these laws didn't work, then the quantum ideas were introduced. The picture of the atom that emerged from this mixture was an inconsistent combination of ideas from classical physics and concepts for which there was no place in classical physics. The orbits of the electrons were determined by the classical, Newtonian laws of motion. But of the many possible orbits, only a small fraction were regarded as possible, and these were assigned by rules that contradicted classical mechanics. It became evident that a better theory of atomic structure would have to have a more consistent foundation and that the quantum concepts would have to be fundamental, rather than secondary.

The contribution of the Bohr theory may be summarized as follows. It provided partial answers to the questions raised about atomic structure in Chapters 17 and 18. Although the theory turned out to be inadequate it supplied clues to the way in which quantum concepts should be used. It indicated the path that a new theory would have to take. A new theory would have to supply the right answers that the Bohr theory gave and would also have to supply the right answers for the problems the Bohr theory couldn't solve. A successful theory of atomic structure has been developed and has been generally accepted by physicists. It is called "quantum mechanics" because it is built directly on the foundation of quantum concepts; it will be discussed in the next chapter.

SG 19 16
SG 19 17
SG 19 18

Q16 The Bohr model of atoms is widely given in science books. What is wrong with it?

Study Guide

19.1 (a) Suggest experiments to show which of the Fraunhofer lines in the spectrum of sunlight are due to absorption in the sun's atmosphere rather than to absorption by gases in the earth's atmosphere.

(b) How might one decide from spectroscopic observations whether the moon and the planets shine by their own light or by reflected light from the sun?

19.2 Theoretically, how many series of lines are there in the emission spectrum of hydrogen? In all these series, how many lines are in the visible region?

19.3 The Rydberg constant for hydrogen, R_H, has the value 1.097×10^7/m. Calculate the wavelengths of the lines in the Balmer series corresponding to $n = 8$, $n = 10$, $n = 12$. Compare the values you get with the wavelengths listed in Table 19.1. Do you see any trend in the values?

19.4 (a) As indicated in Fig. 19.5 the lines in one of hydrogen's spectral series are bunched very closely at one end. Does the formula $\frac{1}{\lambda} = R_H \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$ suggest that such bunching will occur?

(b) The series limit must correspond to the last possible line(s) of the series. What value should be taken for n_i in the above equation to compute the wavelength of the series limit?

(c) Compute the series limit for the Lyman, Balmer and Paschen series of hydrogen.

(d) Consider a photon with a wavelength corresponding to the series limit of the Lyman series. What energy would it carry? Express the answer in joules and in electron-volts ($1 \text{ eV} = 1.6 \times 10^{-19}$ J).

19.5 In what ways do the Thomson and Rutherford atomic models agree? In what ways do they disagree?

19.6 In 1903, the German physicist, Philipp Lenard (1864-1947), proposed an atomic model different from those of Thomson and Rutherford. He had observed that, since cathode-ray particles can penetrate matter, most of the atomic volume must offer no obstacle to their penetration. In Lenard's model there were no electrons and no positive charges separate from the electrons. His atom was made up of particles called dynamides, each of which was an electric doublet possessing mass. (An electric doublet is a combination of a positive charge and a negative charge very close together.) All the dynamides were supposed to be identical, and an atom contained as many of them as were needed to make up its mass. They were distributed throughout the volume of the atom, but their radius was so small compared with that of the atom that most of the atom was actually empty.

(a) In what ways does Lenard's model agree with those of Thomson and Rutherford? In what ways does it disagree with those models?
(b) Why would you not expect α particles to be scattered through large angles if Lenard's model were valid?

19.7 In a recently published book the author expresses the view that physicists have interpreted the results of the experiments on the scattering of α particles incorrectly. He thinks that the experiments show only that atoms are very small, not that they have a heavy, positively charged nucleus. Do you agree with his view? Why?

19.8 Suppose that the atom and the nucleus are each spherical, that the diameter of the atom is of the order of 1 Å (Ångstrom unit) and that the diameter of the nucleus is of the order of 10^{-12} cm. What is the ratio of the diameter of the nucleus to that of the atom?

19.9 The nucleus of the hydrogen atom is thought to have a radius of about 1.5×10^{-13} cm. If the nucleus were magnified to 0.1 mm (the radius of a grain of dust), how far away from it would the electron be in the Bohr orbit closest to it?

19.10 In 1903 a philosopher wrote,

> The propounders of the atomic view of electricty [disagree with theories which] would restrict the method of science to the use of only such quantities and data as can be actually seen and directly measured, and which condemn the introduction of such useful conceptions as the atom and the electron, which cannot be directly seen and can only be measured by indirect processes.

On the basis of the information now available to you, with which view do you agree; the view of those who think in terms of atoms and electrons, or the view that we must use only such things as can be actually seen and measured?

19.11 How would you account for the production of the lines in the absorption spectrum of hydrogen by using the Bohr theory?

19.12 Many substances emit visible radiation when illuminated with ultraviolet light; this phenomenon is an example of fluorescence. Stokes, a British physicist of the nineteenth century, found that in fluorescence the wavelength of the emitted light usually was the same or longer than the illuminating light. How would you account for this phenomenon on the basis of the Bohr theory?

19.13 In Query 31 of his Opticks, Newton wrote:

> All these things being consider'd, it seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which he formed them and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them; even so very hard, as never to wear or break in pieces; no ordinary power being able to divide what God himself made one in the first creation. While the particles continue entire, they may compose bodies of one and the same nature and texture in all ages: But should they wear away, or break in pieces, the nature of things depending on them would be changed. Water and earth, composed of old worn particles and fragments of particles, would not be of the same nature and texture now, with water and earth composed of entire particles in the beginning. And therefore. that nature may be lasting, the changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles; compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch in a few points.

Compare what Newton says here about atoms with

- a) the views attributed to Leucippus and Democritus concerning atoms (see the prologue to this unit);
- b) Dalton's assumptions about atoms (see the end of the prologue to this unit);
- c) the Rutherford-Bohr model of the atom.

19.14 Use the chart on p. 91 to explain why atoms of potassium (Z = 19) have electrons in the N shell even though the M shell isn't filled.

19.15 Use the chart on p. 91 to predict the atomic number of the next inert gas after argon. That is, imagine filling the electron levels with pairs of electrons until you reach an apparently stable, or complete, pattern.

Do the same for the next inert gas.

19.16 Make up a glossary, with definitions, of terms which appeared for the first time in this chapter.

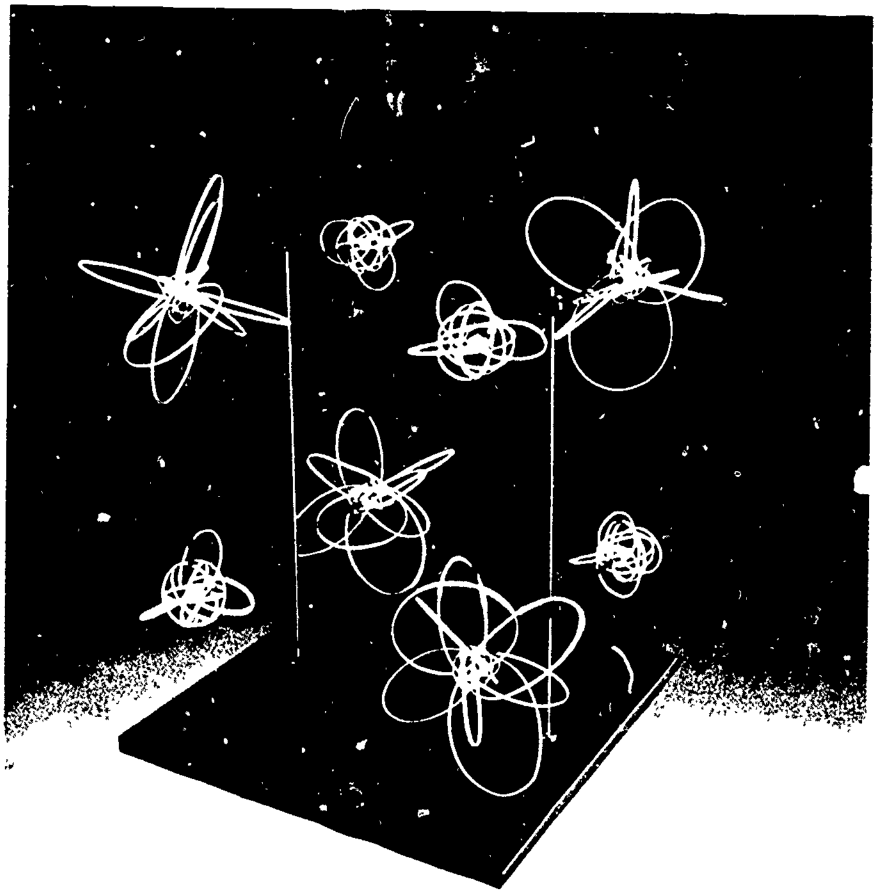
19.17 The philosopher John Locke (1632-1704) proposed a science of human nature which was strongly influenced by Newton's physics. In Locke's atomistic view, elementary ideas are produced by elementary sensory experiences and then drift, collide and interact in the mind. Thus the association of ideas was but a specialized case of the universal interactions of particles.

Does such an "atomistic" approach to the problem of human nature seem reasonable to you? What argument for and against this sort of theory can you think of?

19.18 In a recently published textbook of physics, the following statement is made:

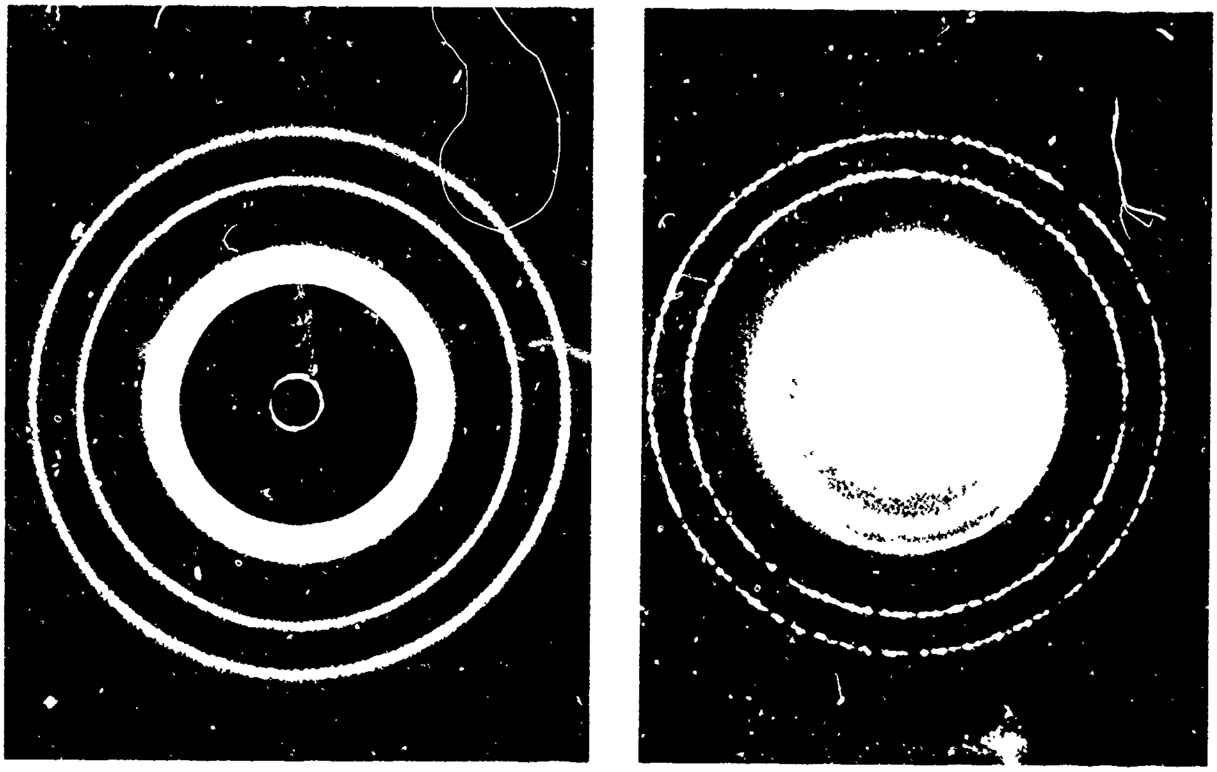
> Arbitrary though Bohr's new postulate may seem, it was just one more step in the process by which the apparently continuous macroscopic world was being analyzed in terms of a discontinuous, quantized, microscopic world. Although the Greeks had speculated about quantized matter (atoms), it remained for the chemists and physicists of the nineteenth century to give them reality. In 1900 Planck found it necessary to quantize the energy of the atomic-sized oscillators responsible for blackbody radiation. In 1905 Einstein quantized the energy of electromagnetic waves. Also, in the early 1900's a series of experiments culminating in Millikan's oil-drop experiment conclusively showed that electric charge was quantized. To this list of quantized entities, Bohr added angular momentum.

- a) What other properties or things in physics can you think of that are "quantized?"
- b) What properties or things can you think of outside physics that might be said to be "quantized?"



This sculpture is meant to represent the arrangement of sodium and chlorine ions in a crystal of common salt. Notice that the outermost electrons of the sodium atoms have been lost to the chlorine atoms, leaving sodium ions with completed K and L shells and chlorine ions with completed K, L and M shells.

The diffraction pattern on the left was made by a beam of x rays passing through thin aluminium foil. The diffraction pattern on the right was made by a beam of electrons passing through the same foil.



20.1 *Some results of relativity theory.* Progress in atomic and nuclear physics has been based on two great revolutions in physical thought: quantum theory and relativity. In Chapters 18 and 19 we saw how quantum theory entered into atomic physics. The further development of quantum theory, quantum mechanics, will be the main subject of this chapter. But we cannot get into quantum mechanics without learning something about relativity. Some of the results of the relativity theory are needed to understand certain phenomena of atomic physics which are basic to quantum mechanics. These results will also be essential to our treatment of nuclear physics in Unit 6. We shall, therefore, devote this section to a brief discussion of the theory of relativity, introduced by Einstein in 1905—the same year in which he published the theory of the photoelectric effect.

The theory of relativity ties together ideas and experimental information that have been touched on earlier in this course. One important piece of information involves the speed of light. Measurements showed a remarkable and surprising result: the speed of light in vacuum (free space) is independent of any motion of the source of the light or of the person making the measurement. The result is always the same, 3.0×10^8 m/sec, regardless of whether the measurer is stationary in his laboratory or is traveling at high speed; or whether the source of light is stationary or moving with respect to the observer. Although the result may appear strange, it has been confirmed by many independent experiments.

Einstein combined the constancy of the speed of light in vacuum with a basic philosophical idea about the role of reference frames (discussed in Unit 1) in physical theory. He postulated that all reference frames that move with uniform velocity relative to each other are equivalent: no one of these frames is preferable to any other. This means that the laws of physics must be the same in all such reference frames. Another way of saying this is that the law of physics are *invariant* with respect to uniform motion, that is, they are not affected by uniform motion. It would be very inconvenient if this were not the case: for example, if Newton's laws of motion did not hold in a train moving at constant speed relative to the surface of the earth.

The combination of the idea of *invariance* with the constancy of the speed of light led Einstein to many remarkable results concerning our ideas of space and time, and to modifications of Newtonian mechanics. We cannot here go through the details of Einstein's work because too much time would be needed. We can, however, state some of the theoretical results he obtained and see if they agree with experiment. It is, after all, the comparison between theory and experiment which is a chief test of the relativity theory, as it is with any other theory in physics.

The most striking results of the relativity theory appear for bodies moving at very high speeds, that is, at speeds that are not negligible compared to the speed of light. For bodies moving at speeds small compared to the speed of light, relativity theory yields the same results as Newtonian mechanics as nearly as we can measure. This must be the case because we know that Newton's laws account very well for the motion of the bodies with which we are familiar in ordinary life. We shall, therefore, look for differences between relativistic mechanics and Newtonian mechanics in experiments involving high-speed particles. For the purposes of this course the differences are presented as deviations from classical physics and in the language of classical physics. Relativity involves, however, a large shift in viewpoint and in ways of talking about physics.

We saw in Sec. 18.2 that J. J. Thomson devised a method for determining the speed v and the ratio of charge to mass q_e/m for electrons. Not long after the discovery of the electron by Thomson it was found that the value of q_e/m was not really constant, but varies with the speed of the electrons. Several physicists found, between 1900 and 1910, that electrons have the value $q_e/m = 1.76 \times 10^{11}$ coul/kg only for speeds that are very small compared to the speed of light; the ratio has smaller values for electrons with greater speeds. The relativity theory offered an explanation for these results. According to the theory of relativity, the electron charge does not depend on the speed of the electrons; but the mass of an electron should vary with speed, increasing according to the formula

See "Mr Tompkins and Simultaneity" in <u>Project Physics Reader 5</u>.

$$m = \frac{m_o}{\sqrt{1 - v^2/c^2}} .$$

See "Mathematics and Relativity" in <u>Project Physics Reader 5</u>.

In this formula, v is the speed of the electron, c is the speed of light in vacuum and m_o is the rest mass, the electron mass when the electron is not moving, that is, when $v = 0$. More precisely, m_o is the mass of the electron when it is at rest with respect to an observer, to the person doing the experiment; m is the mass of the electron measured while it moves with speed v relative to the observer. We may call m the <u>relativistic</u> mass. It is the mass determined, for example, by means of J. J. Thomson's method.

SG 20.1

The ratio of relativistic mass to rest mass, m/m_o, which is equal to $1/\sqrt{1 - v^2/c^2}$, is listed in Table 20.1 for values of v/c which approach unity. The value of m/m_o becomes very large as v approaches c.

See "Relativity" in <u>Project Physics Reader 5</u>.

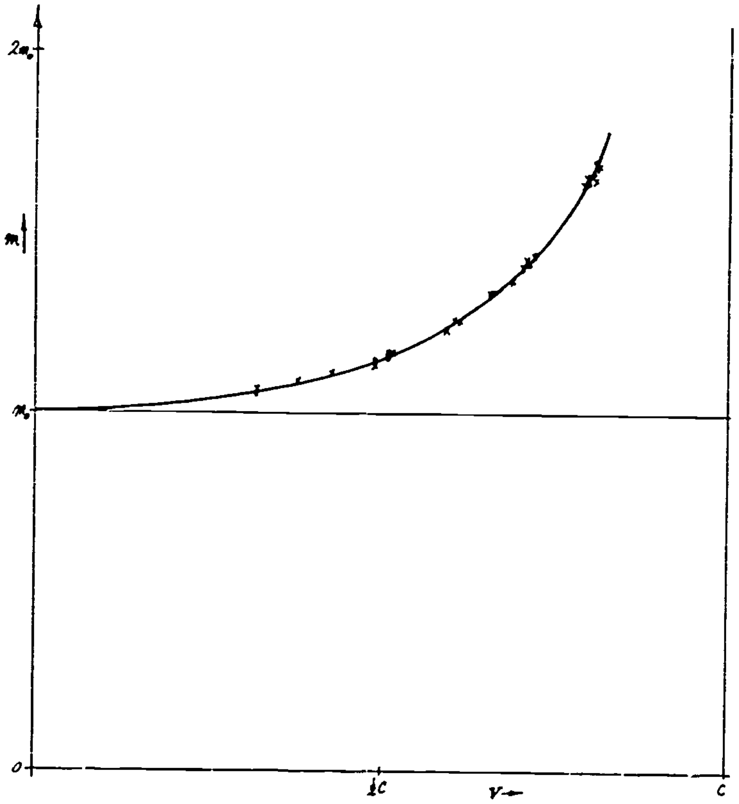
Table 20.1 The Relativistic Increase of Mass with Speed

v/c	m/m_o	v/c	m/m_o
0.0	1.000	0 95	3.203
0.01	1.000	0.98	5.025
0.10	1.005	0.99	7.089
0.50	1.155	0.998	15.82
0.75	1.538	0.999	22.37
0.80	1.667	0.9999	70.72
0.90	2.294	0.99999	223.6

See "Parable of the Surveyors" in <u>Project Physics Reader 5</u>.

See "Outside and Inside the Elevator" in <u>Project Physics Reader 5</u>.

The formula for the relativistic mass has been tested experimentally; some of the earlier results, for electrons with speeds so high that the value of v reaches about 0.8 c, are shown in the graph at the right. At that value of v the relativistic mass m is about 1.7 times the rest mass m_o. The curve shows the theoretical variation of m as the value of v increases, and the dots and crosses are results from two different experiments. The agreement of experiment and theory is excellent. The increase in mass with speed accounts for the shrinking of the ratio q_e/m with speed, which was mentioned earlier.



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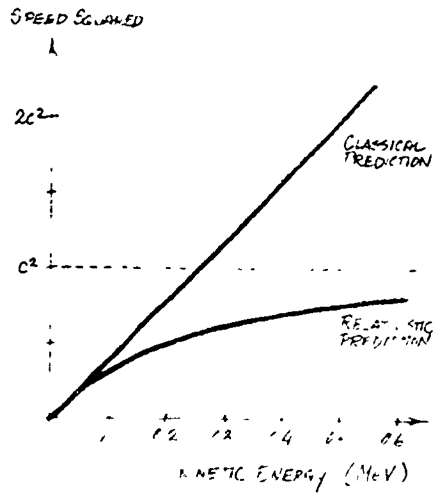
The theory of relativity says that the formula for variation of mass is valid for <u>all</u> moving bodies, not just electrons and other atomic particles. But larger bodies, such as those with which we are familiar in everyday life, move with speeds so small compared to that of light that the value of v/c is very small. The value of v^2/c^2 is then extremely small, and the values of m and m_o are so nearly the same that we cannot tell them apart. In other words, the relativistic increase in mass can be detected only for particles of sub-atomic size, which can move at very high speeds.

The effects discussed so far are mainly of historical interest because they helped convince physicists of the correctness of relativity theory. Experiments done more recently provide even more striking evidence of the breakdown of Newtonian physics for particles with very high speeds. Electrons can be given very high energies by accelerating them by means of a high voltage V. Since the electron charge is known, the energy increase, q_eV, is known. The rest mass m_o of an electron is also known (see Sec. 18.3) and the speed v can be measured. It is, therefore, possible to compare the values of the energy q_eV with $\frac{1}{2}m_ov^2$. When experiments of this kind are done, it is found that when the electrons have speeds that are small compared to the speed of light, $\frac{1}{2}m_ov^2 = q_eV$. We used this relation in discussing photoelectric effect. We could do so because photoelectrons do, indeed, have small speeds and m and m_o are very nearly identical for them. But, when the speed of the electron becomes large so that v/c is no longer small compared to 1.0, it is found that $\frac{1}{2}m_ov^2$ does not increase in proportion to q_eV; the discrepancy increases as q_eV increases. The increase in kinetic energy still equals the amount of electrical work done, q_eV, but some of the energy increase becomes measurable as the increase in mass instead of a marked increase in speed. The value of v^2, instead of steadily increasing with kinetic energy, approaches a limiting value: c^2.



In the Cambridge Electron Accelerator (CEA) operated in Cambridge, Massachusetts, by Harvard University and the Massachusetts Institute of Technology, electrons are accelerated in many steps to an energy which is equivalent to what they would gain in being accelerated by a potential difference of 6 × 10^9 volts—an enormous energy for electrons. (Unit 6 deals further with accelerators, and the operation of the CEA apparatus is also the subject of a movie "Synchrotron".) The speed attained by the electrons is

$v = 0.999999996\,c$; at this speed the relativistic mass m is over 10,000 times greater than the rest mass m_o!

Relativity theory leads to a new formula for kinetic energy, expressing it in terms of the increase in mass:

$$KE = (m - m_o)c^2$$

$$\text{or} \qquad KE = mc^2 - m_oc^2.$$

It can be shown in a few steps of algebra that $mc^2 - m_oc^2$ is almost exactly equal to $\frac{1}{2}m_ov^2$ when v is very small compared to c. But at very high speeds, $mc^2 - m_oc^2$ agrees with experimental values of the amount of work done on a particle and $\frac{1}{2}m_ov^2$ does not. Einstein gave the following interpretation of the terms in the relativistic formula for KE: mc^2 is the <u>total</u> energy of the particle, and m_oc^2 is an energy the particle has even when it is at rest:

$$\begin{array}{ccccc} KE & = & mc^2 & - & m_oc^2 \\ \text{kinetic energy} & = & \text{total energy} & - & \text{rest energy} \end{array}$$

The rest energy m_0c^2 includes the potential energy, if there is any. Thus a compressed spring has a somewhat larger rest mass and rest energy than the same spring when relaxed.

Or, putting it the other way around, the total energy E of a particle is the sum of its rest energy and its kinetic energy:

$$\begin{aligned} E &= mc^2 \\ &= m_oc^2 + KE. \end{aligned}$$

This equation, Einstein's mass-energy relation, has great importance in nuclear physics. It suggests that kinetic energy can be converted into rest mass, and rest mass into kinetic energy or radiation. In Chapters 23 and 24, we shall see how such changes come about experimentally, and see additional experimental evidence which supports this relationship.

SG 20.4

SG 20.5

The theory of relativity was developed by Einstein from basic considerations of the nature of space and time and of their measurement. He showed that the Newtonian (or classical) views of these concepts led to contradictions and had to be revised. The formulas for the variation of mass with speed and the mass-energy relation resulted from the logical development of Einstein's basic considerations. The predictions of the theory have been verified experimentally, and the theory represents a model, or view of the world, which is an improvement over the Newtonian model.

SG 20.6

SG 20.7

Q1 What happens to the measurable mass of a particle as its kinetic energy is increased?

Q2 What happens to the speed of a particle as its kinetic energy is increased?

20.2 Particle-like behavior of radiation. The first use we shall make of a result of relativity theory is in the further study of light quanta and of their interaction with atoms. The photoelectric effect taught us that a light quantum has energy hf, where h is Planck's constant and f is the frequency of the light. This concept also applies to x rays which, like visible light, are electromagnetic radiation, but of higher frequency. The photoelectric effect, however, didn't tell us anything about the momentum of a quantum. We may raise the question: if a light quantum has energy does it also have momentum?

The theory of relativity makes it possible for us to define the momentum of a photon. We start with the mass-energy relation for a particle, $E = mc^2$, and write it in the form:

$$m = \frac{E}{c^2}.$$

We may then speculate that the magnitude of the momentum p is

$$p = mv = \frac{E}{c^2}v.$$

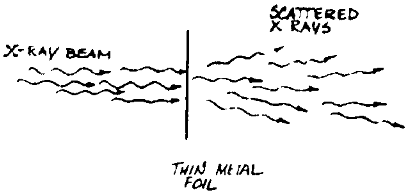
The last term is an expression for the momentum from which the mass has been eliminated. If this formula could be applied to a light quantum by setting the speed v equal to the speed of light c in the above equation, we would get

$$p = \frac{Ec}{c^2} = \frac{E}{c}.$$

Now, $E = hf$ for a light quantum, and if we substitute this expression for E in $p = E/c$, we would get for the momentum of a light quantum:

$$p = \frac{hf}{c}.$$

Does it make sense to define the momentum of a photon in this way? It does if the definition can be applied successfully to the interpretation of experimental results. The first example of the successful use of the definition was in the analysis of the Compton effect which will now be considered.

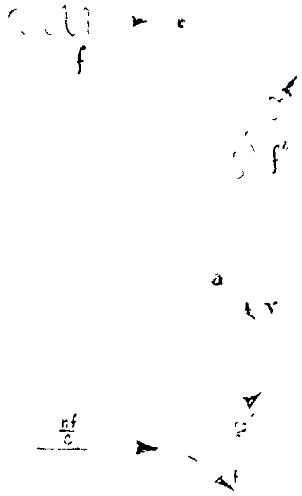


According to classical electromagnetic theory, when a beam of light (or x rays) strikes the atoms in a target (such as a thin sheet of metal), the light will be scattered in various directions but its frequency will not be changed. Light of a certain frequency may be absorbed by an atom, and light of another frequency may be emitted; but, if the light is simply scattered, there should be no change in frequency—provided that the classical wave theory is correct.

According to quantum theory, however, light is made up of photons. Compton reasoned that if photons have momentum, then in a collision between a photon and an atom the law of conservation of momentum should also apply. According to this law (see Chapter 10), when a body of small mass collides with a massive object, it simply bounces back or glances off with very little change in energy. But, if the masses of the two colliding objects are not very much different, a significant amount of energy can be transferred in the collision. Compton calculated how much energy a photon should lose in a collision with an atom, assuming that the energy and momentum of the photon are defined as hf and hf/c, respectively. The change in energy is too small to observe if a photon simply bounces off an entire atom. If, however, a photon strikes an electron, which has a small mass, the photon should transfer a significant amount of energy to the electron.

Arthur H. Compton (1892-1962) was born in Wooster, Ohio and graduated from the College of Wooster. After receiving his doctor's degree in physics from Princeton University in 1916, he taught physics and then worked in industry. In 1919-1920 he did research under Rutherford at the Cavendish Laboratory of the University of Cambridge. In 1923, while studying the scattering of x rays, he discovered and interpreted the changes in the wavelengths of x rays when the rays are scattered. He received the Nobel Prize in 1927 for this work.

In experiments up to 1923, no difference had been observed between the frequencies of the incident and scattered light (or x rays) when electromagnetic radiation was scattered by matter. In 1923 Compton, using improved experimental techniques, was able to show that when a beam of x rays of a given frequency is scattered, the scattered beam consists of two parts: one part has the same frequency as the incident x rays; the other part has slightly lower frequency. This reduction in frequency of some of the scattered x rays is called the Compton effect. The change of frequency corresponds to a transfer of energy from photons to electrons in accordance with the laws of conservation of momentum and energy. The observed change in frequency is just what would be predicted if the photons were particles having momentum $p = \frac{hf}{c}$. Furthermore, the electrons which were struck by the photons could also be detected, because they were knocked out of the target. Compton found that the momentum of these electrons was just what would be expected if they had been struck by a particle with momentum $p = \frac{hf}{c}$.



Compton's experiment showed that a photon can be regarded as a particle with a definite momentum as well as energy; it also showed that collisions between photons and electrons obey the laws of conversation of momentum and energy.

Photons act much like particles of matter, having momentum as well as energy; but they also act like waves, having frequency and wavelength. In other words, the behavior of electromagnetic radiation is sometimes similar

20 3

to what we are used to thinking of as particle behavior and sometimes similar to what we are used to thinking of as wave behavior. This behavior is often referred to as the wave-particle dualism of radiation. The question, "Is a photon a wave or a particle?" can only be answered: it may not be either, but can appear to act like either, depending on what we are doing with it.

How does the momentum of a photon depend on the frequency of the light?

What did the Compton effect prove?

20.3 Wave-like behavior of matter.

In 1924, a French physicist, Louis de Broglie, suggested that the wave-particle dualism which applies to radiation might also apply to electrons and other atomic particles. Perhaps, he said, this wave-particle dualism is a fundamental property of all quantum processes, and what we have always thought of as material particles sometimes act like waves. He then sought an expression for the wavelength of an electron and found one by means of a simple argument.

We start with the formula for the magnitude of the momentum of a photon,

$$p = \frac{hf}{c}.$$

The speed and frequency of a photon are related to the wavelength by the relation

$$c = f\lambda,$$

$$\text{or} \qquad \frac{f}{c} = \frac{1}{\lambda}$$

If we replace $\frac{f}{c}$ in the momentum equation by $\frac{1}{\lambda}$, we get:

$$p = \frac{h}{\lambda},$$

$$\text{or} \qquad \lambda = \frac{h}{p}.$$

The de Broglie wavelength of a material particle does not refer to light, but to some new wave property associated with the motion of matter itself.

De Broglie suggested that this relation, derived for photons, would also apply to electrons with the momentum $p = mv$. He, therefore, wrote for the wavelength of an electron:

$$\lambda = \frac{h}{mv},$$

SG 20.4

where m is the mass of the electron and v its speed.

What does it mean to say that an electron has a wavelength equal to Planck's constant divided by its momentum? If this statement is to have any physical meaning, it must be possible to test it by some kind of experiment. Some wave property of the electron must be measured. The first such property to be measured was diffraction.

By 1920 it was known that crystals have a regular lattice structure; the distance between rows or planes of atoms in a crystal is about 10^{-10}m. After de Broglie proposed his hypothesis that electrons have wave properties, several physicists suggested that the existence of electron waves might be shown by using crystals as diffraction gratings. Experiments begun in 1923 by C. J. Davisson and L. H. Germer in the United States, yielded diffraction patterns similar to those obtained for x rays, as illustrated in the two drawings at the left below. The experiment showed not only that electrons do have wave properties, but also that their wavelengths are correctly given by de Broglie's relation, $\lambda = h/mv$. These results were confirmed in 1927 by G. P. Thomson, who directed an electron beam through thin gold foil to produce the more familiar type of diffraction pattern like the one at the right in the margin. By 1930, diffraction from crystals had been used to demonstrate the wave-like behavior of helium atoms and hydrogen molecules, as illustrated in the drawing at the right below.

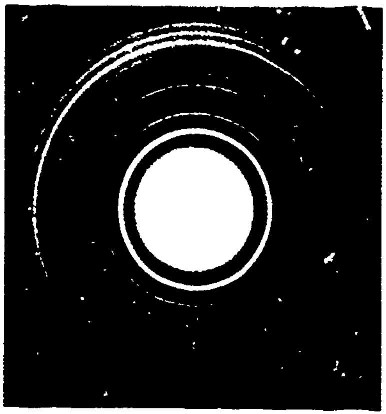
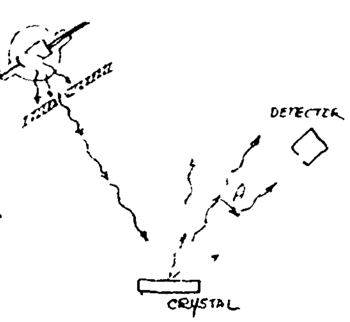
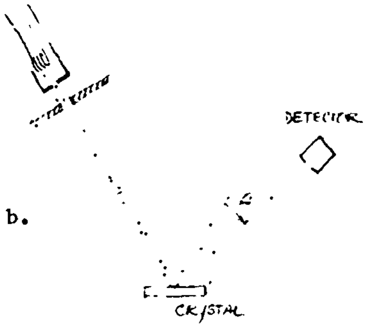
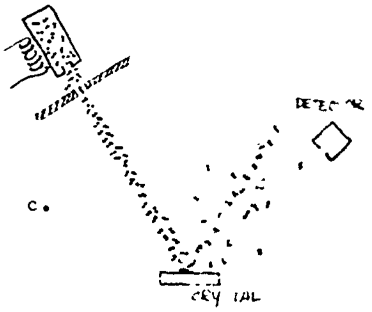


Fig. 20.3 Diffraction pattern produced by directing a beam of electrons through polycrystalline aluminum. With a similar pattern, G.P. Thomson demonstrated the wave properties of electrons—28 years after their particle properties were first demonstrated by J.J. Thomson, his father.



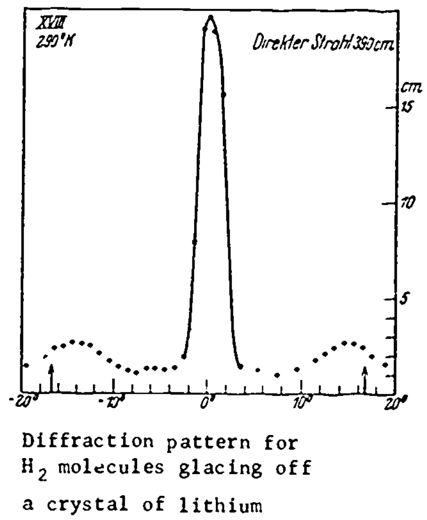




a. One way to demonstrate the wave behavior of x rays is to direct a beam at the surface of a crystal. The reflections from different planes of atoms in the crystal interfere to produce reflected beams at angles other than the ordinary angle of reflection.

b. A very similar effect can be demonstrated for a beam of electrons. The electrons must be accelerated to an energy that corresponds to a deBroglie wavelength of about 10^{-10} m (which requires an accelerating voltage of only about 100 volts).

c. More surprisingly still, a beam of molecules directed at a crystal will show a similar diffraction pattern. The diagram above shows how a beam of hydrogen molecules (H_2) can be formed by slits at the opening of a heated chamber; the average energy of the molecules is controlled by adjusting the temperature of the oven. The graph, reproduced from Zeitschrift für Physik, 1930, shows results obtained by I. Estermann and O. Stern in Germany. The detector reading is plotted against the deviation to either side of angle of ordinary reflection.



Diffraction pattern for H_2 molecules glacing off a crystal of lithium fluoride.

The de Broglie wavelength: examples.

A body of mass 1 kg moves with a speed of 1 m/sec. What is its de Broglie wavelength?

$$\lambda = \frac{h}{mv}$$

$$h = 6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

$$mv = 1 \text{ kg}\cdot\text{m/sec}$$

$$\lambda = \frac{6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}}{1 \text{ kg}\cdot\text{m/sec}},$$

or

$$\lambda = 6.6 \times 10^{-34} \text{ m.}$$

The de Broglie wavelength is much too small to be detected. We would expect to detect no wave aspects in the motion of this body.

An electron of mass 9.1×10^{-31} kg moves with a speed of 2×10^{6} m/sec. What is its de Broglie wavelength?

$$\lambda = \frac{h}{mv}$$

$$h = 6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

$$mv = 1.82 \times 10^{-24} \text{ kg}\cdot\text{m/sec}$$

$$\lambda = \frac{6.6 \times 10^{-34} \text{ joule}\cdot\text{sec}}{1.82 \times 10^{-24} \text{ kg}\cdot\text{m/sec}},$$

or

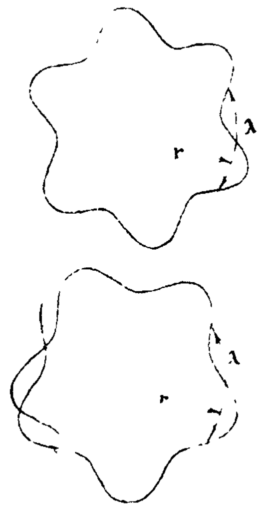
$$\lambda = 3.6 \times 10^{-10} \text{ m.}$$

The de Broglie wavelength is of atomic dimensions; for example, it is of the same order of magnitude as the distances between atoms in a crystal. We would expect to see wave aspects in the interaction of electrons with crystals.

SG 20.12
SG 20.13

According to de Broglie's hypothesis, which has been confirmed by these experiments, wave-particle dualism is a general property not only of radiation but also of matter. It is now customary to use the word "particle" to refer to electrons and photons while recognizing that they both have properties of waves as well as of particles.

Fig. 20.4 Only certain wavelengths will "fit" around a circle.



De Broglie's relation, $\lambda = \frac{h}{mv}$, has an interesting yet simple application which makes more reasonable Bohr's postulate that the angular momentum of the electron in the hydrogen atom can only have certain values. Bohr assumed that the angular momentum can have only the values:

$$mvr = n\,\frac{h}{2\pi}, \text{ where } n = 1, 2, 3, \ldots$$

Now, suppose that an electron wave is somehow spread over an orbit of radius r—that, in some sense, it "occupies" an orbit of radius r. We may ask if standing waves can be set up as indicated, for example, in Fig. 20.4. The condition for such standing waves is that the circumference of the orbit is equal in length to a whole number of wavelengths, that is, to $n\lambda$. The mathematical expression for this condition is:

$$2\pi r = n\lambda.$$

If we now replace λ by $\frac{h}{mv}$, according to de Broglie's relation, we get

$$2\pi r = n\frac{h}{mv},$$

or

$$mvr = n\frac{h}{2\pi}.$$

But, this is just Bohr's quantization condition! The de Broglie relation for electron waves allows us to derive the quantization that Bohr had to assume.

The result obtained indicates that we may picture the electron in the hydrogen atom in two ways: either as a particle moving in an orbit with a certain angular momentum, or as a standing de Broglie type wave occupying a certain region around the nucleus.

Q5 Where did de Broglie get the relation $\lambda = \frac{h}{mv}$ for electrons?

Q6 Why were crystals used to get diffraction patterns of electrons?

20.4 Quantum mechanics. The proof that things (electrons, atoms, molecules) which had been regarded as particles also show properties of waves has served as the basis for the currently accepted theory of atomic structure. This theory, quantum mechanics, was introduced in 1925; it was developed with great rapidity during the next few years, primarily by Heisenberg, Born, Schrödinger, Bohr and Dirac. The theory appeared in two different mathematical forms proposed independently by Heisenberg and Schrödinger. These two forms were shown by Dirac to be equivalent. The form of the theory that is closer to the ideas of de Broglie, discussed in the last section, was that of Schrödinger. It is often referred to as "wave mechanics."

Schrödinger sought to express the dual wave and particle nature of matter mathematically by means of a wave equation. Maxwell had formulated the electromagnetic theory of light in terms of a wave equation, and physicists were familiar with this theory and its applications. Schrödinger reasoned that a wave equation for electrons would have to resemble the wave equation for light, but would have to include Planck's constant to permit quantum effects. Now, the equations we are talking about are not algebraic equations. They involve higher mathematics and are called "differential equations." We cannot discuss this mathematical part of wave mechanics, but the physical ideas involved require only a little mathematics and are essential to an understanding of modern physics. So, in the rest of

Paul Adrien Maurice Dirac (1902-), an English physicist, was one of the developers of modern quantum mechanics. His relativistic theory of quantum mechanics (1930) was the first indication that "anti-particles" exist, such as the positron. He shared the Nobel Prize for physics in 1933 with Schrödinger. In 1932, at the age of 30, Dirac was appointed Lucasian Professor of Mathematics at Cambridge University, the post held by Newton.

Max Born (1882-) was born in Germany, but left that country in 1933 when Hitler and the Nazis gained control. Born was largely responsible for introducing the statistical interpretation of wave mechanics. From 1933 to 1953, when he retired, he worked at Cambridge, England and Edinburgh, Scotland. He was awarded the Nobel Prize in physics in 1954.

Prince Louis Victor de Broglie (1892-) comes of a noble French family. His ancestors served the French kings as far back as the time of Louis XIV. He was educated at the Sorbonne in Paris, served as a radio specialist in World War I, and was awarded the Nobel Prize in physics in 1929.

Werner Karl Heisenberg (1901 -), a German physicist, was one of the developers of modern quantum mechanics (at the age of 23). He discovered the uncertainty principle, and after the discovery of the neutron in 1932, proposed the proton-neutron theory of nuclear constitution. He was awarded the Nobel Prize in physics in 1932. During World War II, Heisenberg was in charge of German research of the application of nuclear energy.

Erwin Schroedinger (1887-1961) was born in Austria. After service in World War I, he became a professor of physics in Germany. He developed wave mechanics in 1926, left Germany in 1933 when Hitler and the Nazis came to power. From 1940 to 1956, when he retired, he was professor of physics at the Dublin Institute for Advanced Studies. He shared the Nobel Prize in physics with Dirac in 1933 for his work on wave mechanics.

this chapter, we shall discuss some of the physical ideas of the theory to try to make them seem plausible, and we shall consider some of the results of the theory and some of the implications of these results.

Schrodinger was successful in deriving an equation for the motions of electrons. This equation, which has been named after him, defines the wave properties of electrons and also includes their basic particle aspects. The mathematical solution of the Schrodinger equation shows that only certain electron energies are possible in an atom. For example, in the hydrogen atom, the single electron can only be in those states for which the energy of the electron has the values:

$$E_n = -\frac{2\pi^2 m q_e^4}{n^2 h^2},$$

with n having only whole number values. These values of the energies are just the ones given by the Bohr theory. But, in Schrödinger's theory, this result follows directly from the mathematical formulation of the wave and particle nature of the electron. The existence of these stationary states has not been assumed, and no assumptions have been made about orbits. The new theory yields all the positive results of the Bohr theory without having any of the inconsistent hypotheses of the earlier theory. The new theory also accounts for the experimental information for which the Bohr theory failed to account.

See "The New Landscape of Science" in Project Physics Reader 5.

On the other hand, quantum mechanics does not supply a physical model or picture of what is going on inside the atom. The planetary model of the atom has had to be given up, and has not been replaced by another simple picture. There is now a highly successful mathematical model, but no easily understood physical model. The concepts used to build quantum mechanics are more abstract than those of the Bohr theory; it is hard to get an intuitive feeling for atomic structure. But the mathematical theory of quantum mechanics is much more powerful than the Bohr theory, and many problems have been solved with quantum mechanics that were previously unsolvable. Physicists have learned that the world of atoms, electrons and photons cannot be thought of in the same mechanical terms as the world of everyday experience. In fact the world of atoms has presented us with some new and fascinating concepts which will be discussed in the next two sections.

The set of energy states of hydrogen could be derived from Bohr's postulate of quantized angular momentum. Why was the derivation from Schrodinger's equation so much better?

Quantum (or wave) mechanics has had great success. What is its major drawback?

20.5 Quantum mechanics - the uncertainty principle. The success of wave mechanics emphasizes the fundamental importance of the dual wave-and-particle nature of radiation and matter. The question now arises of how a particle can be thought of as "really" having wave properties. The answer is that invisible matter of the kinds involved in atomic structure doesn't have to be thought of as "really" being either particles or waves. Our ideas of waves and particles are taken from the world of visible things and may just not apply on the atomic scale. The suitability of applying wave and particle concepts to atomic problems has to be studied and its possible limitations determined.

See "Dirac and Born" in Project Physics Reader [illegible].

When we try to describe something that no one has ever seen or can ever see directly, it is questionable whether the concepts of the visible world can be taken over [illegible]. It appeared natural before 1925 to try to talk about the transfer of energy in either wave terms or particle terms, because that was all physicists knew and understood at the time. No one was prepared to find that both wave and particle descriptions could apply to light and to matter. But this dualism cannot be wished away, because it is based on experimental results

If we didn't feel uncomfortable with the dualism, we could just accept it as a fact of nature and [illegible] there. But, scientists were as uncomfortable with the dualism as you undoubtedly are, and searched for a way out of the situation. Because there is no argument with the facts, the way out has to be with our view of nature, our [illegible] scientists. To look for this way we shall describe some experiments which show up a fundamental limitation on our ability to describe phenomena. Following that, we shall give a simplified version of the present view of physics, concerning the wave-particle dualism.

Max Born, one of the founders of quantum mechanics, has written: "The ultimate origin of the difficulty lies in the fact (or philosophical principle) that we are compelled to use the words of common language when we wish to describe a phenomenon, not by logical or mathematical analysis, but by a picture appealing to the imagination. Common language has grown by everyday experience and can never surpass these limits. Classical physics has restricted itself to the use of concepts of this kind; by analyzing visible motions it has developed two ways of representing them by elementary processes: moving particles and waves. There is no other way of giving a pictorial description of motions—we have to apply it even in the region of atomic processes, where classical physics breaks down."

Up to this point we have always talked as if we could measure any physical property as accurately as we pleased, if not in the laboratory at least in our own [illegible] in which ideal instruments could be "used." Wave mechanics shows that, even in thought experiments, there are limitations on the accuracy with which atomic measurements may be made.

20.5

Suppose we want to measure the position and velocity of a car; and let us suppose that the car's position is to be measured from the end of a garage. The car moves slowly out of the garage along the driveway. We mark the position of the front end of the car at a given instant by making a scratch on the ground; at the same time, we start a stopwatch. Then we run to the far end of the driveway, and at the instant that the front end of the car reaches another mark on the ground we stop the watch. We then measure the distance between the marks and get the average speed of the car by dividing the distance traversed by the time elapsed. Since we know the direction of the car's motion, we know the average velocity. Thus we know that at the moment the car reached the second mark it was at a known distance from its starting point and had traveled at a known <u>average velocity</u>.

How did we get this information? We could locate the position of the front end of the car because sunlight bounced off the front end into our eyes and permitted us to see when the car reached a certain mark on the ground. To get the average speed we had to locate the front end twice.

$$\lambda = \frac{c}{f} = \frac{3 \times 10^8 \text{ m/sec}}{10^6\text{/sec}} = 300 \text{ m.}$$

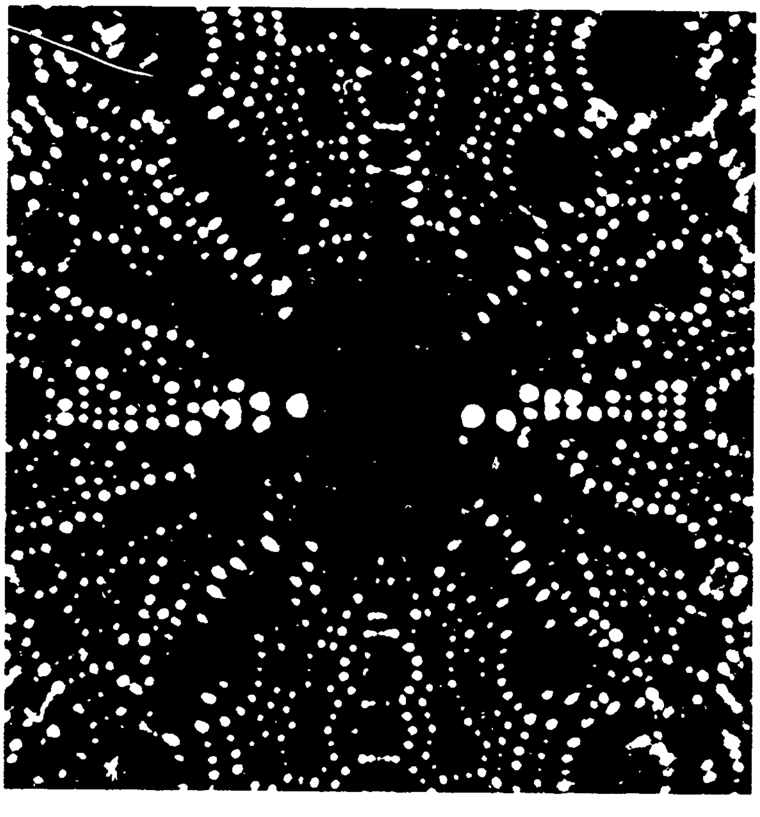
Note that we used sunlight in our experiment. Suppose that we had decided to use radio waves instead of light of visible wavelength. At 1000 kilocycles per second, a typical value for radio signals, the wave length is 300 meters. With radiation of this wavelength, which is very much greater than the dimensions of the car, it is impossible to locate the car with any accuracy, because the wavelength has to be comparable with or smaller than the dimensions of the object before the object can be located. <u>Radar</u> uses wavelengths from 3 cm to about 0.1 cm. Hence a radar apparatus could have been used instead of sunlight, but radar waves much longer than 3 cm would result in appreciable uncertainty about the positions and average speed of the car.

Let us now replace the car, driveway and garage by an electron leaving an electron gun and moving across an evacuated tube. We try to measure the position and speed of the electron. But some changes have to be made in the method of measurement. The electron is so small that we cannot locate its position by using visible light. The reason is that the wavelength of visible light is at least 10^4 times greater than the diameter of an atom.

To locate an electron within a region the size of an atom (10^{-10} m) we must use a light beam whose wavelength is comparable to the size of the atom, if not much smaller. Otherwise we will be uncertain about the position by an

The extreme smallness of the atomic scale is indicated by these pictures made with techniques that give the very limits of magnification—about 10,000,000 times in this reproduction.

Electron micrograph of a section of a single gold crystal. The entire section of crystal shown is only 100Å across—smaller than the shortest wavelength of ultraviolet light that could be used in a light microscope. The finest detail that can be resolved is just under 2Å, so that the layers of gold atoms (spaced slightly more than 2Å) show as a checked pattern; individual atoms are beyond the resolving power.



Field-ion micrograph of the tip of a microscopically thin tungsten crystal. As above, the entire section shown is only about 100Å across. The bright spots indicate the locations of atoms along edges of the crystal, but should not be thought of as pictures of the atom.

amount many times greater than the diameter of the electron. Now a photon of such a wavelength has a very great energy and momentum; and, from our study of the Compton effect, we know that the photon will give the electron a strong kick. As a result, the velocity of the electron will be seriously changed, and in an unknown direction. Hence, although we have "located" the electron, we have altered its velocity (both in magnitude and direction). To say this more directly: the more accurately we locate the electron (by using photons of shorter wavelength) the less accurately we can know its velocity. If we try to disturb the electron less by using less energetic (longer wavelength) photons, we lose resolving power and acquire a greater uncertainty in the position of the electron. To summarize: we are unable to measure both the position and velocity of an electron to a prescribed accuracy. This conclusion is known as the uncertainty principle, and was discovered by Heisenberg. The uncertainty principle can be expressed quantitatively in a simple formula. If Δx is the uncertainty in position, and Δp is the uncertainty in momentum, then the product of the two must be equal to, or greater than, Planck's constant divided by 2π:

$$(\Delta x)(\Delta p) \geq \frac{h}{2\pi}$$

[illegible]
SG 20.5
[illegible]

The same reasoning holds for the car, but the limitation is of no practical consequence with such a massive object. It is only in the atomic world that the limitation is important.

Q9 If light photons used in finding the velocity of an electron disturb the electron too much, why can't the observation be improved by using weaker photons?

Q10 If the wavelength of light used to locate a particle is too long, why can't the location be found more precisely by using light of shorter wavelength?

20.6 Quantum mechanics - probability interpretation.

The way in which physicists now think about the dualism involves the idea of probability. Even in situations in which no single event can be predicted with certainty, it may still be possible to make predictions of the statistical probabilities of certain events. For example, automobile manufacturers don't know which 8 million people will buy cars this year. But they do know that about that many people will find need for a new car. Similarly, on a holiday weekend during which perhaps 25 million cars are on the road, the statisticians report a high probability that about 600 people will be killed in accidents. It isn't known which cars in which of

The uncertainty principle: examples.

A *large* mass.

Consider a car, with a mass of 1000 kg, moving with a speed of about 1 m/sec. Suppose that the uncertainty Δv in the speed is 0.1 m/sec (10% of the speed). What is the uncertainty in the position of the car?

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

$$\Delta p = m\Delta v = 100 \text{ kg}\cdot\text{m/sec}$$

$$h = 6.63 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

$$\Delta x \geq \frac{6.63}{6.28} \times \frac{10^{-34} \text{ joule}\cdot\text{sec}}{10^{2} \text{ kg}\cdot\text{m/sec}}$$

or

$$\Delta x \geq 1 \times 10^{-36} \text{ m.}$$

The uncertainty in position is much too small to be observable. In this case we can determine the position of the body with as high an accuracy as we would ever need.

A *small* mass.

Consider an electron, with a mass of 9.1×10^{-31} kg, moving with a speed of about 2×10^{6} m/sec. Suppose that the uncertainty Δv in the speed is 0.2×10^{6} m/sec (10% of the speed). What is the uncertainty in the position of the electron?

$$\Delta x \Delta p \geq \frac{h}{2\pi}$$

$$\Delta p = m\Delta v = 1.82 \times 10^{-25} \text{ kg}\cdot\text{m/sec}$$

$$h = 6.63 \times 10^{-34} \text{ joule}\cdot\text{sec}$$

$$\Delta x \geq \frac{6.63}{6.28} \times \frac{10^{-34} \text{ joule}\cdot\text{sec}}{1.82 \times 10^{-25} \text{ kg}\cdot\text{m/sec}},$$

or

$$\Delta x \geq 5 \times 10^{-10} \text{ m.}$$

The uncertainty in position is of the order of atomic dimensions, and is significant in atomic problems.

The reason for the difference between these two results is that Planck's constant h is very small: so small that the uncertainty principle becomes important only on the atomic scale.

The main use of the uncertainty principle is in *general* arguments in atomic theory rather than in particular numerical problems. We don't really need to know exactly where an electron is, but we sometimes want to know if it *could* be in some *region* of space.

the 50 states will be the ones involved in the accidents, but the average behavior is still quite accurately predictable.

It is in this way that physicists think about the behavior of photons and material particles. As we have seen, there are fundamental limitations on our ability to describe the behavior of an individual particle. But the laws of physics often enable us to describe the behavior of large collections

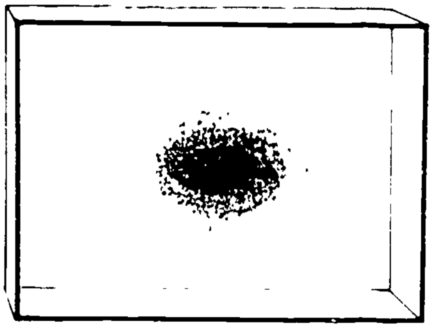
See "The Fundamental Idea of Wave Mechanics" in *Project Physics Reader 5*.

Probability in Quantum Mechanics

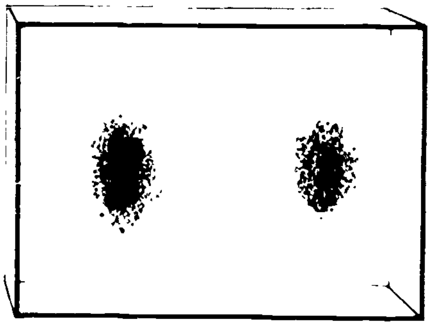
We have already described how probabilities were used in the kinetic theory of gases (Chapter 11). Because a gas contains so many molecules—more than a billion billion in each cubic centimeter of the air we breathe—it is impractical to calculate the motion of each molecule. Instead of applying Newton's laws to trace the paths of these molecules the scientists who developed the kinetic theory assumed that the net effect of all of the collisions among molecules would be a random, disordered motion that could be treated statistically. In the kinetic theory a gas is described by stating its average density and average kinetic energy, or, where more detail is wanted, by showing the relative numbers of molecules with different speeds.

Probability is used in a different way in quantum theory. The description of a single molecule or a single electron is given in terms that yield only statistical predictions. Thus quantum mechanics predicts the probability of finding a single electron in a given region. The theory does not specify the position and the velocity of the electron, but the probability of its having certain positions and certain velocities. The theory asserts that to ask for the precise position and velocity of a particle is to demand the unknowable.

As an example, consider the case of a particle confined to a box with rigid sides. According to classical mechanics the path of the particle can be traced from a knowledge of its position and velocity at some instant. Only if we introduce a large number of particles into the box is there a need to use probabilities.

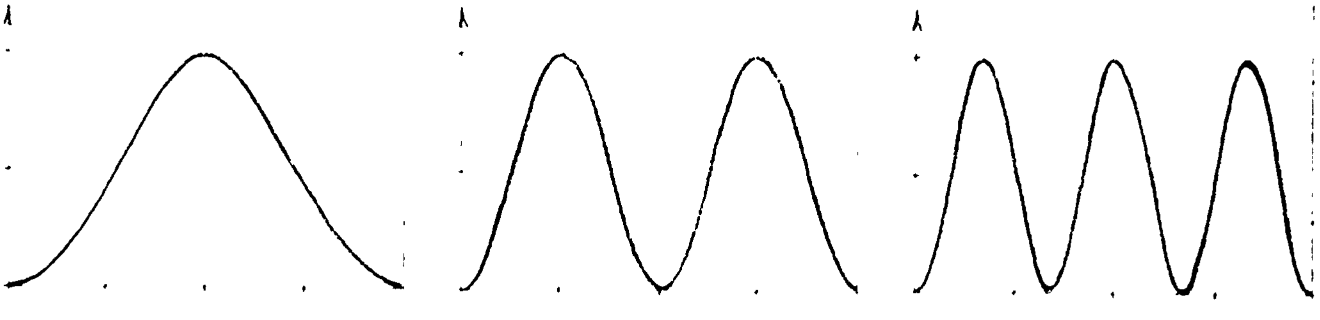


The quantum mechanical treatment of a single particle confined to a box is much different. It is not possible, according to the theory, to describe the particle as moving from one point to another within the box; only the probability of detecting the particle at various regions can be predicted. Moreover, the theory indicates that the particle is limited to certain discrete values of kinetic energy. The way the probability of finding the particle varies from point to point within the box depends on the energy. For example, in the lowest possible energy state the particle has the probability distribution indicated by the shading in the top drawing at the left; the darker the shading, the greater the probability of the particle's being there. The probability falls to zero at the sides of the box. The lower drawing at the left represents the probability distribution for the second energy level; notice that the probability is zero also for the particle to be on the center line.

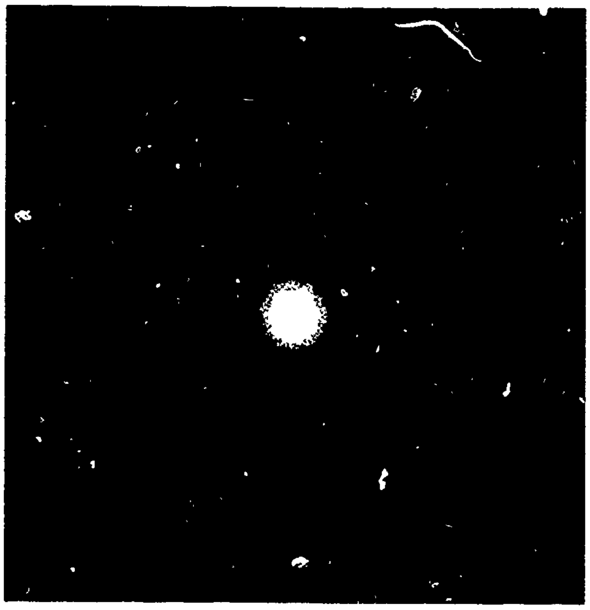


As these drawings suggest, the probability distributions are the same as the intensity of standing waves that have nodes on the faces of the box. The standing wave intensity patterns for three of the lower energy levels are graphed below. The momentum and kinetic energy of the electron are connected to the wavelength of the standing waves through the deBroglie relations: $p = h/\lambda$ and $KE = h^2/2m\lambda^2$. Since only certain wavelengths can be fitted into the box, the particle can have only certain values of momentum and energy.

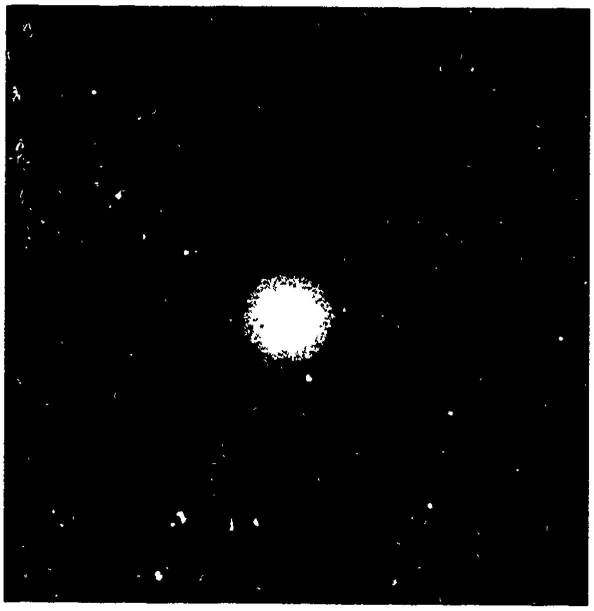
This quantum effect of discrete energy levels will occur, in theory, for any confined particle. Yet for a particle large enough to be seen with a microscope there does not appear to be any lower limit to its energy or any gaps in possible values of its energy. This is because the energy for the lowest state of such a particle is immeasurably small and the separation of measurably larger energies is also immeasurably small. The existence of discrete energy states can be demonstrated experimentally only for particles of very small mass confined to very small regions—that is, particles on the atomic scale.



Nowhere is the discreteness of energy states more pronounced than for electrons bound in atoms. The electron mass is extremely small and an atom makes an extremely small "box." There is thus clearly a lower limit to the energy of an electron in an atom and there are distinct gaps between energy levels.

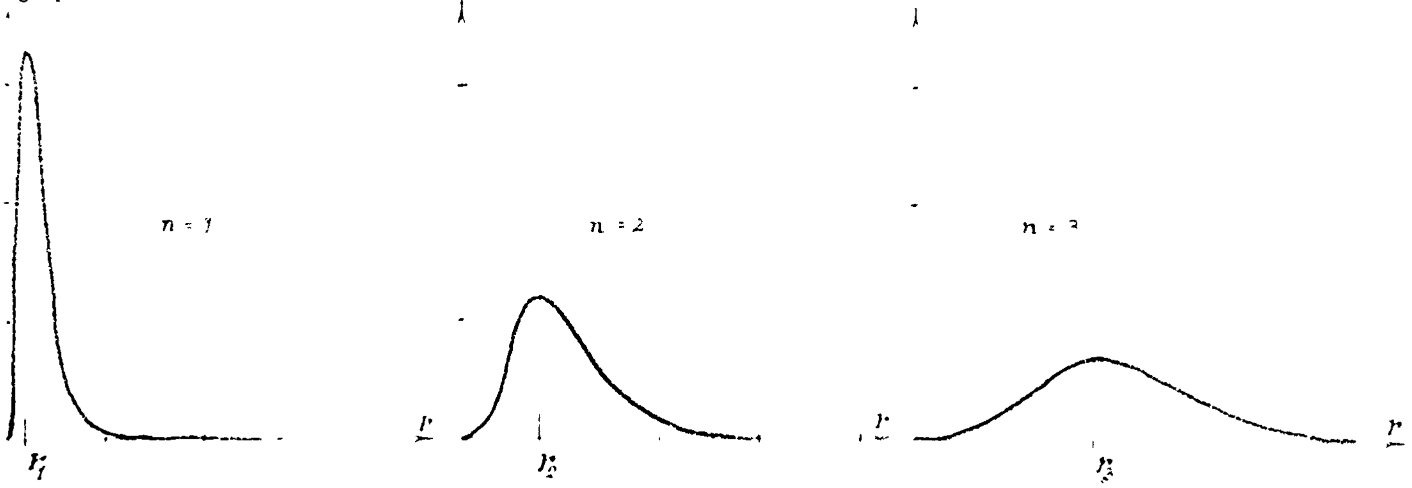


According to modern quantum theory, the hydrogen atom does not consist of a localized negative particle moving around a nucleus as in the Bohr model. Indeed, the theory does not provide any picture of the hydrogen atom. However, quantum theory does yield probability distributions similar to those on the preceding page. A description of this probability distribution is the closest thing that the theory provides to a picture. The probability distribution for the lowest energy state of the hydrogen atom is represented in the upper drawing at the right, where whiter shading at a point indicates greater probability. The probability distribution for a higher energy state, still for a single electron, is represented in the lower drawing at the right.



Quantum theory is, however, not really concerned with the position of any individual electron in any individual atom. Instead, the theory gives a mathematical representation that can be used to predict interaction with particles, fields and radiation. For example, it can be used to calculate the probability that hydrogen will emit light of a particular wavelength; the intensity and wavelength of light emitted by a large number of hydrogen atoms can then be compared with these calculations. Comparisons such as these have shown that the theory agrees with experiment.

Although the atom of modern quantum mechanics differs fundamentally from the Bohr model, there are points of correspondence between the two theories. The probability of finding the electron somewhere on a sphere at a distance r from the nucleus is plotted for the lowest energy state of the hydrogen atom at the left below. The most probable distance (r_1) is equal to the radius of the electron orbit given by the Bohr theory. The same correspondence occurs for higher energy states, as shown in the other two graphs.

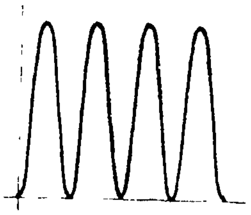


of particles with high accuracy. The solutions of the Schrödinger equation give us the probabilities for finding the particles at a given place at a given time.

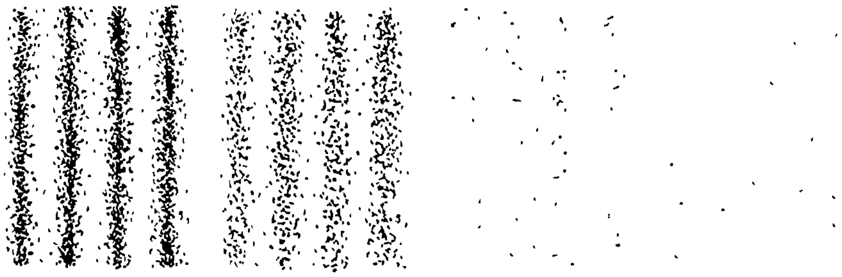
To see how probability enters the picture we shall first examine a well-known problem from the point of view of waves. Then we shall examine the same situation from the point of view of particles.

Imagine a television screen with a stream of electrons scanning it. The electron waves from the gun cover the screen with varying intensities to make the picture pattern. If the overall intensity of the waves is reduced by reducing the flow of electrons from the gun, the wave theory predicts that the picture pattern will remain, but that the entire picture will be fainter. If we were actually to do this experiment, we would find that, as the intensity becomes very weak, the picture pattern fades into a collection of separate faint flashes scattered over the screen. The naked eye is not sensitive enough to see the scattered flashes.

The waves give us the probability of finding electrons at various places at various times. If the number of electrons is small, the prediction becomes very poor. We can predict with any accuracy only the average behavior of large numbers of electrons.



This graph for a pattern of stripes would be interpreted in a wave model as the relative wave intensity, and in a particle model as the relative probability of a particle arriving.



A similar analysis holds for photons and their associated light waves. If light waves are projected onto a movie screen, the pattern is similar for all light intensities which give large numbers of photons. If the projector's light bulb is screened or otherwise reduced in intensity so that the light is extremely weak, the pattern falls apart into a collection of flashes. Here, too, the wave gives the probability of finding photons at various places at various times, and this probability gives us the correct pattern for large numbers of photons.

If a camera were pointed at the screen and the shutter left open for long enough time so that many photons (or electrons, in the previous example) arrived at the screen, the resultant picture would be a faithful reproduction of the high intensity picture. Even though individual particles arrive at random places on the screen, the rate at which they arrive doesn't affect the final result provided that we wait until the number that has finally arrived is very large. SG 20 19

We see then that we can deal only with the average behavior of atomic particles; the laws governing this average behavior turn out to be those of wave mechanics. The waves, it seems, are waves of probability. The probability that a particle will have some position at a given time travels through space in waves which interfere with each other in exactly the same way that water waves do. So, for example, if we think of electron paths crossing each other, we consider the electrons to be waves and compute the interference patterns which determine the directions in which the waves will be going after they have passed each other. Then, as long as there is no more interaction of the waves with matter, we can return to our description in terms of particles and say that the electrons end up going in such and such directions with such and such speeds. SG 20 20

We quote Max Born who was the originator of the probability interpretation of the wave-particle dualism:

> Every process can be interpreted either in terms of corpuscles or in terms of waves, but...it is beyond our power to produce proof that it is actually corpuscles or waves with which we are dealing, for we cannot simultaneously determine all the other properties which are distinctive of a corpuscle or of a wave, as the case may be. We can, therefore, say that the wave and corpuscular descriptions are only to be regarded as complementary ways of viewing one and the same objective process....

SG 20 21

Despite the successes of the idea that the wave represents the probability of finding its associated particle in some specific condition of motion, many scientists found it hard to accept the idea that men cannot know exactly what any one particle is doing. The most prominent of such disbelievers was Einstein. In a letter to Born written in 1926, he remarked, SG 20 22

> The quantum mechanics is very imposing. But an inner voice tells me that it is still not the final truth. The theory yields much, but it hardly brings us nearer to the secret of the Old One. In any case, I am convinced that He does not throw dice.

Thus, Einstein refused to accept probability-based laws as final in physics, and here for the first time he spoke of the dice-playing God—an expression he used many times later as he expressed his belief that there are deterministic laws yet to be found. Despite the refusal of Einstein (and others) to accept probability laws in mechanics, neither he nor any other physicist has succeeded in replacing Born's probability interpretation of quantum mechanics.

Scientists agree that quantum mechanics works; it gives the right answers to many questions in physics, it unifies ideas and occurrences that were once unconnected, and it has been wonderfully productive of new experiments and new concepts. On the other hand, there is less agreement about the significance of quantum theory. Quantum theory yields probability functions, not particle trajectories. Some scientists see in this aspect of the theory an important revelation about the nature of the world; for other scientists this same fact indicates that quantum theory is incomplete. Some in this second group are trying to develop a more basic, non-statistical theory for which the present quantum theory is only a limiting case. There is no doubt that quantum theory has profoundly influenced man's views of nature. It would be a mistake to assume that quantum mechanics provides some sort of ultimate physical theory, although up to this time no one has developed a successful nonstatistical theory of atomic and nuclear physics.

Finally, it must be stressed again that effects which are completely unnoticeable because of the large masses of the visible world are very important for the small particles of the atomic world. The simple concepts (such as wave, particle, position, velocity) which work satisfactorily for the world of everyday experience are not appropriate, and the attempt to borrow these concepts for the atomic world has produced our problems of interpretation. We have been lucky enough to have unscrambled many of the apparent paradoxes, although we may at first be unhappy to have lost a world in which waves were only waves and particles were only particles.

Q11 In wave terms, the bright lines of a diffraction pattern are regions where there is a high field intensity produced by constructive interference. In the probability interpretation of quantum mechanics, the bright lines of a diffraction pattern are regions where there is a high ....?

Q12 If quantum mechanics can predict only probabilities for the behavior of any one particle, how can it predict many phenomena, for example, half-lives and diffraction patterns, with great certainty?

Doodles from the scratch pad of a modern theoretical physicist, Prof. C. N. Yang.

20.1 How fast would you have to move to increase your mass by 1%?

20.2 The centripetal force on a mass moving with relativistic speed v around a circular orbit of radius R is $F = mv^2/R$, where m is the relativistic mass. Electrons moving at a speed 0.60 c are to be deflected in a circle of radius 1.0 m what must be the magnitude of the force applied? ($m_0 = 9.1 \times 10^{-\text{[illegible]}}$ kg.)

20.3 The formulas ($p = m_0v$, $KE = \frac{1}{2}mv^2$) used in Newtonian physics are convenient approximations to the more general relativistic formulas. The factor $1/\sqrt{1-v^2/c^2}$ can be expressed as an infinite series of steadily decreasing terms by using a binomial series expansion. When this is done we find that

$$\sqrt{1-v^2/c^2} = 1 + 1/2\,\frac{v^2}{c^2} + 3/8\,\frac{v^4}{c^4} + 5/16\,\frac{v^6}{c^6} + 35/128\,\frac{v^8}{c^8} + \ldots.$$

a) Show, by simple substitution, that when $\frac{v}{c}$ is less than 0.1, the values of the terms drop off so rapidly that only the first few terms need be considered.

b) The greatest speeds of man-sized objects are rarely more than 3,000 m/sec, so $\frac{v}{c}$ is less than $10^{-\text{[illegible]}}$. Substitute the series expression for $1/\sqrt{1-v^2/c^2}$ into the relativistic formulas,

$$p = \frac{m_0v}{\sqrt{1-v^2/c^2}} \quad \text{and}$$

$$KE = mc^2 - m_0c^2$$

and cross off terms which will be too small to be measurable. What formula would you use for momentum and kinetic energy in describing the motion of man-sized objects?

20.4 According to relativity theory, changing the energy of a system by ΔE also changes the mass of the system by $\Delta m = \Delta E/c^2$. Something like 10^6 joules per kilogram of substance are commonly released as heat energy in chemical reactions.

a) Why then aren't mass changes detected in chemical reactions?

b) Calculate the mass change associated with a change of energy of $10^{\text{[illegible]}}$ joules.

20.5 The speed of the earth in its orbit is about 18 miles/sec (3×10^4 m/sec). Its "rest" mass is 6.0×10^{24} kg.

a) What is the kinetic energy ($\frac{1}{2}m_0v^2$) of the earth in its orbit?

b) What is the mass equivalent of that kinetic energy?

c) By what percentage is the earth's "rest" mass increased at orbital speed?

d) Refer back to Unit 2 to recall how the mass of the earth is found; was it the rest mass or the mass at orbital speed?

20.6 In 1926, Sir John Squire proposed the following continuation of Pope's verse on Newton:

Pope: Nature and Nature's laws lay hid in night
God said, 'Let Newton be!' and all was light.

Squire: It did not last: The Devil howling 'Ho,
Let Einstein be,' restored the status quo.

What does this mean, and do you agree?

20.7 In relativistic mechanics the formula $p = mv$ still holds, but the mass m is given by $m = m_0/\sqrt{1-v^2/c^2}$. The rest mass of an electron is $9.1 \times 10^{-}$[illegible] kg.

a) What is its momentum when it is moving down the axis of a linear accelerator from left to right at a speed of 0.4 c with respect to the accelerator tube?
b) What would Newton have calculated for the momentum of the electron?
c) By how much would the relativistic momentum increase if the speed of the electron were doubled?
d) What would Newton have calculated its change in momentum to be?

20.8 Calculate the momentum of a photon of wavelength 4000 Å. How fast would an electron have to move in order to have the same momentum?

20.9 What explanation would you offer for the fact that the wave aspect of light was shown to be valid before the particle aspect was demonstrated?

20.10 Construct a diagram showing the change that occurs in the frequency of a photon as a result of its collision with an electron.

20.11 The electrons which produced the diffraction photograph on p. 109 had de Broglie wavelengths of 10^{-10} meter. To what speed must they have been accelerated? (Assume that the speed is small compared to c, so that the electron mass is 10^{-30} kg.)

20.12 A billiard ball of mass 0.2 kilograms moves with a speed of 1 meter per second. What is its de Broglie wavelength?

20.13 Show that the de Broglie wavelength of a classical particle of mass m and kinetic energy KE is given by

$$\lambda = \frac{h}{\sqrt{2m(KE)}}$$

What happens when the mass is very small and the speed is very great?

20.14 Suppose that the only way you could obtain information about the world was by throwing rubber balls at the objects around you and measuring their speeds and directions of rebound. What kinds of objects would you be unable to learn about?

20.15 A bullet can be considered as a particle having dimensions approximately 1 centimeter. It has a mass of about 10 grams and a speed of about 3×10^4 centimeters per second. Suppose we can measure its speed to within one part of 10^4. What is the corresponding uncertainty in its position according to Heisenberg's principle?

20.16 Show that if Planck's constant were equal to zero, quantum effects would disappear and particles would behave according to Newtonian physics. What effect would this have on the properties of light?

20.17 Bohr once said,

> If one does not feel a little dizzy when discussing the implications of Planck's constant h it means that one does not understand what one is talking about.

What might he have meant? (Refer to examples from Chapters 18, 19 and 20.) Do you agree with Bohr's reaction?

20.18 A particle confined in a box cannot have a kinetic energy less than a certain amount; this least amount corresponds to the longest de Broglie wavelength which produces standing waves in the box, that is, the box size is one-half wavelength. For each of the following situations find the longest de Broglie wavelength that would fit in the box; then use $p = h/\lambda$ to find the momentum p, and use $p = mv$ to find the speed v.

a) a dust particle (about $10^{-[illegible]}$ kg) in a display case (about 1 m across).

b) an argon atom ($6.6 \cdot 10^{-[illegible]}$ kg) in a light bulb (about $10^{-[illegible]}$ m across).

c) a protein molecule (about $10^{-[illegible]}$ kg) in a bacterium (about 10^{-6} m across).

d) an electron (about $10^{-[illegible]}$ kg) in an atom (about $10^{-[illegible]}$ m across).

20.19 Some philosophers (and some physicists) have claimed that the Uncertainty Principle proves that there is free will. Do you think this extrapolation from atomic phenomena to the world of animate beings is justified? Discuss.

20.20 A physicist has written

> It is enough that quantum mechanics predicts the average value of observable quantities correctly. It is not really essential that the mathematical symbols and processes correspond to some intelligible physical picture of the atomic world.

Do you regard such a statement as acceptable? Give reasons.

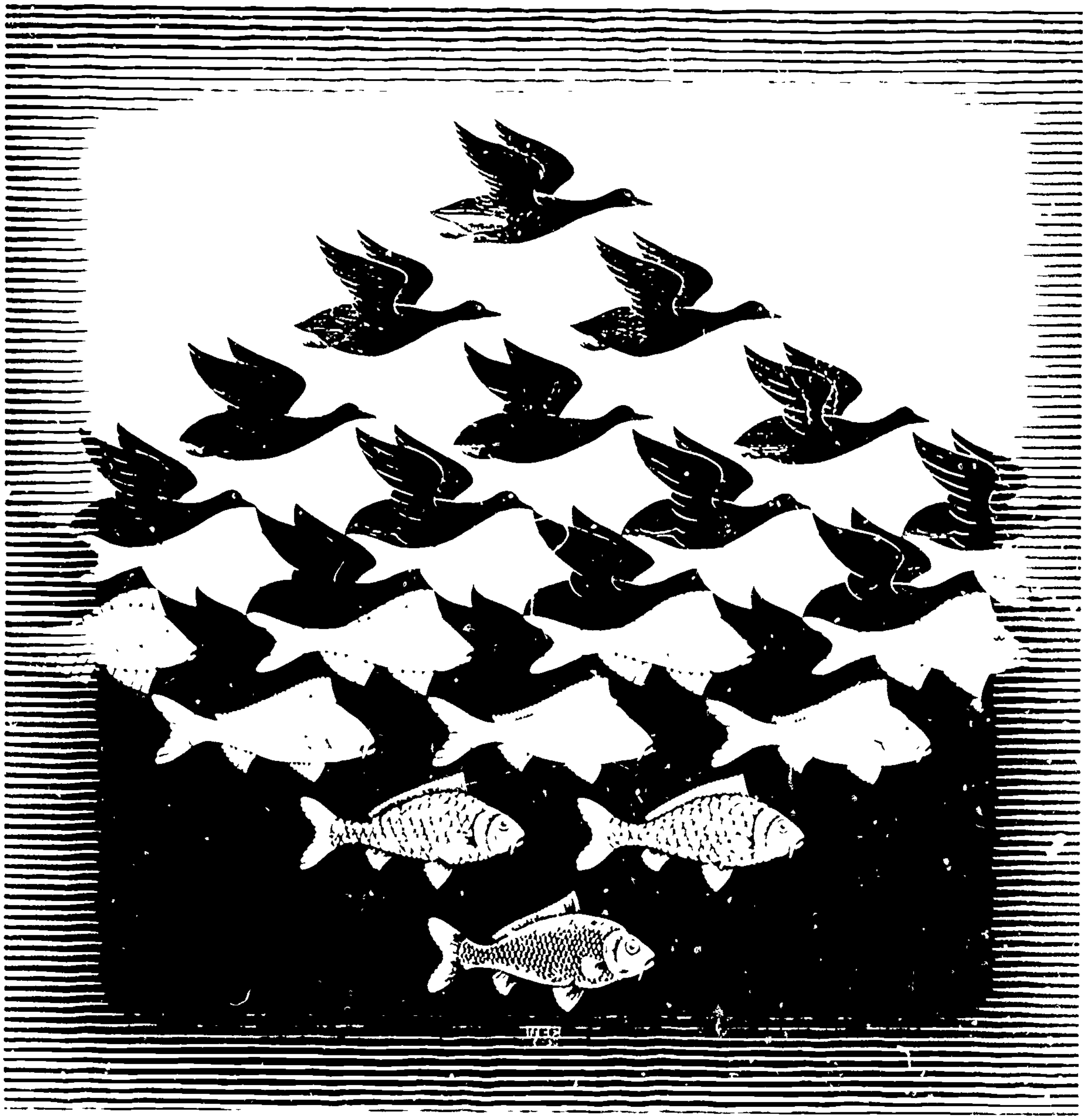
20.21 The great French physicist Pierre Laplace (1748-1827) wrote,

> Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it—an intelligence sufficiently vast to submit these data to analysis—it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atom; for it, nothing would be uncertain and the future, as the past, would be present to its eyes. A Philosophical Essay on Probabilities.

Is this statement consistent with modern physical theory?

20.22 In Chapters 19 and 20 we have seen that it is impossible to avoid the wave-particle dualism of light and matter. Bohr has coined the word complementarity for the situation in which two opposite views seem equally valid, depending on which aspect of a phenomenon one chooses to consider. Can you think of situations in other fields (outside of atomic physics) to which this idea might apply?

20.23 In Units 1 through 4 we discussed the behavior of large-scale "classical particles" (for example, tennis balls) and "classical waves" (for example, sound waves), that is, of particles and waves that in most cases can be described without any use of ideas such as the quantum of energy or the de Broglie matter-wave. Does this mean that there is one sort of physics ("classical physics") for the phenomena of the large-scale world and quite a different physics ("quantum physics") for the phenomena of the atomic world? Or does it mean that quantum physics really applies to all phenomena but is not distinguishable for classical physics when applied to large-scale particles and waves? What arguments or examples would you use to defend your answer?



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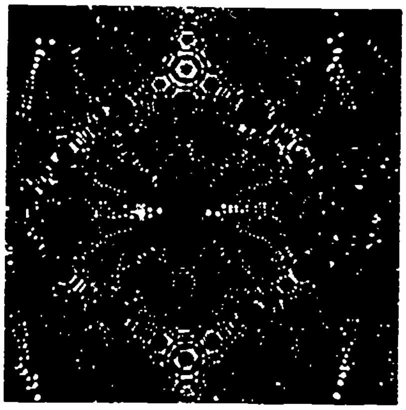
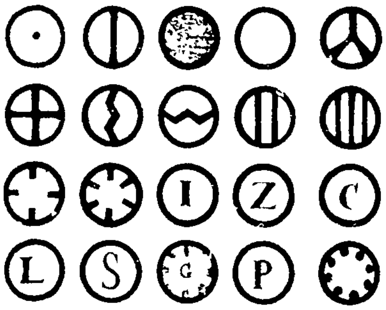


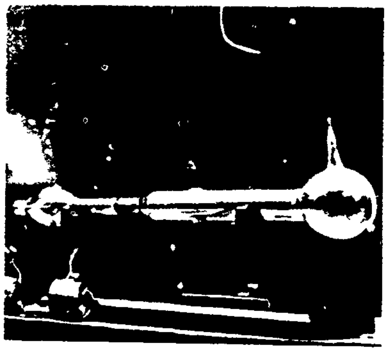
Epilogue We have traced the concept of the atom from the early ideas of the Greeks to the quantum mechanics now generally accepted by physicists. The search for the atom started with the qualitative assumptions of Leucippus and Democritus who thought that their atoms offered a rational explanation of things and their changes. For many centuries most natural philosophers thought that other explanations, not involving atoms, were more reasonable. Atomism was pushed aside and received only occasional consideration until the seventeenth century. With the growth of the mechanical philosophy of nature in the seventeenth and eighteenth centuries, particles (corpuscles) became important. Atomism was reexamined, mostly in connection with physical properties of matter. Boyle, Newton and others speculated on the role of particles in the expansion and contraction of gases. Chemists speculated about atoms in connection with chemical change. Finally, Dalton began the modern development of atomic theory, introducing a quantitative aspect that had been lacking—the relative atomic mass.

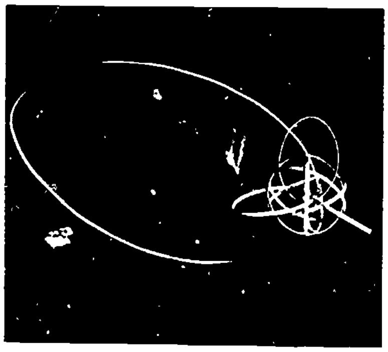
Chemists, in the nineteenth century, found that they could correlate the results of many chemical experiments in terms of atoms and molecules. They also found a system in the properties of the chemical elements. Quantitative information about atomic masses provided a framework for the system—the periodic table of Mendeleev. During the nineteenth century, physicists developed the kinetic theory of gases. This theory—based on the assumption of very small corpuscles, or particles, or molecules, or whatever else they might be called—helped strengthen the position of the atomists. Other work of nineteenth-century physics helped pave the way to the study of the structure of atoms, although the reasons for this work had no direct connection with the problem of atomic structure. The study of the spectra of the elements and of the conduction of electricity in gases, the discovery of cathode rays, electrons, and x rays, all eventually led to the atom.

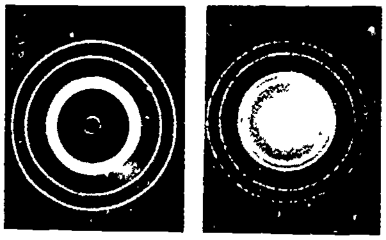
Nineteenth-century chemistry and physics converged, at the beginning of the twentieth century, on the problem of atomic structure. It became clear that the uncuttable, infinitely hard atom was too simple a model: that the atom itself is made up of smaller particles. And so the search for a model with structure began. Of the early models, that of Thomson—the pudding with raisins in it—attracted much interest; but it was inadequate. Then came Rutherford's nuclear atom, with its small, heavy, positively charged nucleus, surrounded, somehow, by negative charges. Then the atom of Bohr, with its electrons moving in orbits like planets in a miniature solar system. The Bohr theory had many successes and linked chemistry and spectra to the physics of atomic structure. But then the Bohr theory fell, and with it the easily grasped pictures of the atom. There is an end—at least for the present—to the making of simple physical models. Now is the time for mathematical models, for equations, not for pictures. Quantum mechanics enables us to calculate how atoms behave: it helps us understand the physical and chemical properties of the elements. What we used to call "atomic physics," Dirac now calls "the theory of chemistry," presumably because "chemistry" is that which is understood, while physics still has secrets.



The next stage in our story is the nucleus of the atom. Is it uncuttable? Is it infinitely hard? Or is the nucleus made up of smaller components? Do we have to worry about its composition and structure?







Index

Brief Answers to Study Guide

Chapter 17

17.1 80.3% zinc
19.7% oxygen

17.2 47.9% zinc

17.3 13.9 × mass of H atom
same

17.4 986 g nitrogen
214 g hydrogen

17.5 9.23 × mass of H atom

17.6 (a) 14.1
(b) 28.2
(c) 7.0

17.7 Discussion

17.8 Na:1
Ca:2
Al:3
Sn:4
P:5

17.9 (a) Ar-K
Co-Ni
Te-I
Th-Pa
U-Np
Es-Fm
Md-No
(b) Discussion

17.10 Discussion

17.11 Discussion

17.12 0.113 g hydrogen
0.895 g oxygen

17.13 (a) 0.05 g zinc
(b) 0.30 g zinc
(c) 1.2 g zinc

17.14 (a) 0.88 g chlorine
(b) 3.14 g iodine
(c) Discussion

17.15 Discussion

17.16 Discussion

17.17 Discussion

17.18 Discussion

Chapter 18

18.1 (a) 2.0×10^{7} m/sec
(b) 1.8×10^{11} coul/kg

18.2 Proof

18.3 Discussion

18.4 Discussion

18.5 1.5×10^{14} cycles/sec
ultraviolet

18.6 4×10^{-19} joules
4×10^{-18} joules

18.7 2.6×10^{-19} joules
1.6 eV

18.8 4.9×10^{14} cycles/sec

18.9 (a) 2.5×10^{20} photons
(b) 2.5 photons/sec
(c) 0.4 sec
(d) 2.5×10^{-10} photons
(e) 0.1 amp

18.10 1.3×10^{17} photons

18.11 1.2×10^{19} cycles/sec

18.12 Discussion

18.13 1.2×10^{5} volts
1.9×10^{-14} joules
1.2×10^{5} eV

18.14 Glossary

13.15 Discussion

Chapter 19

19.1 Discussion

19.2 Five listed in text, but theoretically an infinite number. Four lines in visible region.

19.3 $n_i = 8$ 3880 Å
$n_i = 10$ 3790 Å
$n_i = 12$ 3730 Å
Discussion

19.4 (a) Discussion
(b) $n_i = \infty$
(c) Lyman series 910 Å
Balmer series 3650 Å
Paschen series 8200 Å
(d) $E = 21.8 \times 10^{-19}$ joules
$E = 13.6$ eV

19.5 Discussion

19.6 Discussion

19.7 Discussion

19.8 Ratio = 10^{-4}

19.9 3.5 meters

19.10 Discussion

19.11 Discussion

19.12 Discussion

19.13 Discussion

19.14 Discussion

19.15 $Z = 36$, $Z = 54$

19.16 Glossary

19.17 Discussion

19.18 Discussion

Chapter 20

20.1 0.14 c or 4.2×10^{7} m/sec

20.2 3.7×10^{-14} newtons

20.3 $m_o v^2$ and $m_o v$

20.4 (a) changes are too small
(b) 10^{-12} kg

20.5 (a) 27×10^{32} joules
(b) 3×10^{16} kg
(c) 5×10^{-7} %
(d) Rest mass

20.6 Discussion
20.7 (a) 1.2×10^{-22} kg·m/sec
(b) 1.1×10^{-22} kg·m/sec
(c) 2.4×10^{-22} kg·m/sec
(d) 1.1×10^{-22} kg·m/sec

20.8 $p = 1.7 \times 10^{-27}$ kg·m/sec
$v = 1.9 \times 10^{3}$ m/sec

20.9 Discussion

20.10 Diagram

20.11 6.6×10^{6} m/sec

20.12 3.3×10^{-33} m

20.13 Proof

20.14 Discussion

20.15 $\Delta x = 3.3 \times 10^{-31}$ m

20.16 Discussion

20.17 Discussion

20.18 (a) 2 m, $3.3 \times 10^{-24}\ \frac{\text{kg}\cdot\text{m}}{\text{sec}}$, $3.3 \times 10^{-25}\ \frac{\text{m}}{\text{sec}}$

(b) 0.2 m, $3.3 \times 10^{-33}\ \frac{\text{kg}\cdot\text{m}}{\text{sec}}$, $5 \times 10^{-8}\ \frac{\text{m}}{\text{sec}}$

(c) 2×10^{-6} m, $3.3 \times 10^{-28}\ \frac{\text{kg}\cdot\text{m}}{\text{sec}}$, $3.3 \times 10^{-6}\ \frac{\text{m}}{\text{sec}}$

(d) 2×10^{-10} m, $3.3 \times 10^{-24}\ \frac{\text{kg}\cdot\text{m}}{\text{sec}}$, $3.3 \times 10^{6}\ \frac{\text{m}}{\text{sec}}$

20.19 Discussion

20.20 Discussion

20.21 Discussion

20.22 Discussion

20.23 Discussion

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Answers to End of Section Questions

Chapter 17

Q1 The atoms of any one element are identical and unchanging.

Q2 conservation of matter; the constant ratio of combining weights of elements

Q3 no

Q4 It was the highest known element—and others were rough multiples.

Q5 relative mass; and combining number, or "valence"

Q6 2,3,6,1,2

Q7 density, melting point, chemical activity, valence

Q8 atomic mass

Q9 when the chemical properties clearly suggested a slight change or order

Q10 Sometimes the next heavier element didn't have the expected properties—but did have the properties for the next space over.

Q11 its position in the periodic table, determined by many properties but usually increasing regularly with atomic mass

Q12 Water, which had always been considered a basic element, and had resisted all efforts at decomposition, was easily decomposed.

Q13 New metals were separated from substances which had never been decomposed before.

Q14 the amount of charge transferred by the current, the valence of the elements, and the atomic mass of the element

Chapter 18

Q1 They could be deflected by magnetic and electric fields.

Q2 because the mass is 1800 times smaller

Q3 (1) Identical electrons were emitted by a variety of materials; and (2) the mass of an electron was much smaller than that of an atom.

Q4 All other values of charge he found were multiples of that lowest value.

Q5 Fewer electrons are omitted, but with the same average energy as before.

Q6 The average kinetic energy of the emitted electrons decreases until, below some frequency value, none are emitted at all.

Q7 The energy of the quantum is proportional to the frequency of the wave, $E = hf$.

Q8 The electron loses some kinetic energy in escaping from the surface.

Q9 The maximum kinetic energy of emitted electrons is 2.0 eV.

Q10 When x rays passed through material, say air, they caused electrons to be ejected from molecules, and so produced + ions.

Q11 (1) not deflected by magnetic field; (2) show diffraction patterns when passing through crystals; (3) produced a pronounced photoelectric effect

Q12 (1) diffraction pattern formed by "slits" with atomic spacing (that is, crystals); (2) energy of quantum in photoelectric effect

Q13 For atoms to be electrically neutral, they must contain enough positive charge to balance the negative charge of the electrons they contain; but electrons are thousands of times lighter than atoms.

Chapter 19

Q1 It is composed of only certain frequencies of light.

Q2 by heating or electrically exciting a gas (However, very dense gas, such as the insides of a star, will emit a continuous range of light frequencies.)

Q3 Certain frequencies of light are missing.

Q4 by passing light with complete range of frequencies through a relatively cool gas

Q5 none (he predicted that they would exist because the mathematics was so neat.)

Q6 careful measurement and tabulation of data on spectral lines

Q7 They have a positive electric charge and are repelled by the positive electric charge in atoms.

Q8 Rutherford's model located the positively charged bulk of the atom in a tiny nucleus—in Thomson's model the positive bulk filled the entire atom.

Q9 the number of positive electron charges in the nucleus

Q10 3 positive units of charge (when all 3 electrons were removed)

Q11 Atoms of a gas emit light of only certain frequencies, which implies that each atom's energy can change only by certain amounts.

Q12 none (He *assumed* that electron orbits could have only certain value, of angular momentum, which implied only certain energy states.)

Q13 Bohr *derived* his prediction from a physical model, from which other predictions could be made. Balmer only followed out a mathematical analogy.

Q14 (a) 4.0 eV (b) 0.1 eV (c) 2.1 eV

Q15 The electron arrangements in noble gases are very stable. When an additional nuclear charge and an additional electron are added, the added electron is bound very weakly to the atom.

Q16 It predicted some results that disagreed with experiment; and it predicted others which could not be tested in any known way.

Chapter 20

Q1 It increases, without limit.

Q2 It increases, approaching ever nearer to a limiting value, the speed of light.

Q3 Photon momentum is directly proportional to the frequency of the associated wave.

Q4 That the idea of photon momentum is consistent with the experimental results of scattering of x rays by electrons.

Q5 by analogy with the same relation for photons

Q6 The regular spacing of atoms in crystals is about the same as the wavelength of low-energy electrons.

Q7 Bohr invented his postulate just for the purpose. Schrödinger's equation was derived from the wave nature of electrons and explained many phenomena other than hydrogen spectra.

Q8 It is almost entirely mathematical—no physical picture or models can be made of it.

Q9 It can. But less energetic photons have longer associated wavelengths, so that the location of the particle becomes less precise.

Q10 It can. But the more energetic photons will disturb the particle more and make measurement of velocity less precise.

Q11 ...probability of quanta arriving.

Q12 As with all probability laws, the *average* behavior of a large collection of particles can be predicted with great precision.

Acknowledgments

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