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INTRODUCTION TO ATOMIC PHYSICS

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INTRODUCTION TO ATOMIC PHYSICS

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To
JAMES FRANCK

PREFACE

The present book grew out of a course, Introduction to Atomic Physics, which the author has been giving at Harvard University since 1931. It is intended for readers who have taken a one-year introductory physics course and are familiar with the elements of chemistry. Calculus is not necessary for the understanding of atomic physics on the introductory level. Here the difficulty is not of a mathematical nature. It is difficult, however, to understand how thoroughly our detailed theory of atomic structure, although apparently remote from observed facts, is based on experimental evidence. Therefore, in this book the relation between theory and observed facts is stressed throughout. In one argument in which calculus is indispensable, the mathematical treatment is relegated to an appendix. For more advanced students many calculus problems are included.

Throughout the book the main emphasis is on *understanding* as opposed to *accepting on authority*. This point of view necessarily limits the scope of a book planned on the precalculus level. For example, the author had to refrain from the discussion of complex spectra on the basis of several quantum numbers, the origin of which would remain mysterious. Isolated facts of minor importance, which only the expert must study, are entirely omitted. In only a few cases are the results of the advanced mathematical treatment needed to provide a comprehensive evaluation of the ability of the theory to account for observations. In such cases, brief reports on further developments are given.

In many chapters of the book a method is applied that the author has tried out in elementary and advanced courses. Certain arguments that are essential parts of the course are relegated to problems. Through difficult problems the student is guided by a set of questions. This method serves two purposes: It is intended to stimulate the interest of the student, and it impresses the student with the *physical idea* that is given in the problem, as distinguished from the *mathematical performance* through which he is asked to go by himself.

In the lecture course offered at Harvard University many experiments are demonstrated. Other experiments that take more time are performed by the student in an advanced laboratory course in atomic physics. Although the experiments are only briefly described in the text, more technical advice is given in an appendix.

The course from which the present book developed originally covered two semesters. After a reorganization, it was reduced to a one-semester course. For such a short course it is recommended that the instructor give only the briefest outline of the fundamentals of chemistry and the kinetic theory of gases. In later sections, too, some detail may be replaced by summaries. Depending on the preference of the instructor, the following sections are suggested for omission or an abbreviated treatment: 6.2, 8.2*c*, 15.6*b*, 16.1–16.2, 17.10, 17.11, 19.1*d*, 19.1*h*, 20.7, 22.6*d*, 22.6*e*, 22.9, 23.3.

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OTTO OLDENBERG

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INTRODUCTION

When trying to understand atomic theory, we become aware of the contrast between this comparatively new branch and the older branches of physical theory. In *mechanics* the theory gives relations between quantities that are directly observable. In *optics* a definite gap opens up between the observation and the theory. For example, we observe certain regular light and dark fringes and explain them by the theoretical concept of light as a wave motion that is not directly accessible to our senses as the surface waves of water are. Ever so much wider is this gap between observations and theoretical concepts in *atomic physics*. This seems to us the greatest difficulty in the study of atomic physics.

Even at the beginning of this century, in the earlier development of atomic theory, the gap seemed so wide that a distinguished chemist, although operating every day with the concept of atoms, warned his students that they should not believe too literally in the existence of such atoms which nobody had ever seen as individual particles. Contrary to this skepticism, at present we are asked to believe that we know the parts of the most complicated atoms and how the parts work together. We are told, for example, that each mercury atom consists of a nucleus of well-known mass and electric charge, built of 80 "protons" and about 120 "neutrons," surrounded by 80 "electrons," each electron, in turn, with a well-known mass and charge, arranged in well-known groups and capable of changing its position when absorbing or emitting light according to well-known laws that differ widely from the laws familiar to the beginner in the introductory course on physics. We even claim that we can describe the nucleus in considerable detail. This detailed picture contrasts with the fact that nobody has ever seen an individual atom, much less taken it apart and examined its parts as a watchmaker examines the gears of a watch. Our senses tell us only such facts as, for example, that certain colored light is emitted by the electric discharge through mercury vapor.

What is the method of research that leads us so far away from the solid basis of observations? We illustrate it by two historical examples indicating two opposite approaches. On the basis of our present attitude, both are subject to criticism. Nevertheless, they help us in understanding the modern approach.

In the Islamic world, about a thousand years ago, there was an important development of research in physics. The concave mirror, the

convex mirror, refraction of light, and many other phenomena were systematically observed and described. This method of careful description of experiments has led to important discoveries. Can it lead to the discovery of atoms and their properties? This does not seem possible since atoms are far beyond the range of direct observation. Even today, in spite of a vastly improved experimental technique, nobody has ever seen an individual atom.

Nevertheless the idea of atoms is eleven centuries older than Islamic science. This brings us to the other example illustrating the opposite approach. The ancient Greeks had the aspiration to penetrate into mysteries that they imagined beyond the limit of immediate observation. Around 400 B.C., Democritus taught that matter consists of an almost infinite number of invisible and *indivisible* particles, which differ from each other only in form, position, and arrangement. *Atomos* is the Greek word for indivisible. This then was the first appearance of the concept of atoms. Are we justified in saying that Democritus discovered the atomic structure of matter? Our present critical attitude does not allow us to accept that, because he did not offer any evidence proving the truth of his new idea, which was based solely on his intuition and his faith in a simple structure underlying the complexity of everyday observations.

By another example let us illustrate the fact that the indiscriminate use of the intuition may equally well lead in the wrong as in the right direction. This is evident from the Greek ideas of the cosmos. Around 350 B.C. Aristotle taught that the earth does not move and that it lies exactly at the center of the universe. A century later his teaching was opposed by Aristarchus who claimed that the earth revolves about the sun in the circumference of a circle, the sun lying in the middle of the orbit. Although at present we accept this latter picture of the cosmos, Aristarchus is generally not considered to be the discoverer of the heliocentric system because he did not offer a proof that demonstrated the superiority of his system over the geocentric system of Aristotle. The Copernican system is the universally accepted name for the new concept. Copernicus, 1800 years later, applied the same basic idea; but he went a great step further by using this idea for the explanation of certain observations of great complexity. He explained the planetary orbits, which to the terrestrial observer seem most involved, as simple orbits about the sun, seen from one of the planets, the earth. The history of this discovery shows why we do not consider Democritus as the discoverer of the atomic structure of matter. He had no way of proving the truth of his idea by correlating it with observed facts. This last step was taken 22 centuries later by Dalton. This criticism, based on more than 2,000 years of further scientific development, does not detract from our admi-

ration for the great step forward in human thought made by the Greek philosophers. They had the freedom of mind to abandon such naïve ideas as that the residence of the human race must be the center of the universe. Beyond the range of the human eye they visualized a realm of nature in which different laws may be in effect, *e.g.*, where the familiar experience that matter is divisible without limit may not be true. They imagined that an orderly structure of nature of a totally different kind may exist at the very small and the very large scale. The origin of these ideas is evident from the Greek origin of the words "atom" and "cosmos."

After criticizing the Islamic and the ancient Greek physicists as representatives of two opposite lines of thought, we want to know what we consider to be the most fruitful approach. The answer is a combination of both these methods. Modern atomic theory is a product of the imagination which has led us very far beyond what we perceive with our senses, but we claim that we have a criterion for the value of a theory. We judge it by its power to make a multitude of observed facts derivable from a unified basis. An example of this point of view will be given by each chapter of the present book. We accept on authority only the observed facts; *e.g.*, spectral lines observed. In the lecture course as many as possible of such facts are demonstrated by experiments. The theory, *e.g.*, Bohr's theory of the hydrogen atom, cannot be derived from the observed facts. Therefore, the theory is by no means as certain as these facts. Even in our introductory treatment we must adopt the critical attitude indispensable in research, judging the value of a theory by its power to give a consistent picture of many observed facts. This point of view will guide us throughout this book. We may state our criterion in a more extreme form: We accept a theory if it allows us to predict the result of an experiment hitherto untried. Thus a discouraged student of atomic theory may gain confidence when he recalls its recent success: The theory predicted that the element uranium, after a most complicated treatment, would lead to a reaction in which an unheard-of energy would suddenly be liberated. The value of this theory is generally recognized.

There is still another aspect to understanding atomic theory. How is it possible that human beings discovered a structure so far remote from what our senses perceive? How reliable is our theoretical knowledge? These questions will best be answered by the historical approach, which we shall use wherever it is compatible with the systematic argument.

In a book devoted to a systematic survey it is not possible to trace the slow development of each new experiment and new idea in full detail. For example, it would be misleading to say that the charge on the electron was first measured in 1905 by Millikan using the oil-drop method. On one hand, this statement disregards the results of the

earlier workers using clouds of water drops; on the other hand, it discounts the great difficulties overcome by Millikan and his numerous coworkers during their efforts spread over a decade and continued much later. This example illustrates the fact that numerous brief historical statements given throughout the book must be taken with a grain of salt.

During his complicated journey through the vast territory of atomic physics, the student should keep in mind the significance within the whole of any detailed view. In this endeavor he will be assisted by the survey printed as Table 1. Here the bearing of any group of experiments on our theoretical knowledge is evident from the correlation between the *observation*, given in the left column, and the *theory* in the right column. We arrange our discussion from the point of view of the theory. This gives the student practice in invoking experiments from different fields of physics and chemistry in the support of the same theoretical idea. We start from the arguments for atomic structure in the widest sense, the structure of *matter* as revealed in chemistry (Part I) and the study of *gases* (Part II). Next we study the structure of *electricity* (Part III) and the structure of *light* (Part IV). The following detailed discussion of the structure of individual atoms is naturally subdivided into the structure of the *external electrons* (Part V) and that of the *nucleus* (Part VI). Finally, in Part VII, we give a brief outline of *wave mechanics* which, instead of Newtonian mechanics, governs the motion of the smallest particles studied in atomic physics.

Table 1. *Atomic Physics*

Observation	*Theory*
Part I. Structure of Matter as Revealed in Chemistry	
Facts of chemistry	Atoms and their relative weights, Dalton, 1803; Avogadro's rule, 1811
Part II. Gases	
Pressure, temperature, specific heat of a gas; Brownian motion	Kinetic theory of gases, beginning 1848
Part III. Structure of Electricity	
A. Determinations of ϵ/μ	
Electric discharge through liquids; Faraday's laws, 1833	ϵ/μ of ions in liquids; existence of a fundamental charge, 1881
ϵ/μ of cathode-ray particles	Cathode ray consists of free electrons, J. J. Thomson, 1897
ϵ/μ of positive-ray particles	Positive ray consists of free + ions
ϵ/μ decreases for high velocities	Mass equivalent to energy, Einstein, 1905
B. Determination of ϵ	
Millikan's oil-drop experiment, 1909	Determination of the fundamental charge; masses of atoms and molecules
C. Electrons in metals.	
Electron emission from glowing metals	Free electrons in metals; work function
Part IV. Structure of Light	
Photoelectric effect, 1887, 1916 Compton effect, 1923	Light consists of quanta of energy $h\nu$, Planck, 1900; Einstein, 1905
Part V. Electronic Structure of Atoms	
A. The nuclear atom	
Scattering of α particles	The heavy, positively charged nucleus surrounded by electrons, Rutherford, 1911
B. Electronic structure	
Spectrum of hydrogen atoms	Bohr's theory, 1913
Spectra of heavier atoms	Energy levels of *external* electrons
Methods of observation	Elementary processes
Periodic table of elements	Stability of rare-gas electronic structure
X rays	The *internal* electron groups
Part VI. Nuclear Structure	
Isotopes, 1920	Nuclei built of a few types of particles, energies of formation
Natural radioactivity, 1896	Spontaneous disintegration of heavy nuclei
Artificial transmutation of elements, 1919, 1932	Artificial transmutation of nuclei, neutrons, 1932, positrons
Cosmic rays, 1912	Highest energy rays of cosmic origin, positrons, 1932, mesotrons, 1937

Table 1. *Atomic Physics (Continued)*

Part VII. Wave Nature of Matter

Diffraction of electrons, 1927	The motion of matter governed by waves, de Broglie, 1922; Heisenberg, Schrödinger, 1925

PART I

STRUCTURE OF MATTER AS REVEALED IN CHEMISTRY

CHAPTER 1

THE ATOMIC HYPOTHESIS AND AVOGADRO'S RULE

In the study of atomic physics, we must first make clear the argument by which certain experiments are explained by the existence of atoms. Conventionally, these experiments and their interpretation are considered as belonging not to physics but to chemistry. We assume that the reader is familiar with the elements of chemistry. Hence we restrict ourselves to a brief review of the complicated argument which, starting from observations, leads to the atomic theory of matter, Avogadro's hypothesis, and the molecular formulas.

1.1. Qualitative Analysis; Existence of Elements. Most substances can be analyzed into constituents, as water is analyzed into hydrogen and oxygen. However, a certain group of substances, like hydrogen and oxygen, cannot be analyzed any further. [This statement should be qualified in view of the more recent discovery of isotopes (Chap. 20). The reader will find that most statements of physics are only approximations valid within a limited range.] Substances that withstand further chemical analysis are called "elements." This argument leads only to the existence of such elements. It does not say whether these elements have a *continuous* or *discontinuous*, *i.e.*, atomic, structure.

1.2. Quantitative Analysis by Weight; Existence of Atoms. When water is analyzed into its constituents, the same ratio of masses is always found, *i.e.*, 2.016 hydrogen to 16.000 oxygen. This is an example of the general *law of constant proportions*, which states that *the same compound always contains the same elements in the same mass proportion.*

There is another compound, hydrogen peroxide, which, when analyzed into hydrogen and oxygen, yields another mass ratio, 1.008 hydrogen to 16.000 oxygen. For the time being we are not interested in the fact that each of these ratios is approximately a ratio of integers ($\frac{1}{8}$ and $\frac{1}{16}$, respectively); this will be discussed in the chapter on nuclear physics (Sec. 20.2). Instead, here we are interested in the fact that one of these ratios (1.008 : 8.00) is exactly twice as large as the other (1.008 : 16.000). Numerous similar results obtained with other compounds have led to the *law of multiple proportions* which states that, *when the same two elements combine to form more than one compound, the different masses of one of the elements*

that unite with a constant mass of the other bear a simple ratio to one another.

Dalton, in 1803, took the great step that led to the basis of theoretical chemistry by introducing the atomic hypothesis and so explaining the two empirical laws just mentioned. He assumed that each element consists of atoms, *i.e.*, very small particles, all of the same kind and of the same mass. In a compound substance a few atoms of different kinds combine. For the above example, Dalton made the simplest assumption that water consists of 1 hydrogen and 1 oxygen atom, abbreviated as HO. Correspondingly, hydrogen peroxide would be written as HO_2. The reader may invent such molecular formulas for the various compounds of nitrogen (N) and oxygen (O) which have been observed in the following proportions: 14:16, 28:16, 14:32, 28:48, or 28:80.

The argument just presented fails to furnish *unique* molecular formulas. HO is only the simplest formula for water. But it would be compatible with the law of multiple proportions to write instead H_2O or HO_2, or any other such combination. In each case the formula for hydrogen peroxide would have to be changed accordingly. Other experiments are needed to eliminate this ambiguity.

1.3. Quantitative Analysis of Gases by Volume; Avogadro's Rule. This new evidence was furnished in 1808 by Gay-Lussac. While the laws concerned with *weights* of substances are independent of the state (solid, liquid, or gaseous) of these substances, Gay-Lussac measured the *volumes of gases*, all at the same temperature and pressure. He found, for example, that 1 cm^3 of hydrogen and 1 cm^3 of chlorine form 2 cm^3 of hydrogen chloride. The general law describing all such experiments states that the *ratios of the volumes of gases used and produced in a chemical reaction are represented by small whole numbers.* This law is interpreted and, at the same time, the ambiguity of the molecular formulas partly resolved, when we adopt Avogadro's hypothesis (1811) which assumes that *under the same conditions of temperature and pressure equal volumes of all gases contain the same number of molecules.*

The law of Gay-Lussac deals with volumes of gases that may well be recorded by the experimenter. Avogadro's rule, however, is of a different character in that it is concerned with molecules, *i.e.*, with something unobservable. This is typical of a hypothesis in atomic physics. Let us tentatively adopt it and consider what it has to say regarding the formation of hydrogen chloride mentioned above. We shall see that this general hypothesis leads to definite results only if we supplement it by specific assumptions for one or the other type of molecule.

If we assume that 1 cm^3 *of any gas* contains n molecules then, in the example given above, n hydrogen molecules must provide all the hydrogen needed for $2n$ hydrogen chloride molecules. Thus we are forced to assume

that in each hydrogen molecule there are twice as many atoms of hydrogen as there are in each hydrogen chloride molecule. The simplest, though not the only possible, assumption is that each hydrogen molecule contains 2 atoms of hydrogen (written H_2) while each hydrogen chloride molecule contains only one. The same argument applies to the relation between chlorine and hydrogen chloride. Thus we obtain the molecular formulas H_2 for hydrogen, Cl_2 for chlorine, and HCl for hydrogen chloride. This tentative result, that hydrogen gas consists of diatomic molecules H_2, helps us in the next problem, *i.e.*, finding the formulas for water vapor and oxygen. Here our starting point is the observation that 2 cm^3 hydrogen and 1 cm^3 oxygen form not 3 but only 2 cm^3 water vapor. The reader will find that the corresponding argument leads to H_2O for water and O_2 for oxygen as the simplest formulas.

Certain more complicated formulas, however, are not excluded as far as this argument goes. Hence it is an important additional fact that no gas analysis has ever been performed that would force us to assume more than 2 atoms in a hydrogen molecule, etc. Therefore, we accept the simplest formulas here derived as correctly describing the molecules.

Later it will be mentioned that these results regarding the constitution of molecules are well confirmed by two independent observations dealing with *spectra* (Sec. 16.2) and *positive rays* (Sec. 8.3). For example, it can be shown that hydrogen, excited by an electric discharge, emits light which when analyzed in a spectrograph shows all the properties characteristic of *diatomic* molecules. Therefore, there is no doubt that the conventional molecular formulas correctly represent the molecular constitution.

It is evident that Avogadro's argument is by no means a rigorous conclusion from the experimental data. As a matter of fact, HO was widely written as the formula for the water molecule up to the middle of the nineteenth century. Attention is called to this generally adopted procedure in which a hypothesis is tested by drawing conclusions, which are then compared with observed facts. This first example of the method is unusually complicated by the need for the additional assumptions of molecular formulas. On the other hand, the importance of these formulas and of the elaborate, but not unique, way in which they are derived is evident.

Avogadro's rule may be stated as follows: The number of molecules contained in 1 cm^3 of any gas under standard conditions (0°C and 1 atm pressure) is a universal constant. "Universal" means a constant applying to any gas, independent of its chemical properties. Historically this was an unusual situation in which the *existence* of an important universal constant had been inferred without any estimate of its *numerical value.* Avogadro could only argue that the individual molecules are so small that we cannot see them and so light that we cannot weigh them. Therefore, their number per cubic centimeter must be very large. It took more than

half a century before the first estimate of their size and weight was obtained (Sec. 6.1). Accurate measurements of these quantities have been made more than a century after Avogadro's discovery (Sec. 9.2).

A summary of this discussion will be found at the end of Chap. 2.

PROBLEM

1.1. *Molecular formula.* (*a*) 2 cm^3 *nitric oxide* are analyzed into 1 cm^3 nitrogen and 1 cm^3 oxygen. What are the simplest molecular formulas for nitrogen and nitric oxide? Take the formula for molecular oxygen for granted. Explain your answer. (*b*) What ratio of volumes do you predict when gaseous nitrogen tetroxide, N_2O_4, is analyzed into nitrogen and oxygen?

CHAPTER 2

SOME RESULTS AND DEFINITIONS OF CHEMISTRY

2.1. Valence. In chemistry it has been found that sodium (Na) and related elements may form compounds with oxygen (oxides) of the molecular constitution Na_2O, indicating that 1 oxygen atom has the power of binding 2 sodium atoms. However, calcium (Ca) and related elements form oxides described by CaO. Such power of atoms is generally described as their "valence." Oxygen is called "bivalent" and sodium "univalent." A crude picture of the valence of oxygen, just sufficient for the beginner physicist, is given by two little hooks with which each oxygen atom is endowed while each sodium atom carries only one hook. Thus a "saturated" molecule is formed when each of the two hooks of 1 oxygen atom is interlinked with the one hook of a sodium atom. Correspondingly, calcium would be called "bivalent" because it forms the compound CaO. Chlorine (Cl) and related compounds are univalent because with sodium they form compounds of the type NaCl.

For a thorough understanding of chemical compounds this picture of the valence is too primitive because it fails to give an explanation for the fact that some elements manifest different values of valence in different compounds. Later, in our discussion of the periodic table of elements, we shall refine our picture of the valence.

2.2. Atomic and Molecular Weights. The mass ratio of 1 cm^3 hydrogen (H_2) and 1 cm^3 oxygen (O_2) is 1.008 : 16. Since, according to Avogadro's rule, both contain the same number of molecules, we must attribute this ratio to the masses of the individual molecules: mass of H_2/mass of O_2. It is convenient to express such ratios on the basis of an arbitrarily selected unit. Historically, two different units have been used. It is obvious that the mass ratio of a hydrogen atom H and a hydrogen molecule H_2 is 1 : 2. Since the hydrogen atom is the lightest of all atoms, it may be adopted as the arbitrary unit. In this system H_2 would have the molecular weight 2.000 and O_2 a little less than 32. Instead, at present a slightly different system is universally adopted based on $\frac{1}{16}$ of an oxygen atom as the arbitrary unit. (We shall use the letter m as indicating any molecular weight on this basis.) This gives the oxygen molecule the molecular weight of exactly 32.000 and the hydrogen molecule the molecular weight 2.016. The

relative masses of the atoms, called "atomic weights," are accordingly 1.008 for H and, by definition, 16.000 for O. There are two reasons for the curious choice of $\frac{1}{16}$ of an oxygen atom as a unit. First, it has a practical advantage as many atomic weights have been determined by the analysis of oxides, *i.e.*, by comparison with oxygen atoms. Second, it leads to the strange result, unexplained through more than a century, that many, but not all, atomic weights are whole numbers. This important observation will be discussed in the chapter on isotopes (Sec. 20.2).

The term "atomic weight" makes us believe that we should express this quantity somehow with the help of the familiar mass unit, gram. In this respect, however, the universally adopted term "atomic weight" is misleading. This quantity is defined as the *ratio of two masses* (or of two weights). Therefore, it makes no difference in what units the individual masses are measured. The conventional expression for this situation is "the molecular weight has no dimension." (Another familiar example of a quantity that has no dimension is the specific gravity of a substance, defined as the ratio of its density to that of water.)

2.3. A New Unit of Mass. In chemistry it became convenient to define a new unit of mass replacing the familiar gram. One "gram molecule" or "mole" is defined as the number of grams given by the molecular weight, *i.e.*, m grams. Hence, 1 mole O_2 = 32.000 g O_2. The relation between this new mass unit and the gram is evident from the simple example:

$$96 \text{ g } O_2 = 3 \text{ moles } O_2$$

or, in general.

$$\text{Mass (grams)} = \text{mass (moles)} \times m \tag{2.1}$$

where mass (g) and mass (mole) mean the figures expressing the same mass in the units of grams or moles, respectively. Correspondingly, when dealing with atoms, the chemist defines 1 gram atom as the number of grams given by the atomic weight. This leads to the analogous relation

$$\text{Mass (grams)} = \text{mass (gram atoms)} \times \text{atomic weight} \tag{2.2}$$

The usefulness of this new unit will be evident when we express the number N of molecules contained in 1 mole, *i.e.*, in m grams. Each molecule has a mass μ measured in grams. Let us compare two gases, *e.g.* hydrogen and oxygen, indicated by the subscripts 1 and 2, respectively. For each gas we write the number of grams contained in 1 mole.

$$m_1 = N_1\mu_1 \qquad \text{and} \qquad m_2 = N_2\mu_2$$

or, instead,

$$N_1 = \frac{m_1}{\mu_1} \qquad \text{and} \qquad N_2 = \frac{m_2}{\mu_2}$$

Since the molecular weight m of any substance is defined as proportional to the mass μ, it follows that $m_1/\mu_1 = m_2/\mu_2$ and $N_1 = N_2$. Hence, the

number of molecules contained in 1 mole is the same for all substances. Now we may drop the subscript and write this universal constant N, called "Avogadro's number." Since N represents a number per mole, it has the unit of an absolute number divided by a mass in moles (or mole^{-1}). In the important equation

$$m = N\mu \tag{2.3}$$

only m and μ are specific for the substance. This new statement that *the number of molecules N contained in one mole is a universal constant* is not a law describing results of new experiments but only a logical conclusion from our definition of the molecular weight m as proportional to the mass μ of the individual molecule. This statement is simpler than Avogadro's rule given above, in which we refer the number of molecules to a unit *volume* because there we have to stipulate standard conditions. Here we refer the number to a unit *mass* (1 mole). It is obvious that the number so defined is independent of the conditions because a certain mass of a gas does not lose any of its molecules when we cool or compress or liquefy or freeze it. At the present stage of our argument the numerical value of Avogadro's number N remains unknown (Sec. 9.2).

The usefulness of the mole as our new unit of mass is illustrated by an example. Suppose a chemist wants to mix hydrogen and oxygen in such a proportion that, when water is formed, each oxygen atom finds the necessary 2 hydrogen atoms as partners. From the molecular formulas and atomic weights he computes that he must mix 4.072 g H_2 and 32.000 g O_2 in order to produce 36.072 g H_2O. The same result is more easily stated as 2 moles H_2 and 1 mole O_2 form 2 moles H_2O.

Here the ways of the chemist and the physicist separate. The chemist studies the various compounds; the physicist, among other problems, studies the behavior of gases, the emission and absorption of light, the effects of electric currents. Through the greater part of a century these two ways seemed to lead into independent realms of science separated so completely that research was carried on in separate laboratories. However, no border line exists at present between chemistry and physics. In particular, within the past twenty years these two lines of research joined again with the discovery of a theory which describes on a unified basis all properties of atoms, in particular their spectra and their chemical behavior. This theory, which requires advanced mathematics, will be discussed only very briefly in Chap. 26.

SUMMARY OF CHAPTERS 1 AND 2

Quantitative chemical analysis *by weight* leads to two fundamental laws of chemistry: the law of constant proportions and the law of multiple proportions. These laws, summarizing the results of experiments, are under-

stood on the basis of the hypothesis that matter consists of atoms and molecules.

Quantitative analysis *of gases by volume* leads to the law of Gay-Lussac and its interpretation by Avogadro's hypothesis. Molecular formulas are based on this result. Although they cannot be rigorously derived, a consistent system of such formulas (H_2, Cl_2, O_2, H_2O) has been worked out.

The valence of an atom describes its ability to bind one or several other atoms of certain kinds.

The atomic and molecular weights give the weights (or masses) of atoms and molecules in terms of an arbitrary unit, $\frac{1}{16}$ of the weight (or mass) of an oxygen atom.

A new unit of mass is introduced, which simplifies many laws and computations of chemistry. One gram atom is the number of grams given by the atomic weight, and 1 gram molecule or mole is the number of grams given by the molecular weight. The number of molecules N contained in 1 mole is a universal constant, Avogadro's number.

PROBLEMS

2.1. *Formula of rock salt.* Rock salt is analyzed by weight into 39.3 per cent sodium and 60.7 per cent chlorine. What is its chemical formula?

2.2. *Formula of ethylene.* Ethylene (density under standard conditions = 1.250×10^{-3} g/cm^3) is analyzed by weight into 85.62 per cent carbon and 14.38 per cent hydrogen. What is its chemical formula?

PART II

GASES

We are interested in the study of gases for various reasons. Historically, their properties represent the first major field beyond chemistry in which the atomic theory, based on the work of Joule, Clausius, and Maxwell, succeeded in interpreting a vast group of observed facts. The theory culminated in the first determination of the masses and sizes of molecules. This development began about half a century after Dalton's application of the atomic hypothesis to the fundamental laws of chemistry. In many chemical investigations of gases, results of the kinetic theory are applied. Furthermore, the study of gases is important for spectroscopic investigations since only in gases are the individual atoms practically separated from their neighbors and exhibit their individual properties by sharply defined spectral lines. The properties of gases must be known for the study of electric discharges through gases, exhibiting cathode rays and positive rays, which yield most important results on the nature of electricity and matter. In astrophysics, the kinetic theory of gases enters into the consideration of stellar atmospheres. Finally, the flow of electricity through metals and from glowing metals is understood by the comparison of the electricity contained in the metal with a gas.

In order to make the kinetic theory of gases accessible to an elementary discussion, we shall introduce simplifying assumptions. In Chap. 7 we shall report on the results of the refined mathematical treatment, which are surprisingly well approximated by our simple methods.

CHAPTER 3

EXPLANATION OF PRESSURE AND TEMPERATURE

3.1. Experiments. The first aim of the theory of gases is the interpretation of the ideal-gas law. This law itself represents an empirical equation and, therefore, is independent of any theory. To begin with, we describe the set of experiments leading to that law. The experimenter has methods for measuring the pressure of a gas, its volume, its mass, and its temperature. The pressure p is measured with a mercury manometer (barometer). From its height h the *pressure* p is computed as p = height $\times$ density of mercury. This equation yields the pressure in absolute units (dyne/cm^2). From the volume and mass we compute the *specific volume* v = volume/mass, measured in cm^3/g; v is the reciprocal of the more familiar *density*. The *temperature* t, finally, is defined as the quantity measured by the mercury thermometer, calling its readings for water at the ice point 0 and at the boiling point 100 degrees centigrade (written 100°C). These experiments lead to the result that at a constant temperature the pressure is inversely proportional to the specific volume (Boyle's law); furthermore that the product pv is a linear function of the temperature (Charles' law). In an equation, this experimental result is stated as

$$pv = R'(t + 273)$$

where R' is a constant of proportionality specific for the gas under investigation. The same addend 273 shows up in the corresponding equations for all gases. Therefore, it is convenient to introduce a new letter $T = t + 273$. This we call the absolute temperature, measured in degrees Kelvin (written °K).

In the next group of experiments, we compare the values of R' (the specific gas constants) for various gases and find that R' is inversely proportional to their molecular weights m. This is written as an equation $R' = R/m$, where R is a constant of proportionality correlating the various gases. Hence R is not *specific* for one gas any more but is a *universal* constant called the "universal gas constant." Now we write the ideal-gas law as

$$pv = \frac{R}{m}T \tag{3.1}$$

where it is understood that the mass is measured in grams. [This equation is easily changed, applying Eq. (2.1), into the shape in which it is given in most textbooks of chemistry,

$$pV = RT \tag{3.2}$$

where V is specific volume in cubic centimeters per mole. We shall use Eq. (3.1).]

The numerical value of the universal gas constant R may be computed by introducing any set of values of p, v, m, and T measured for any gas into the ideal-gas law, Eq. (3.1), avoiding excessively high densities. For example, air (average molecular weight $m = 29.0$) at 0°C and a pressure of 1 atm has a density 1.293 g/liter. This leads to the value

$$\begin{aligned} R &= 83.1 \times 10^6 \text{ ergs/(mole degree)} \\ &= 1.987 \text{ cal/(mole degree)} \end{aligned}$$

The unit follows from the consideration that $p \times$ volume = work. The last equation shows that the volume per mole, V, of any gas depends only on p and T, not on the nature of the gas, because the molecular weight m does not enter into the equation. A figure familiar to every chemist is the volume occupied by 1 mole of any gas under standard conditions. This figure is easily computed by introducing $T = 273$°K and $p = 1$ atm $= 1.013 \times 10^6$ dynes/cm^2 into Eq. (3.2). The result is 22.4 liters. This is called the "molar" volume or "gram-molecular" volume of gases.

We must examine the validity of the ideal-gas law more closely. For our purpose it is not important that at high densities deviations are noticeable. At 1 atm, where this law is applied, *e.g.*, in many chemical investigations, it represents a very satisfactory approximation. More difficult is the concept of the temperature. Our definition of the temperature is limited to the range of the mercury thermometer and, therefore, fails below -39 and above about 550°C. Outside these limits, the statement $pv = RT/m$ cannot be based on measurements because we have not defined what we mean there by the word "temperature." All we can do is arbitrarily apply the same statement; in other words, use the same equation as the *definition* of the temperature. For the theory of gases this difficulty is immaterial since we simply consider the equation as describing experiments, *i.e.*, consider the temperature range of the mercury thermometer.

3.2. Kinetic Theory of Gases. The kinetic theory of gases has been developed starting from the concept of heat where heat energy is identified with the energy of motion of the smallest particles, the atoms and molecules. It is an obvious picture that in the solid body each atom is bound to a certain position about which it vibrates. When heating the solid body, we reach the melting point where the motion becomes so violent that the atoms and molecules are free to move, but they are still in touch with one another. When we heat and finally evaporate the liquid, the atoms and

molecules form a vapor or a gas. Since the density of the gas is much smaller than that of the liquid, we must assume that in the gas the molecules do not touch each other but are separated by distances large as compared with their own diameters. Now their heat motion enables them to shoot in straight lines until they collide with one another or the walls of the container. We assume that these are elastic collisions. Furthermore, we assume that there are no mutual forces acting between the molecules except for the repulsion acting while the molecules are in actual collision.

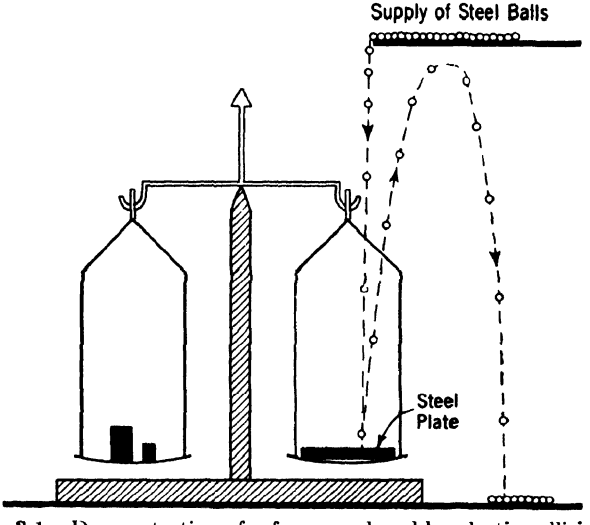


FIG. 3.1. Demonstration of a force produced by elastic collisions.

Hence between collisions each molecule will travel in a straight line (neglecting the parabolic curvature of its path caused by the gravitational force). For the sake of convenience we shall call the smallest particles "molecules" although in some gases they are individual atoms.

For the interpretation of the ideal-gas law we want to understand the pressure of a gas. This, in the kinetic theory, is interpreted as the bombardment of the wall by molecules, a bombardment so rapid that we have no chance to distinguish the individual molecular impacts but notice only their over-all effect as the pressure. This effect of a rapid bombardment is demonstrated by a steel plate which is hit with small steel spheres at so rapid a rate that only the over-all effect is noticeable as a force. If the steel plate is lying on one pan of a balance (Fig. 3.1), its weight being equilibrated by weights on the other pan and, say, 10 steel spheres per second are dropping from a height of 50 cm onto the steel plate, bouncing back in elastic impacts, and finally falling down somewhere on the table, then this rapid bombardment causes a certain steady deflection of the balance, indicating the same effect as that of a uniform force.

We want to compute the weight or force which, instead of the bombardment acting on the same pan, causes the same deflection. For the computation of this force it is convenient to suppose that the plate is mounted with its plane vertical (free to move in the horizontal direction) and is hit by bullets arriving horizontally (Fig. 3.2). This arrangement assures that we consider only the effect on the plate of the bullets (irrespective of the gravitational force). The plate (mass M) is supposed to be very heavy as compared with the bullet (mass m). Then each bullet bounces back in an elastic impact and so very nearly reverses its velocity c and momentum mc. In other words, its momentum changes from $+mc$ to $-mc$, *i.e.*, by the amount $2mc$. We compute the acceleration given to the plate by the bombardment and the uniform force that would give the same acceleration as follows. Each impact imparts a certain momentum MC to the steel plate (C = velocity of plate due to one impact). C is computed from the law of conservation of momentum.

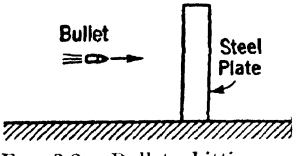


FIG. 3.2. Bullet hitting a steel plate.

$$2mc = MC \qquad \text{or} \qquad C = \frac{2mc}{M}$$

The value of C is very small as compared to c. Hence we may assume that *all* bullets collide with the *same* velocity c disregarding the fact that each impact gives a very small velocity C to the plate. When we shoot n bullets per second against the plate, we give it a velocity per second (acceleration) nC. The force F that would cause the same acceleration of the plate of mass M is, according to Newton's second law,

$$F = MnC = 2mnc \tag{3.3}$$

Finally, it is obvious without computation that the force F is the same when the plate is fixed instead of free to move; this case can be approached by assuming a very large ratio of masses M/m.

The same argument applies to the computation of the pressure exerted by a gas. In order to simplify our equations we introduce the approximation that the gas contained in a cube (side b) consists of three equal groups of molecules, each group shooting parallel to one side between two opposite walls on which the molecules belonging to this group exert a pressure. Each group contains $nb^3/3$ molecules (n = number of molecules per cubic centimeter). We disregard mutual collisions among molecules. Furthermore, we assume that all molecules have the same speed c. To begin with, we apply the preceding computation to the effect of *one* molecule (mass μ) on *one* of the walls as follows:

Distance traveled between consecutive impacts = $2b$
Time between consecutive impacts = $2b/c$

Number of impacts per second $= c/2b$
Force exerted by 1 molecule [see Eq. (3.3)] $= \mu c^2/b$

Next we consider *all molecules* ($nb^3/3$) of our group. They exert the force

$$F = \frac{1}{3}nb^3 \times \frac{\mu c^2}{b} = \frac{b^2\mu n c^2}{3}$$

Consequently, the pressure p (= force/area) results as

$$p = \frac{b^2\mu n c^2}{b^2 3} = \frac{\mu n c^2}{3}$$

Here μn has the significance of the mass contained in the unit volume, *i.e.*, the density or the reciprocal specific volume $1/v$. So we obtain as the final result of our theory

$$pv = \frac{c^2}{3} \tag{3.4}$$

In order to check the validity of our *theory*, we compare its result, *i.e.*, the last equation, with the result of the *experiments*, *i.e.*, the ideal-gas law $pv = RT/m$. Here we are disappointed because the two equations are not the same. Hence, as far as this argument goes, we have no reason to believe that the basic idea of our theory is correct. Our next endeavor will be to make predictions on the basis of the theory that may be checked by experiments. This is the subject of the next chapter. For the time being, all conclusions from our theory are tentative, subject to the condition, "if our theory is correct." If the theory is correct, we can equate the left sides of the ideal-gas law and the theoretical equation (3.4). Thus we conclude

$$\frac{c^2}{3} = \frac{R}{m}T \tag{3.5}$$

This result gives us a chance to compute the numerical values of the speed of molecules. The result, *e.g.*, for oxygen at 0°C, is

$$c = 460 \text{ m/sec}$$

a surprisingly large value, larger than the speed of sound in air.

On this basis we easily express the kinetic energy of each molecule (mass μ) as

$$E_k = \frac{1}{2}\mu c^2 = \frac{3}{2}\mu\frac{R}{m}T$$

or, remembering $m = N\mu$ [Eq. (2.3)],

$$E_k = \frac{3}{2}\frac{R}{N}T \tag{3.6}$$

Since R and N are both universal constants, we conclude that, if our theory is correct, at the same temperature all molecules have the same kinetic energy although their masses and speeds may differ widely.

The last equation gives us an understanding of the physical significance of the temperature. The absolute temperature is proportional to the kinetic energy of the rectilinear motion of the molecules. Originally we introduced the absolute temperature, $T = t + 273$, only for the mathematical simplification of the ideal-gas law [Eq. (3.1)]. Here we find that on the absolute scale (or Kelvin scale) the zero has a physical significance; it means the ultimate disappearance of molecular motion.

A summary of this discussion will be found at the end of Chap. 7.

PROBLEMS

3.1. *Ideal-gas law.* A bulb of 5.00-cm radius contains 0.400 g of nitrogen at 20°C. Compute the pressure (in atm).

3.2. *Composition of air.* Under standard conditions the density of oxygen is 1.4290×10^{-3}, that of nitrogen 1.2507×10^{-3}, and that of air 1.2928×10^{-3} g/cm³. Compute the percentages, by volume, of oxygen and nitrogen present in air assuming that air contains no other gas.

3.3. *Mass of air.* Compute the total mass of air contained in a lecture room, 5 m high, 12 m wide, and 15 m long at a pressure of 1 atm and a temperature of 20°C. (For density of air see preceding problem.)

3.4. *Force exerted by bombardment, elastic collisions.* Construct a demonstration apparatus in which a rapid bombardment by steel balls produces a force on the pan of a balance. Under the assumption of elastic reflection, from what height h must n (= 10) steel balls be dropped per second to produce the same force F as a 2.5-g weight resting on the pan if each ball hits the pan only once? Take the mass of each steel ball $m = 0.4$ g and neglect friction due to air.

3.5. *Force exerted by bombardment, inelastic collisions.* A sandbag is bombarded by a machine gun shooting horizontally; m = mass of each bullet; n = number of bullets per second; c = velocity of bullets. Compute the force F exerted on the sandbag.

CHAPTER 4

EXPERIMENTAL TESTS

In the preceding chapter we failed to derive a theoretical equation for the pressure of a gas agreeing with the ideal-gas law representing the experiments. There is no contradiction between theory and experiment, but the theory fails to introduce the concept of the temperature and, instead, predicts molecular speeds. Our next concern is to test the kinetic theory by experiments. This is the purpose of the present chapter discussing the direct measurement of these speeds, specific heats of gases, and Brownian motion.

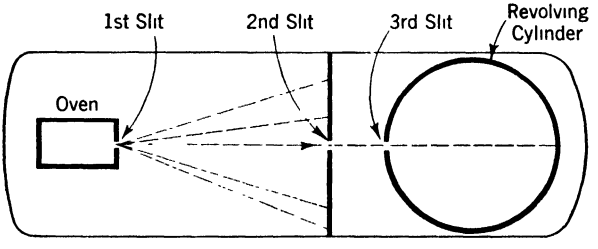


FIG. 4.1. Stern's measurement of molecular velocities, using a drum revolving at high speed.

4.1. Measurement of Molecular Speeds. Molecular speeds were first measured by Stern (1920) about sixty years after the theoretical prediction of these speeds outlined in the preceding chapter. This large time interval indicates the great technical difficulty of the experiment.

For this measurement Stern developed the "atomic beam" method (Fig. 4.1), which in recent years has found other important applications in atomic physics. We shall describe the experimental arrangement used later by Zartman. A small capsule containing a little silver is placed in a highly evacuated chamber and heated by an electric oven to such a high temperature that the silver evaporates. The vapor atoms shoot out of a narrow slit (first slit) into the high vacuum and there continue their straight paths. Most of the silver atoms are deposited on the walls of the container. Some atoms, however, shoot through a second slit, mounted parallel to the first slit, in the middle of the chamber, and continue their paths as a narrow beam. They, in turn, are incident on the outside wall of a metal cylinder with the axis parallel to the slits, which can be rotated

at high speed about its axis. In the wall of this cylinder a third slit is cut parallel to the axis. Suppose the cylinder is at rest and adjusted so that the atomic beam just passes through its slit. Then, gradually, a deposit of silver is formed at the rear inside wall of the cylinder, exactly *opposite to the slit*. Next let us assume a rapid revolution of the cylinder. Then, most of the time, the silver arriving in the beam is deposited on the outside wall of the cylinder and wasted for our experiment. We are interested in the small fraction of the silver atoms that happen to pass through the third slit in the moments when it just faces the beam. These atoms need some time (diameter/velocity of atoms) to travel to the opposite wall of the cylinder. During this brief time interval the cylinder rotates by a small angle so that now the deposit is formed not opposite the slit but in a *position slightly shifted* by the distance s. The same time interval just mentioned may be expressed as s/velocity of surface. Hence,

$$\text{Speed of atoms} = \text{speed of surface} \times \frac{\text{diameter}}{s}$$

Stern's results agree within the limit of his accuracy with the theoretical prediction giving an outstanding confirmation of the kinetic theory of gases. We shall mention the method again when discussing the distribution of molecular speeds (Sec. 7.1).

4.2. Specific Heats of Gases. The conventional definition of specific heat states: The specific heat of any substance is the quantity of heat required to raise the temperature of 1 g of the substance 1°C. Instead of the mass unit gram, we introduce the mass unit mole and so write

$$\text{Specific heat} = \frac{\text{increase of heat energy of 1 mole}}{\text{increase of temperature}} \tag{4.1}$$

It has been found that the specific heats of gases depend upon the method of measurement. We may measure them either at constant pressure or at constant volume. When the gas is contained in a cylinder closed by a piston, we keep the *volume* constant by screwing the piston to a certain position, or we keep the *pressure* constant by placing a certain weight on the piston. The specific heat of a gas at constant pressure c_p turns out to be larger than the value obtained at constant volume c_v. The difference is explained by the idea that, when heating a gas *at constant volume*, we simply impart heat energy to the molecules. However, when we do the same *at constant pressure*, we must do additional work in raising the piston. Since we are interested in the energy content of the molecules, we do not pay attention to the work required to raise the piston and simply consider c_v, the specific heat of the gas at constant volume.

We begin with the results of experiments. In Table 4.1 we list a few representative values of c_v. This table makes it evident why we prefer to

Table 4.1. *Specific Heats of Gases*

Gas	c_v cal/(mole degree)
He	3.02
A	2.95
Hg vapor	2.94
O_2	5.00
N_2	4.98
CO	5.01
HCl	4.90

express the specific heats in terms of 1 mole instead of 1 g; it brings out a simple relation. All gases known to the chemist as monatomic, *i.e.*, as having molecules identical with single atoms (the rare gases, mercury vapor), have specific heats of nearly 3 cal/(mole degree) although they differ widely in their atomic weights. Most gases consisting of diatomic molecules have specific heats near 5 cal/(mole degree). A further fact is that these values of c_v are independent of the temperature and pressure. These are the observed facts that we wish to explain.

The kinetic theory suggests the idea that the heat energy required to raise the temperature of the gas is stored in the heated gas as kinetic energy of the individual molecules. This idea leads to a simple theoretical prediction based on the theoretical expression for the kinetic energy of 1 molecule [Eq. (3.6)].

$$E_k \text{ of 1 molecule} = \frac{3}{2}\frac{R}{N}T$$

Consequently the total heat energy of 1 mole (or N molecules)

$$E_k \text{ of 1 mole} = N\frac{3}{2}\frac{R}{N}T = \frac{3}{2}RT$$

The specific heat c_v is computed as the increase of this energy when we heat the gas from T_1 to T_2 divided by this increase of temperature [Eq. (4.1)]; hence,

$$c_v = \frac{\frac{3}{2}R(T_2 - T_1)}{T_2 - T_1} = \frac{3}{2}R \tag{4.2}$$

This is a surprisingly simple result. It correctly states that the specific heats of gases are independent of the pressure and the temperature, as p and T do not enter into the last equation. Beyond that, the last equation gives the numerical value

$$c_v = \tfrac{3}{2} \times 1.987 = 2.98 \text{ cal/(mole degree)}$$

This value agrees within the limits of error of the measurements with the specific heats of the monatomic gases (Table 4.1). So far we have found an experimental confirmation of the kinetic theory. It seems marred,

however, by the larger values of the specific heats measured for the diatomic gases. This discrepancy indicates that we must refine our assumption, stating that the heat energy of a gas is identical with the kinetic energy of the molecules as expressed in Eq. (3.6). Here we shall only report on the argument without further mathematical derivation. The kinetic energy [expressed in Eq. (3.6)] represents only the energy due to the *rectilinear motion*. For the specific heat, however, it is a plausible assumption that the diatomic molecule may perform a *rotation* in addition to the rectilinear motion. This makes each diatomic molecule a larger reservoir of energy which takes up more heat energy and so is responsible for a larger specific heat. The quantitative treatment, which we omit, leads to a specific heat of 4.96 cal/(mole degree) for the diatomic gas, in good agreement with the measurements.

This is the difference between the two experiments in which the kinetic energy of molecules manifests itself: In the *specific heat* of a gas we must consider the *total energy content* of the molecule, including rectilinear motion and rotation (in other cases, not discussed here, also vibration); but the *pressure* of a gas is fully explained by the *rectilinear motion* alone of the molecules impinging on a wall, where single atoms and diatomic molecules produce the same effect.

It should be added that in Table 4.1 several odd cases of specific heats are disregarded, in particular the fact that the specific heat of hydrogen, H_2, although showing nearly the regular value at room temperature, shows considerable variations with the temperature. These are unexplained on the simple basis of our kinetic theory and require the quantum theory for their explanation. Although additional assumptions are necessary for the interpretation of a part of the experimental facts, one may well say that the specific heats of gases provide an experimental confirmation of the kinetic theory of gases.

The history of the theory of specific heats is typical of the development of a theory. When we find that the theory only partly represents the facts, we do not throw it away but try to refine it by additional assumptions. At present the very complicated behavior of hydrogen gas at various temperatures can be quantitatively accounted for by the advanced development of the quantum theory, which is not discussed here.

4.3. Brownian Motion. The last experiment to be cited in support of our theory has a wider importance in that it demonstrates the perpetual heat motion of the smallest particles in gases as well as in liquids. As early as 1827, just after the introduction of achromatic lenses, the English botanist Brown discovered that small dust particles suspended in water, when viewed through a microscope, show a perpetual, entirely irregular motion. The same type of motion can be seen in a gas when we observe through a microscope a small oil drop slowly falling down. This irregular

motion is incidentally observed in Millikan's oil-drop experiment (Chap. 9). Only the larger drops are falling uniformly while the smaller ones appear to perform an irregular dance about the average line of their fall.

Long after the observation made by Brown, this mysterious irregular motion was identified with the heat motion common to all particles. Why is it noticeable only in the smallest drops? Individual *gaseous molecules* have sizes so small and speeds so high that there is not the slightest chance of observing them under the microscope. The *smallest oil drop* just observable under intense illumination through the microscope behaves like a giant molecule. Since it has a mass ever so much larger than that of the ordinary molecule, its random heat motion is so much slower that it is clearly discernible. On the other hand, the *larger oil drops*, more easily observed under the microscope, have such low speeds of heat motion that this motion is not noticeable. It is a fortunate coincidence that there exists a range where the drops are large enough to be visible and small enough to have an easily observed heat motion. In the Brownian motion of tiny crystal fragments suspended in liquids one can distinguish the violent motion of the smallest fragments and the slower motion of the larger fragments. Odd-shaped fragments show a rotation as well as a linear motion. These motions take place only over the smallest distances observable under the microscope. Hence the rotation is not observed over several revolutions but only over a few degrees followed by another short random rotation.

Brownian motion can be well demonstrated by microscopic projection. This is the most direct and striking demonstration of heat motion.

A summary of this material will be found at the end of Chap. 7.

PROBLEMS

4.1. *Measurement of molecular speed.* In his refinement of Stern's method (Fig. 4.1, Sec. 4.1), Zartman used a drum of radius $r = 5.0$ cm revolving at the rate of 241 rps. Although he actually measured the velocity distribution of bismuth (partly molecular, partly atomic), we are interested only in the average velocity. The shift between the zero position and the average displaced position of the metal deposited is measured as 1.8 cm. To what molecular velocity does this correspond?

4.2. *Specific heat.* Compute the numerical value of the universal gas constant, in erg/(mole degree), and the specific heat at constant volume, in cal/(mole degree), of helium from the following data: Under standard conditions the density of helium is 1.785×10^{-4} g/cm^3. Helium is a monatomic gas of atomic weight $m = 4.00$.

*

CHAPTER 5

MEAN FREE PATH AND VISCOSITY

So far, in discussing the kinetic theory of gases, we considered only collisions of molecules *with the walls*, disregarding *mutual* collisions among molecules because they are irrelevant for the computation of the pressure exerted by the gas. In the present chapter dealing with the viscosity, mutual collisions are all-important.

5.1. Mean Free Path. Early in the history of the kinetic theory the mean free path was introduced on the basis of the following argument. If we uncork an ammonia bottle in one corner of a room, we might expect the ammonia smell to be noticeable instantaneously all over the room since the theory tells us that the molecules have a speed of several hundred meters per second. As a matter of fact, however, the propagation of the vapor, made evident by the smell, takes a time interval of, say, 1 min. This delay was explained by Clausius who assumed that each molecule, although endowed with high speed, travels only a short distance in a straight line until, by a collision with another molecule, it is deflected. Therefore, its path may look like the crooked line sketched in Fig. 5.1. Mutual collisions retard the propagation across a room. The figure indicates the meaning of the free path between collisions. As we cannot observe an individual free path of a molecule, all we can do is define its average, called the "mean free path," and correlate it with the various properties of the gas, the size of molecules, the number of molecules per cubic centimeter, and in Sec. 5.2, the coefficient of viscosity.

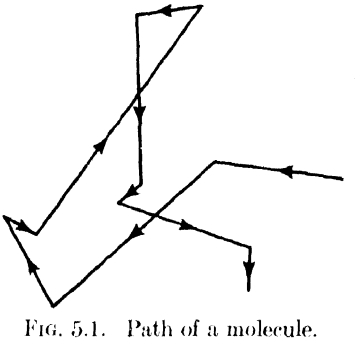


FIG. 5.1. Path of a molecule.

Without computation it is evident that the mean free path L decreases when the number of molecules per unit volume or their radius r increases. This relation is quantitatively expressed as follows (see Fig. 5.2). As an approximation we suppose that only one molecule is moving, all other molecules being at rest. This molecule, when moving over an arbitrary distance d, carves out a volume = cross section $\times$ distance = $\pi r^2 d$. How many other molecules does it hit on its way? It hits not only those whose centers are in the volume carved out, but in addition those which intrude into the

volume carved out with any small part of their volumes. The centers of all these molecules are located in the volume with twice the radius, *i.e.*, the volume $\pi(2r)^2 d$. Calling n the number of molecules per cubic centimeter, there are $n\pi(2r)^2 d$ molecules. This is the number of collisions suffered by the molecule moving through the distance d. Hence the number of collisions in the unit distance is $4\pi nr^2 d/d = 4\pi nr^2$, and its reciprocal is the mean distance between consecutive collisions, which is identical with the mean free path L.

$$L = \frac{1}{4\pi nr^2} \tag{5.1}$$

This equation shows that the mean free path is inversely proportional to

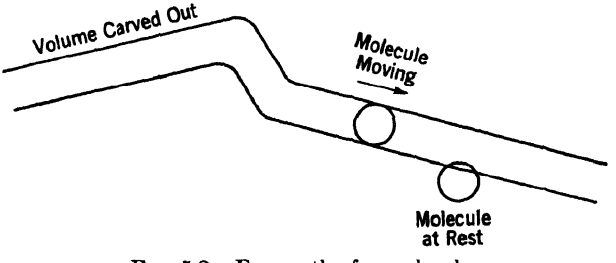


FIG. 5.2. Free path of a molecule.

the number of molecules per cubic centimeter, n, hence inversely proportional to the density or, at constant temperature, inversely proportional to the pressure of the gas.

The long mean free path prevailing at very low pressure can be demonstrated by the evaporation in high vacuum of a silver bead. An obstacle placed in the path of the evaporating silver atoms throws a sharp shadow, which is observed in the silver deposit on the wall.

5.2. Viscosity. We shall study the viscosity of a gas in order to find evidence concerning the mean free path and, indirectly, the masses and sizes of molecules. Later, discussing Millikan's oil-drop experiment, we shall meet the same quantity again.

When moving a body through a liquid or through air, we feel a resistance due to friction. Various liquids provide different resistances, and the resistance of any one is much higher than that of a gas. This property of gases and liquids is called "viscosity." We introduce a definition of the coefficient of viscosity when considering the following experiment which, at the same time, serves for its most precise measurement. The apparatus (Fig. 5.3) consists of two metal cylinders, one, a little smaller than the other, mounted coaxially inside the other. The larger cylinder revolves at a uniform speed of about 1 rpm. The smaller cylinder is suspended on a delicate spring. When the outer cylinder revolves, the inner one tends to follow. This indicates that the gas between the cylinders transmits a

force from one wall to the other. This force turns out to be independent of the material of the cylinders. This is explained by the assumption that the layer of gas touching the cylinder does not move with respect to that cylinder. This has the same effect as if, for any material of the cylinder, its surface consisted of molecules of the gas. The force transmitted depends only on the gas used. Therefore, all we have to consider is the "internal friction," since there is no noticeable friction characteristic, for example, for the combination air-copper. The velocity of flow of the various layers between the two cylinders is simply a linear function of the distance, as may be observed by watching dust particles suspended in the gas.

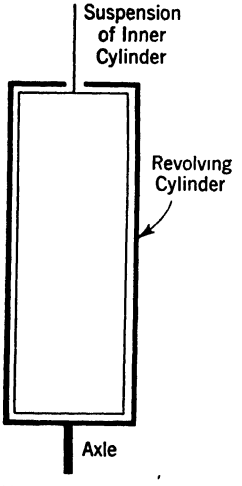


FIG. 5.3. Measurement of viscosity. As the outer cylinder revolves, the torque transmitted to the inner cylinder is measured.

It has been found by experiment that in each gas the force transmitted from the revolving to the nonrevolving cylinder is proportional to the area and the linear velocity u of the revolving cylinder, and inversely proportional to the distance s between the cylinders. The quotient u/s is called the "velocity gradient." This relation is expressed with the help of a factor of proportionality η, called the coefficient of viscosity, which is characteristic for the gas.

$$\frac{\text{Force}}{\text{Area}} = \eta \frac{u}{s} \tag{5.2}$$

From this equation, the unit of η is easily derived as follows

$$\text{Unit of } \eta = \frac{\text{dyne}}{\text{cm}^2} \times \frac{\text{sec}}{\text{cm}} \times \text{cm} = \text{cm}^{-1}\ \text{g}\ \text{sec}^{-1}$$

For air under standard conditions the value is

$$\eta = 1.8 \times 10^{-4}\ \text{cm}^{-1}\ \text{g}\ \text{sec}^{-1}.$$

The experiments reported are interpreted in the kinetic theory of gases as follows: Let us consider a gas which is enclosed between two parallel, plane, horizontal surfaces, a distance s apart, with the lower surface at rest while the upper moves with a uniform horizontal velocity u. We assume that the layer of gas touching one or the other surface partakes of the motion of that surface and that the intermediate layers have flow velocities described by the constant gradient u/s. In addition to this, each particle has a velocity of thermal agitation, the average value of which is much higher than that of the flow. As in the theory of the ideal-gas law, we simplify the description of the thermal agitation by assuming that the

molecules are moving only along three coordinates, two thirds parallel to the surfaces and one third normal to them. This assumption, however, applies only to the high velocity of the thermal agitation and does not prevent us from attributing to the last third of the molecules the additional, low *horizontal* velocity due to the flow. Our aim is to describe the viscosity in terms of the action of those molecules which move between layers flowing with different velocities. Since those molecules whose velocity of thermal agitation is in planes *parallel* to the two surfaces do not travel to other such planes and hence do not contribute to the viscosity, we shall not mention them any more.

The viscosity is explained by the action of those molecules which move in the direction *normal* to the surfaces. We shall express the force which these molecules produce in the direction of the flow in terms of Newton's second law

$$\text{Force} = \frac{\text{change of momentum}}{\text{time interval}}$$

When the molecules move downward they pass from fast flowing layers into slower ones. We assume that a molecule in any layer, by collisions, takes up the horizontal flow velocity of the layer. A molecule moving downward causes a loss of momentum of flow of an upper layer because this layer loses the body of mass μ flowing with the velocity of the particular layer, hence endowed with the corresponding momentum in the direction of the flow. At the same time the lower layer gains the same momentum. First we compute the combined action of many molecules per unit area and time, all moving *downward*. Next, we shall apply the corresponding argument to the molecules moving *upward*, in our example from a layer of lower into one of higher flow velocity. The *resulting* change of momentum per unit area and time, hence the resulting force per unit area, is given by the difference between these two contributions. The same resulting force, which is exerted by each layer on its lower neighbor, ultimately acts on the lower surface and there is observed as the effect of the viscosity of the gas. The equal and opposite force is exerted by the lower on the upper surface as is postulated by Newton's third law which states that to every force there is an equal and opposite reaction.

We compute the momentum per unit area and time transferred through an arbitrarily selected horizontal plane. If we call n the total number of molecules per unit volume, then $n/6$ molecules per unit volume are moving downward and the same number upward. The number of molecules passing downward through a unit area of any layer in a unit time is the sum of all those contained in a cylinder whose base is equal to a unit area and whose length is equal to the distance traveled by a molecule in a unit time, *i.e.*, $nc/6$ (c = velocity of thermal agitation).

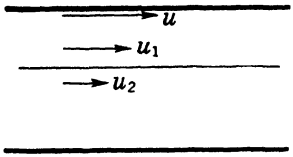


FIG. 5.4. Flow velocity in a gas.

Molecules passing downward through such a plane will, on the average, travel a distance given by the mean free path L before they suffer collisions. On the average the molecules come from a layer at a distance L above the plane considered (Fig. 5.4) and leave this layer while endowed with the corresponding momentum in the direction of the flow μu_1. Hence, we express the resulting momentum per unit area and time transferred by all molecules, traveling downward and upward through the plane, as follows:

$$\text{Horizontal momentum transferred from layer above} = \frac{nc}{6}\mu u_1$$

$$\text{Horizontal momentum transferred from layer below} = \frac{nc}{6}\mu u_2$$

where u_2 is the flow velocity of the layer one mean free path below the plane considered. Since we assume that $u_1 > u_2$, there is a resulting momentum transferred downward:

$$\text{Horizontal momentum per unit area and time} = \frac{nc}{6}\mu(u_1 - u_2).$$

This is identical with the horizontal force per unit area exerted on each lower layer by its upper neighbor

$$\frac{\text{Force}}{\text{Area}} = \frac{nc}{6}\mu(u_1 - u_2)$$

In particular, this gives the force per unit area exerted on the lower surface of our apparatus which is due to the motion of the upper surface and is transmitted through the gas.

In our approximation, the layers endowed with the flow velocities u_1 and u_2, respectively, are the distance $2L$ apart. Hence, we can write the velocity gradient $(u_1 - u_2)/2L = u/s$. Introducing this expression into the last equation we obtain

$$\frac{\text{Force}}{\text{Area}} = \frac{nc}{3}\mu L\frac{u}{s}$$

Since $n\mu$ is the density, or the reciprocal specific volume $1/v$, we rewrite the last equation

$$\frac{\text{Force}}{\text{Area}} = \frac{cL}{3v}\frac{u}{s} \tag{5.3}$$

The result of the kinetic theory agrees with that of the experiment in that both give force/area as proportional to the velocity gradient u/s. Considering the other factors, however, our theory leaves us in the same situation as that of the ideal gas law (Sec. 3.2); our theoretical result [Eq. (5.3)] is not simply identical with the result of measurements [Eq.

(5.2)]. Therefore, only in a tentative way subject to experimental tests can we compare the two results for force/area and so finally obtain the relation

$$\eta = \frac{cL}{3v} \tag{5.4}$$

If our theory is correct, we can compute the mean free path L from the measured quantities η and v and the thermal speed c, computed earlier [Eq. (3.5)]. The result for air under standard conditions is $L = 0.9 \times 10^{-5}$ cm.

In discussing the experimental confirmation of the theory of viscosity, we only mention the pressure effect. The theory predicts that in the expression for the viscosity η [Eq. (5.4)] the factor $1/v$ is proportional to the pressure, the factor L inversely proportional, the other factor independent; hence the viscosity η should be independent of the pressure. In the early history of this theory, before measurements were available, this prediction was considered to be in obvious disagreement with common sense. It was argued that in high vacuum no force at all is transmitted between the two surfaces (Fig. 5.3). Hence the viscosity must be a function which goes down to zero for zero pressure. Clausius reconciled this objection with the kinetic theory by pointing out that the theory is based on mutual collisions between molecules and, therefore, is valid only within a range of pressures in which the mean free path is small as compared to the dimensions of the vessel. The theory is expected to be inapplicable when high vacuum is approached. This view of Clausius was borne out by experiment. The coefficient of viscosity, defined by Eq. (5.2), was observed to be independent of the pressure over a very wide range but not at the very lowest pressures. Thus, ultimately the measurements confirm the theory. For the lowest pressures, a different theory has been developed, disregarding mutual collisions, taking into account only collisions with the walls. We shall not discuss this theory which, for its range, leads to different results and is of importance in modern high-vacuum technique.

A summary of this discussion will be found at the end of Chap. 7.

PROBLEM

5.1. *Viscosity of air.* In the apparatus of Fig. 5.3, Sec. 5.2, the suspended inner cylinder has a radius $r = 6.40$ cm and a length $L = 26.0$ cm. The outer cylinder has a radius 0.200 cm larger and revolves once in 60.0 sec. The torque so exerted on the inner cylinder is 4.08 dyne cm. Compute the viscosity of air. In actual practice accurate results are obtained by means of a more refined apparatus.

CHAPTER 6

MASSES AND SIZES OF ATOMS; AVOGADRO'S NUMBER

6.1. Measurements on Gases. In our discussion of chemistry (Part I) we were able to determine only relative atomic and molecular weights, *i.e.*, weights based on an arbitrary standard ($\frac{1}{16}$ of an oxygen atom). In the kinetic theory we went a step further by introducing the masses μ of the molecules (measured in grams) and their radii r. Can we compute these quantities on the basis of measurements on gases? In order to answer this question, we must find out whether the theory provides as many independent equations as there are unknowns. If so, we shall be able to compute the unknowns. Here we consider as *unknown* any quantity not directly accessible to observation, *i.e.*, the velocity c of the molecules, their mean free path L, their mass μ, their radius r, and their number per unit volume n. On the other hand, *known* are the quantities whose numerical values can be measured, as the pressure p, the density of the gas δ_g (or its reciprocal, the specific volume v), and the coefficient of viscosity η. Let us assume that all these quantities have been measured for one specific gas, *e.g.*, air, under well-defined conditions.

The first two steps of the computation of the unknowns have been mentioned already. The theoretical expression for the pressure $pv = c^2/3$ [Eq. (3.4)] permits us to compute the numerical value of the velocity c. Next, the theory of the viscosity leads to the equation $\eta = cL/3v$ [Eq. (5.4)] in which now the mean free path L is the only unknown. Hence, for the future, we list the numerical values of c and L among the *known* quantities. The computation of the other unknowns is more involved. We have only two more equations at our disposal: $\delta_g = n\mu$ and $L = 1/4\pi nr^2$ [Eq. (5.1)]. Since they contain *three unknowns* (n, μ, and r) we must find one more independent equation. This is done as follows: Suppose we liquefy the gas, in our example air. In the liquid all molecules touch one another and so fill the space uniformly.

As we assume spherical molecules, we might take into account the empty space left between tightly packed spheres. But it seems futile to do so since the shape of the molecules is unknown. It is better to admit that we are dealing with an approximation.

The density of the liquid δ_l, which is easily measured, is defined as the ratio of mass/volume. The same ratio that is conveniently measured for

several cubic centimeters of the liquid would be obtained for any smaller quantity, in particular for the smallest quantity existing, *i.e.*, the individual molecule. So we obtain one more equation

$$\delta_l = \frac{\mu}{4\pi r^3/3}$$

in which we express the volume of the molecule as that of a sphere. Since this equation contains only the same unknowns as the last two equations mentioned, we are now able to compute all unknowns. Omitting the simple algebra, we list the results for air at atmospheric pressure and the temperature 22°C. (Good measurements of the viscosity are available only for this temperature.)

The known quantities are taken from tables of physical constants: $p = 1.013 \times 10^6$ dynes/cm^2, $\delta_a = 1.196 \times 10^{-3}$ g/cm^3 (at 295°K), $\eta = 1.824 \times 10^{-4}$ cm^{-1} g sec^{-1}, $\delta_l = 0.920$ g/cm^3. The unknowns result as follows:

$$c = 5.0 \times 10^4 \text{ cm/sec} \qquad L = 0.91 \times 10^{-5} \text{ cm}$$
$$r = 3.5 \times 10^{-8} \text{ cm} \qquad \mu = 1.7 \times 10^{-22} \text{ g}$$
$$n = 0.70 \times 10^{19} \text{ cm}^{-3}$$

It is a surprising conclusion that in "high vacuum," as produced at the laboratory (10^{-7} mm mercury), there are still 4×10^9 molecules per cubic centimeter.

In this computation of the molecular constants we do not use the molecular weight. This enters only into the computation of the number of molecules per mole, *i.e.*, Avogadro's number N. N is computed from $m = N\mu$ [Eq. (2.3)] yielding $N = 1.7 \times 10^{23}$ mole^{-1}, assuming an average molecular weight 29.0 for air molecules.*

This determination of the molecular constants typifies the method of atomic physics. We *measure* quantities that are all defined independent of the concept of molecules. For example, the viscosity is defined in terms of a force, a velocity, and a distance. Next we *interpret* these quantities on the basis of processes in which molecules are involved. Thus we derive equations from which we finally *compute* the numerical values of the characteristic constants of molecules although these values are very far beyond the range of direct observation.

The argument presented here led to the first determination of these constants (Loschmidt, 1865). The results of this method are by no means so accurate as the results of modern methods based on electric measurements (Sec. 9.2). Nevertheless the reader will realize how great the progress due to this theory has been when he remembers that in the earlier period it was known only that molecules are smaller than any distance we

*The method presented here lends itself to the determination of the molecular constants in the laboratory (see Appendix 2).

can see under the microscope and lighter than any weight we can weigh on a balance. For forty years the figures given above were the only results available regarding molecular dimensions. Their lack of accuracy is due only partly to the crudeness of our mathematical treatment. There is still another reason for this lack. We introduce the radius r of the molecules and so assume that each molecule is a sphere with a sharply defined surface. Later we shall learn that all atoms and molecules consist of electric charges and, therefore, are surrounded by electric fields. Hence the size of a molecule is not so well defined as the size of a billiard ball but as ill defined as the size of a ball of soft wool, possibly of odd shape. From the kinetic theory of gases we can never hope to derive accurate numerical values of the *masses* of molecules because their poorly defined *sizes* enter into the equations. However, with electrical methods (Sec. 20.4) relative values of molecular masses are determined to six or seven significant figures.

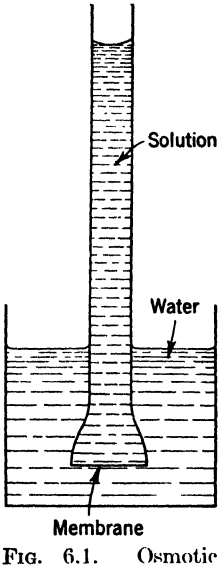


FIG. 6.1. Osmotic pressure.

6.2. Molecules in Solution; Emulsions. An independent determination of Avogadro's number N was performed by Perrin (beginning 1908) who investigated an emulsion, *i.e.*, a liquid in which fine particles are suspended. A discussion of this method will give us an opportunity to apply the laws of the kinetic theory of gases to an entirely different system, to molecules in solution or small particles suspended in a liquid. This new application greatly extends the scope of the kinetic theory of gases. It is known that the cells of living organisms are enclosed by a membrane through which water can pass but which blocks the passage of certain more complex substances dissolved in the water. Such membranes, called "semipermeable," can be artificially produced. The effect of such a membrane on a solution, *e.g.*, of sugar, is demonstrated by the experiment shown in Fig. 6.1. A concentrated sugar solution is put into the inner container closed at the bottom by the semipermeable membrane. When this container is immersed in pure water, the water gradually penetrates from outside into the sugar solution and so raises its level until a well-defined inside pressure is built up.

Van't Hoff (1886) interpreted the process described by assuming that the sugar molecules behave like molecules of a gas. This tends to expand as much as possible within the container which here is represented by the water. But since their motion is blocked by the membrane, all that can happen is that the water passes through the membrane into the solution and so provides a larger container for the sugar. This continues until so high a hydrostatic pressure is built up in the inner container that no more

water passes through the membrane. This value is called the "osmotic pressure" of the solution. It is striking that this correlation between a gas and a solution is even quantitative. According to the gas law, 1 mole of any gas at 20°C in a container of 22.4 liters exerts a pressure of 1.07 atm (Sec. 3.1). Correspondingly 1 mole of sugar dissolved in 22.4 liters of water has an osmotic pressure of nearly 1.07 atm.

This is a special case of van't Hoff's law, which states that the osmotic pressure of a solution is nearly equal to the gas pressure that the dissolved substance would exert if it were a gas of the same temperature occupying the volume offered by the solvent. This discovery opens up a new field for the application of the kinetic theory of gases.

This simple law, however, is restricted to solutions that do not conduct electricity. The osmotic pressures are higher than here predicted in electrically conducting solutions. This deviation from the law can be explained by the assumption that the conductivity of a solution is due to the dissociation of the dissolved molecules into positively and negatively charged particles (Sec. 8.1). The increased number of dissolved particles so generated fully explains the higher value of the osmotic pressure observed.

The comparison of gases and solutions enabled Perrin to make an independent determination of Avogadro's number. First, going back to gases, we consider the distribution of a gaseous atmosphere. A horizontal slice (area A, between two planes at the lower and upper heights h and h') of the atmosphere is assumed to be so thin that the pressure difference between the two heights $p - p'$ is small as compared with the total pressure. We want to express this difference $p - p'$ in terms of the gas law. The pressure difference is caused by the weight of the air contained in the slice; hence,

$$p - p' = \frac{\text{force}}{\text{area}} = \frac{g \times \text{mass}}{A}$$

(for the notation see Sec. 3.1). Since mass = volume/specific volume, we write the same relation, applying the ideal-gas law,

$$p - p' = (h' - h)\frac{Ag}{Av} = (h' - h)\frac{pmg}{RT}$$

On the right side p means an average pressure which is approximately p or p'. Hence

$$p' = p\left[1 - (h' - h)\frac{mg}{RT}\right]$$

Since we presuppose constant temperature, we can replace p'/p by n'/n (n = number of molecules per cubic centimeter),

$$\frac{n'}{n} = 1 - (h' - h)\frac{mg}{RT}$$

The last equation shows that an experimenter who determines the densities of the gas at two adjacent levels can then derive its molecular weight m.

Now we go back to the molecules dissolved in a liquid. According to the correlation between a gas and a solution, the same law is expected to apply to molecules of any kind dissolved in water. For common molecules like sugar, m would be so small that the atmospheric decrease of the concentration would be noticeable only by considering a column of great height. Perrin boldly applied the same law to the distribution in water of heavy particles, large enough to be visible under the microscope. He considered them to be colossal molecules. This was suggested by the fact that the Brownian motion of such particles can well be described by the kinetic theory, simply by treating such particles as huge molecules (Sec. 4.3). In such an "emulsion" a considerable change in the distribution is noticeable within heights of a few centimeters or even millimeters.

This then was the procedure of Perrin. He used microscopic particles of a certain resin (gamboge). First, he separated particles of nearly uniform mass using a centrifuge to hurl the larger particles farther away from the axis than the light ones. This process of separation, which has to be repeated many times, may take several months. Next, by various procedures he determined the mass μ of the individual, rather uniform particles; for example, observing a row of particles, he measured their size under the microscope; furthermore, he measured their density as that of a liquid in which they neither rise nor sink. Finally, in a suspension in water he observed the distribution with height under the microscope, simply counting particles at various heights. This gave the figure for n'/n. (As he actually covered a wider range of height, he had to apply a more general equation derived from our equation above by integration, see Prob. 6.3.)

The equation given above, derived for molecules of a gas had to be modified for the emulsion by introducing the buoyancy due to the suspension of the particles in water. For this purpose, in the above equation (writing $N\mu$ instead of m) we replace the mass of the individual particle μ by (μ − volume × δ_w). A simple calculation leads to the final formula

$$\frac{n'}{n} = 1 - \frac{N\mu}{RT}\left(1 - \frac{\delta_w}{\delta_p}\right)hg$$

where δ_w and δ_p = density of water and particle, respectively. Since all other factors were known, Perrin computed Avogadro's number N.

His result was between 6.5 and 7.2×10^{23} molecules per mole. This is much more accurate than the result reported above (Sec. 6.1) obtained more than forty years earlier. For years this was the best determination of Avogadro's number until it was superseded by the result of Millikan's oil-drop experiment (Chap. 9). Perrin obtained similar results by the measurement of the *Brownian motion* of the same particles that he compared with a statistical theory not to be discussed here.

A summary of this discussion will be found at the end of Chap. 7.

PROBLEMS

6.1. *Molecular quantities.* Argon (molecular weight = atomic weight = 39.9) under standard conditions has a density $\delta_g = 1.783 \times 10^{-3}$ g/cm^3 and a coefficient of viscosity $\eta = 2.10 \times 10^{-4}$ cm^{-1} g sec^{-1}. Liquefied argon has a density $\delta_l = 1.40$ g/cm^3. From these experimental results calculate the following molecular quantities: the velocity c, the mean free path L, the number of collisions per second suffered by a molecule, the number per cm^3 n, the diameter $2r$, and the mass μ. Furthermore, compute Avogadro's number N.

6.2. *High vacuum.* A pressure of 10^{-7} mm of mercury is considered to be "high vacuum." For this pressure and a temperature of 22°C compute the number per cm^3 n of air molecules, their mean free path L, and the mean time t between consecutive collisions, applying the numerical results derived in the text (Sec. 6.1).

6.3. *Perrin's determination of N (calculus problem).* In the text we assumed that Perrin measured the densities n and n' of suspended particles within a difference of height so small that $n - n'$ was small as compared with n. From the formula of the text derive the more general formula that applies for a wide range of height and correspondingly wide range of n.

HINT: (*a*) Starting from the formula for $p - p'$, express $\Delta n (= n - n')$ in terms of $\Delta h (= h' - h)$ and n. For the integration the equation must express the fact that n is decreasing for increasing h. (*b*) Write all quantities referring to n on the left side. (*c*) Write the general integral that contains a constant of integration. (*d*) Determine this constant in terms of the number n_0 which obtains for $h = h_0$. (*e*) Write n as a function of h introducing the exponential function.

COMMENT: The distribution of the pressure in the "isothermal" atmosphere is described by the corresponding law with identically the same exponent.

CHAPTER 7

REPORT ON FURTHER DEVELOPMENTS

This last chapter on the kinetic theory of gases will give a brief report on some further developments of the theory, omitting the mathematical treatment.

7.1. Maxwell's Velocity Distribution. In the theory of the ideal-gas law we simplified the treatment by the assumption that all molecules have the same velocity. This obviously does not agree with the properties of the real gas. When 2 molecules (or billiard balls), both with the same velocity, collide, they will have different velocities after the collision, except in some special cases. Therefore, in the real gas, collisions among the molecules should have the effect of bringing about a distribution of velocities, presumably without sharp limits at low or high velocities. Maxwell (1860) derived the law expressing this distribution of velocities. Suppose that we were able to explore a very large number N of molecules by measuring the velocities c of the individual molecules picked out at random. Their directions do not show any preference; therefore, we pay attention only to the absolute values of their velocities. We divide the whole range of speed arbitrarily into very small steps Δc. For each of these steps we may imagine that we count the number of molecules ΔN having this particular speed. $\Delta N/N$ is the fraction of molecules belonging to each step. We may call $\Delta N/N$ the probability of finding a molecule having the speed associated with a certain small step.

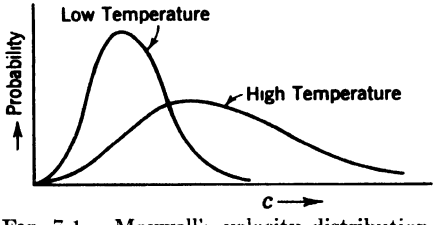


FIG. 7.1. Maxwell's velocity distribution.

Although there is no such technique by which we may explore the speeds of individual molecules in the manner here described, Maxwell succeeded in deriving the mathematical law for this probability as a function of the velocity. We refrain from reporting the complicated formula and instead describe the law by the family of curves given in Fig. 7.1. In our approximation (Sec. 3.2) we found that the one and only molecular speed c introduced into the theory is completely defined by the temperature and the molecular weight, $c = \sqrt{3RT/m}$ [Eq. (3.5)], irrespective of the pressure. Correspondingly, Maxwell found that the temperature and the molecular

weight completely define the velocity distribution. The arithmetical average speed is derived from the distribution law as $\bar{c} = \sqrt{2RT/m}$, a result not very different from the one speed we postulated in our approximation. Figure 7.1 gives the curves for two different temperatures. For the further illustration of the distribution law, Table 7.1 gives the percentage of oxygen molecules at 0°C to be found in the various ranges of velocity.

Table 7.1. *Velocity Distribution of Oxygen Molecules at* 0°C

Velocity Range, m/sec	Per Cent of the Molecules
0–100	1.3
100–200	8.1
200–300	16.7
300–400	21.5
400–500	20.3
500–600	15.2
600–700	9.2
Above 700	7.7

Later, in the theory of electrons in metals, we shall be concerned with the fact that Maxwell's distribution curve has no sharp upper limit. Hence for any given high speed there is always a certain probability of finding some molecules, although this probability is very small for speeds far exceeding the average. This probability increases rapidly with increasing temperature.

Since in Stern's measurement of molecular speeds (Sec. 4.1) the difficult technique was not yet fully developed, only a rather inaccurate determination of the average speed could be made. Later Zartman refined the method and measured the distribution in good agreement with Maxwell's theoretical prediction.

7.2. Mathematical Refinement. The beginning student may be disappointed by the crudeness of our approximations and interested in a comparison of our results with those of a refined analysis that requires a much more advanced mathematical treatment. This comparison is given in Table 7.2.

Table 7.2. *Comparison of Approximate and Refined Methods*

Approximation	Refined Method
$pv = c^2/3$	$pv = \overline{c^2}/3$
$L = 1/4\pi nr^2$	$L = 1/\sqrt{2}\, 4\pi nr^2$
$\eta = cL/3v$	$\eta = \bar{c}L/3v$

In the approximation, c is the one and only molecular velocity considered. In the refined formula $\bar{c}$ means the arithmetical average of all molecular velocities and $\overline{c^2}$ the arithmetical average of the squares of all velocities.

It is surprising how closely the results of our approximations and the refined computation agree. We are sure, to start with, that the approximation would not contain, for example, the factor r^3 where the correct formula would write r^2. This would make the dimensions of the approximate formula wrong and could only be the result of a blunder, not an approximation. But beyond that, even the numerical factors of our approximate equations are not very far off.

SUMMARY OF CHAPTERS 3–7

The first aim of the kinetic theory of gases is the interpretation of the ideal-gas law $pv = RT/m$. The pressure exerted by a gas on a wall is represented by the rapid bombardment of the wall with molecules which leads to the theoretical result $pv = c^2/3$. The comparison of these two equations furnishes a formula for the speed c of molecules. This theory is confirmed (1) by Stern's measurement of molecular speeds, (2) by its application to the specific heat problem, (3) by the Brownian motion.

While in this first section we considered only collisions of molecules *with the walls*, in the next section we consider *mutual* collisions among molecules. The mean free path L of molecules is expressed in terms of their number per unit volume n and their radius r as $L = 1/4\pi nr^2$. The viscosity of a gas is interpreted by the exchange of momentum between adjacent layers of the flowing gas caused by the molecules that exchange places by their thermal motion. This idea leads to the theoretical equation for the coefficient of viscosity $\eta = cL/3v$.

The equations of the kinetic theory (supplemented by an equation for the density of the liquefied gas) furnish the numerical values of the characteristic constants of molecules, their speed c, mean free path L, mass μ, radius r, and number per unit volume n. Furthermore, this yields a value of Avogadro's number N, the number of molecules per mole, which can be determined independently by applying the law of atmospheres to the distribution of small particles suspended in a liquid.

PART III

STRUCTURE OF ELECTRICITY

After studying the atomic structure of *matter* as manifest in chemistry and later applied in the theory of gases, we turn to the experiments that reveal a similar structure of *electricity*. Our first aim is to find mass and charge of the smallest particles observed. Our argument will follow largely the historical development.

CHAPTER 8

DETERMINATIONS OF ϵ/μ

8.1. Faraday's Law of Electrolysis. We shall discuss electrolytic conduction, *i.e.*, electrical conduction through certain liquid solutions, only from a special point of view, namely, that of finding evidence of the structure of electricity. We shall discuss only briefly the experimental evidence expressed in Faraday's law of electrolysis as this law is discussed in elementary courses of chemistry and physics.

When an electromotive force of a few volts is connected with two platinum electrodes dipping into an aqueous solution of hydrogen chloride, HCl, we observe that hydrogen gas is bubbling out at the negative electrode, the cathode, and chlorine gas at the positive electrode, the anode. The volumes of the gases so developed are equal and proportional to the quantity of electricity, *i.e.*, the product of the current and the time. In another experiment, water is decomposed by an electric current. (Here we disregard the fact that pure water does not conduct the current and that we must dissolve, for example, sulfuric acid in the water in order to make it conducting.) In this case the same quantity of electricity used for the decomposition of HCl develops the same volume of hydrogen at the cathode, but only one-half of this volume of oxygen at the anode. Both results have in common the fact that the gases developed at the cathode and anode are equivalent, meaning that, when they are recombined, the original substances HCl and H_2O, respectively, are formed without any residue left.

Hydrogen atoms and all metallic atoms are liberated or deposited at the *negative* electrode. As this indicates that they carry *positive* charges, they are called "electropositive." Correspondingly, chlorine, oxygen, and related atoms that are liberated at the *positive* electrode are called "electronegative."

Faraday correlated these observed facts in the general law

$$\frac{\text{Mass liberated}}{\text{Quantity of electricity}} = \frac{1}{F} \times \frac{\text{atomic weight}}{\text{valence}} \tag{8.1}$$

Here the mass is measured in grams, not gram atoms. 1/F is a constant of proportionality indicating that *for any substance* the ratio mass/quantity of electricity (called "electrochemical equivalent") is proportional to the atomic weight and inversely proportional to the valence. F represents a

new universal constant called the "Faraday constant." The significance of this constant F is evident when we rewrite the equation as follows:

$$F = \frac{\text{quantity of electricity (coulombs)}}{\text{mass (grams)}} \times \frac{\text{atomic weight}}{\text{valence}}$$

Here the units in the parentheses indicate that these are the units applied for the determination of the numerical value of F given below. We simplify this equation with the help of Eq. (2.2) and so obtain

$$F = \frac{\text{quantity of electricity (coulombs)}}{\text{mass (gram atoms)}} \times \frac{1}{\text{valence}} \tag{8.2}$$

This equation shows that the Faraday constant F gives the quantity of electricity (in coulombs) carried by 1 gram atom of a univalent substance. One gram atom of a bivalent substance carries twice this amount, etc. The most accurate determination of this universal constant yields the value $F = 96{,}488$ coulombs/gram atom.

So far we have discussed Faraday's law as it was discovered in 1834; although we have used modern terminology. We shall understand this law better when, according to Stoney (1874), we ask: How large a quantity of electricity is carried by one individual atom? The answer is based on the rule stating that 1 gram atom consists of N atoms.

N atoms of a univalent substance carry F coulombs

1 atom of a univalent substance carries F/N coulombs

1 atom of a bivalent substance carries $2F/N$ coulombs, etc.

The striking result is that *any* univalent charged atom, irrespective of its other chemical properties, carries the same quantity of electricity. This is unexpected because one might guess that different atoms would represent electrical carriers of different capacity. It is still more unexpected that any bivalent charged atom carries exactly twice this amount, etc. This led Stoney to the conclusion that here is a manifestation of a fundamental property of electricity: Electric charges can be subdivided only into very small quantities, each of the value F/N. These units of electric charge Stoney called "electrons." Hence,

$$\text{Charge of electron} = \frac{F}{N} \tag{8.3}$$

Here the question remains open whether these electrons discovered in electrolysis are positive or negative charges or whether electrons of both signs exist and form compounds with the originally neutral atoms. On the basis of this new concept we can briefly restate Faraday's law: *Each valence of a charged atom carries one electron.* The reader may verify that, starting from this statement, we may derive the previous form of Faraday's law.

As far as this argument goes, the value of the electronic charge is un-

known because the value of Avogadro's number N has not yet been determined. Here we refrain from introducing the crude estimate of N based on investigations of gases. Instead we shall use the last equation for the computation of N after having discussed Millikan's independent determination of the charge on the electron.

Considering the present emphasis on atomic physics in which all possible properties of matter are interpreted in terms of properties of atoms, it is a strange historical fact that it took as much as forty years to find that in electrolysis the atoms carry electric charges represented by simple multiples of a fundamental charge. This important theoretical conclusion is based only on Faraday's law (1834), Avogadro's rule (1811), and, we may add, the assumption that the total charge observed is equally distributed over the atoms deposited.

Finally we must express Faraday's results in different terms in order to make them comparable with the results of later experiments on gases and vapors. Faraday measured the electrochemical equivalents, mass (g)/quantity of electricity (coulombs), of the various elements. As this ratio is characteristic for any element, it should be the same for any amount of the element, in particular for the smallest amount that exists, *i.e.*, the individual charged atom. Thus we have determined the ratio of mass to charge (in g/coulomb) of the charged atoms responsible for the conductivity of the solution. We shall indicate such masses and charges of the elementary particles with greek letters μ and ϵ. In investigations of the various electrical rays, it is conventional to characterize them by the reciprocal ratio ϵ/μ, called "specific charge." In electrolysis, for charged hydrogen atoms (written H^+), this ratio is computed as

$$\left(\frac{\epsilon}{\mu}\right)_{H^+} = 9.578 \times 10^4 \text{ coulombs/g}$$
$$= 9.578 \times 10^3 \text{ emu/g}$$

It is evident that this is the largest value of ϵ/μ observed in electrolysis because all other atoms have larger masses; their atomic weights cover the range from unity for hydrogen, the lightest atom, to 238 for uranium, the heaviest atom found in nature.

We shall discuss only briefly Arrhenius's theory of electrolytic conduction (1887). Arrhenius assumed that in the solution, although as a whole it is neutral, charged atoms (called "ions," *i.e.*, migrators) like H^+, Cl^-, exist in equal concentration and are pulled by the electric field to the respective electrodes. Are such ions present once and for all in the solution or do we generate them by applying the electric field between the two metal electrodes? It has been observed that, even for the weakest electric fields, the conductivity of the solution has its full value. Hence we must assume that such ions do exist once and for all. Water solutions in particu-

lar have high conductivities. Therefore, we must attribute to water a particular power of breaking up neutral molecules like HCl or NaCl into equal numbers of positive and negative ions. In our discussion of solutions as compared with gases (van't Hoff's law, Sec. 6.2) we mentioned electrolytic dissociation as an explanation for the abnormally high values of the osmotic pressure.

In the present discussion of electrolysis we limit ourselves to the simplest cases. In textbooks of chemistry more complicated phenomena are discussed caused by the occurrence of more complex ions and secondary reactions at the electrodes.

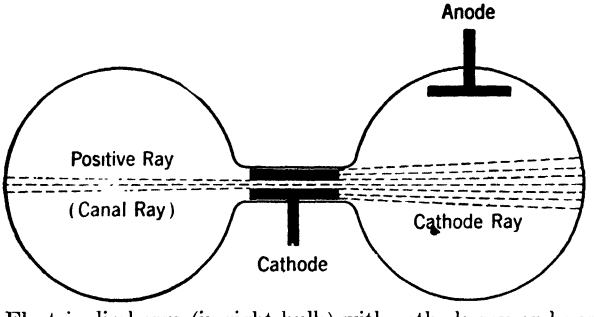


FIG. 8.1. Electric discharge (in right bulb) with cathode ray and positive ray.

8.2. ϵ/μ of Cathode-ray Particles. In electric discharges through gases at low pressure there are observed cathode (or negative) rays and positive rays, both of which are found to be of corpuscular nature. By an experimental technique entirely different from electrolysis, the ratio of charge to mass, ϵ/μ, of these corpuscles is determined and compared with the values obtained in electrolysis.

a. Electric and Magnetic Deflection. Figure 8.1 shows an electric discharge tube consisting of two spherical bulbs connected through a narrow neck. The discharge is produced in the right bulb between the anode (the plate connected with the positive terminal of a power supply) and the cathode (the cylinder occupying the neck, connected with the negative terminal). The function of the left spherical bulb will be discussed in the section on positive rays (Sec. 8.3). A power supply provides several thousands or tens of thousands of volts. The gas consists, for example, of hydrogen or mercury vapor at a pressure of a few thousandths of a millimeter. A discharge fills the whole right bulb uniformly with dim light. Furthermore, there is a straight ray, brighter than the discharge, emanating from the front surface of the cathode, crossing the bulb, and producing fluorescence of the opposite glass surface. This ray is called a "cathode" ray. An obstacle placed in its path casts a shadow on the glass surface and so confirms the fact that the phenomenon is a ray coming from the cathode.

The nature of this ray is revealed when a magnet is brought near by. Even the weak magnetic field surrounding a steel magnet causes a deflection of the cathode ray. When in the apparatus of Fig. 8.1 the north pole of the magnet is placed near the front of the tube, the cathode ray is deflected *downward*. If an electric current in the conventional sense, consisting of *positive* charges, were to emanate from the cathode, it would be deflected *upward*. We conclude that the cathode ray consists of *negatively* charged particles. This is confirmed when we let the cathode ray pass through the space between two parallel metal plates connected to a battery. (The potential difference supplied to these plates should be much smaller than that feeding the discharge; otherwise another independent discharge would be started.) The electric field between the metal plates deflects the cathode ray in a direction indicating *negative* charges coming from the cathode.

A quantitative study of the deflections caused by magnetic and electric fields was made by J. J. Thomson. By way of introduction let us review the forces exerted by such fields on electric charges. The electric field E between plane plates of a condenser (distance d) connected with a battery of electromotive force V is $E = V/d$. The force exerted by this field E on the charge ϵ is $E\epsilon$; it is directed parallel to E. A wire of length L carrying a current I when placed in a magnetic field H directed perpendicular to the wire is acted upon by the force $= iLH$. The direction of this force is perpendicular to that of the wire and that of the magnetic field. We want to apply this fundamental law to the cathode ray which represents a current although it does not flow through a wire. We suppose that this special current consists of many charged particles shooting along the ray. By a computation which is relegated to a problem we derive the force exerted by the magnetic field H on the charge ϵ moving with the velocity v perpendicular to H:

$$\text{Force} = \epsilon v H \tag{8.4}$$

Again the force is perpendicular to both v and H.

Attention is called to the fact that some laws of electrodynamics contain the velocity of light as a factor of proportionality depending on the system of units applied. Our equation, force $= \epsilon v H$, presupposes absolute electromagnetic units. We shall use this system throughout the book unless otherwise stated (see Appendix 1).

For his quantitative study of the magnetic and electric deflection of the cathode ray, Thomson (1897) applied uniform fields limited to a well-defined space. A schematic diagram is given in Fig. 8.2. The electric discharge through a gas at low pressure takes place in the left part of the tube. The cathode ray hits the anode, which consists of a metal plate with a small hole at its center through which a narrow section of the cathode ray is transmitted into the right part of the tube. There the ray is not subjected any more to the strong electric field acting between cathode and anode.

This field-free space is better understood when we assume that the whole inside glass surface on the right side of the anode is covered by a conducting layer, say, a gauze screen, connected with the anode; technically this screen is hardly necessary since the glass surface is somewhat conducting. Thus the inside has the same potential as the anode and hence is free of electric fields anywhere except between the condenser plates to be described presently.

Beyond the perforated anode the ray continues its path with uniform velocity in a straight line except in the limited space indicated in the diagram where a vertical *electric* field may be applied between a pair of condenser plates or a *magnetic* field with lines of force normal to the plane of

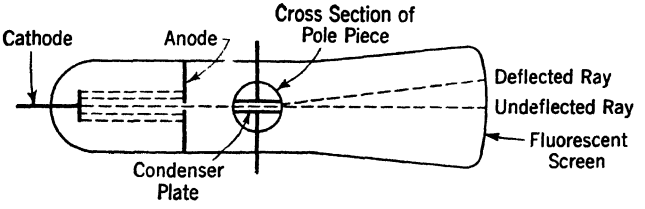


FIG. 8.2. Electric and magnetic deflection of a cathode ray (J. J. Thomson). The magnet is indicated by the circular cross section of the two pole pieces located in front of and behind the plane of the figure.

the paper. (One pole piece of the magnet would be in front of the paper, the other behind the paper. In Fig. 8.2 the circle indicates the cross section of these pole pieces.) We presuppose that both these fields are uniform within a limited space and zero outside. With such an arrangement the cathode ray can be deflected at will upward or downward by either the electric or the magnetic field. The cathode ray is only dimly visible, but its direction can be well demonstrated by the fluorescence it produces on the opposite glass wall which is made brighter if this glass wall is covered with a fluorescent screen.

J. J. Thomson's experiment consists of two consecutive measurements (subscripts 1 and 2). For the first measurement the cathode ray is deflected by a certain electric field E_1. Next by a magnetic field H_1 of the proper value and direction, the cathode ray is brought back into the position it had without any field. For this adjustment of the two fields the resulting force is zero, hence the forces exerted by the one and the other field are equal and opposite. Hence,

$$E_1\epsilon = \epsilon v H_1 \tag{8.5}$$

As the fields E_1 and H_1 can be measured, we derive the velocity v as the unknown, $v = E_1/H_1$. The numerical result is a very high velocity of many thousand kilometers per second, the value depending on the conditions of the experiment, in particular the potential difference applied between cathode and anode.

For the second measurement only a magnetic field, H_2, is applied. For this case the theory predicts a circular path of the charged particles within the range of the magnetic field. Outside of this field, of course, the ray travels in a straight line. The circular path is explained by the fact that the mechanical force exerted by the magnetic field on the moving electric charges is always perpendicular to their instantaneous velocity. Hence the absolute value of the velocity remains unchanged, only its direction is affected. A mechanical analogue is the path of a motorboat with the motor running uniformly and the rudder straight. A man sitting in the bow paddles uniformly in the direction perpendicular to the instantaneous velocity. He does not affect the absolute value of this velocity, only its direction. Thus the boat runs in a circle.

This is the difference between the two fields applied in these experiments: The *electric* field exerts a mechanical force *fixed in space;* this field when applied alone bends the path of charged particles into a parabola, like the path of a bullet shot horizontally. On the other hand, the *magnetic* field exerts a mechanical force *turning with the instantaneous velocity;* this field bends the path of the charged particles into a circle.

For the circular path in the magnetic field H_2 the following condition holds: centripetal force (or mass $\times$ centripetal acceleration) = force exerted by the magnetic field; or, when R = radius of curvature and μ = mass of particle,

$$\frac{\mu v^2}{R} = \epsilon v H_2 \tag{8.6}$$

We apply so weak a magnetic field that the charged particles are by no means bent into a full circle but only slightly deflected from their originally straight path. We observe this deflection on the fluorescent screen and, by a simple geometrical consideration, compute the radius of curvature R of their path; the velocity v has been determined by the first experiment. So here we have one equation with two unknowns ϵ and μ. All we can do is derive one unknown, ϵ/μ, called the "specific charge" of the particles.

$$\frac{\epsilon}{\mu} = \frac{v}{RH_2} \tag{8.7}$$

Thomson's important result is that the specific charge of cathode-ray particles is always the same; in particular it does not depend upon the nature of the gas or the metals contained in the apparatus. The numerical result obtained by the most accurate recent measurements is

$$\epsilon/\mu = 1.7592 \times 10^7 \text{ emu/g}$$

This result reveals the nature of the cathode ray. The ray does not consist of charged gaseous atoms; otherwise ϵ/μ would depend upon the nature of the gas. We are led to a positive statement when we compare the value

of ϵ/μ with the largest value obtained for charged atoms in electrolysis which is the value for hydrogen: 9.578×10^3 emu/g. We notice that for cathode-ray particles the order of magnitude is much larger, 1,837 times the largest value obtained for charged atoms in electrolysis. Should we interpret this large value of ϵ/μ by a large value of the charge ϵ or a small value of the mass μ? The answer can only be guessed as follows: In electrolysis we found that all charged atoms carry the *same fundamental electric charge* or small multiples of it. Their values of ϵ/μ, however, differ because the *masses* differ. We infer that for cathode-ray particles, too, the charge is the same, presumably the fundamental charge. Then the large value of ϵ/μ must be attributed to a small mass of magnitude only 1/1837 that of the hydrogen atom. This excessively small value indicates that here we are dealing with particles fundamentally different from the atoms known in chemistry. Thomson concluded that the cathode ray consists of *free electricity* and thus obtained evidence of *free electrons.** The process in the electric discharge that causes the emission of free electrons from the cathode will be discussed in the chapter, Methods of Observation (Sec. 17.2).

In these experiments the free electrons are always observed as *negatively* charged particles while in electrolysis some atoms carry positive, others negative charges. Recognizing the negative charge as an essential property of free electricity, we come to a new interpretation of charged atoms: Positively charged atoms have *lost* one or several electrons from their neutral structure. Negatively charged atoms have *gained* electrons.

This picture of atoms losing electrons was revolutionary at the time of Thomson's discovery (1897) because it involves the new idea that the electron is an essential part of a neutral atom, a part which in electric discharges or in electrolytic solution may be torn off. The facts of electrolysis are not sufficient to establish this picture because, before Thomson's discovery, it could be assumed that in solution the originally neutral atoms form compounds with positive or negative charges. We need the new concept of free electricity as consisting of *negative* charges in order to conclude that the positively charged atom has *lost an electron*. This idea violates the ancient dogma of the atom as an indivisible particle, a dogma originally conceived by Democritus and used as a workable hypothesis all through the great progress made until the end of the nineteenth century. Thomson's discovery leads the way to our present picture of the structure of atoms as built of electric charges, which may be torn to pieces by various kinds of impact or radiation.

*A few months before Thomson's publication and without his knowledge Wiechert published experiments from which he concluded that the cathode ray consists of "electric atoms" of a velocity of 3×10^9 cm/sec and a mass between 1/200 and 1/4000 of that of the hydrogen atom.

Is free electricity a special kind of matter? This is only a question of words. Free electricity certainly has in common with atoms the property that each elementary particle has a well-defined mass which, at high velocity, shows the characteristic increase predicted by Einstein's principle. Therefore, we may well recognize electrons as a kind of matter as well as positive ions.

More important is the fact that in our argument we attributed a certain variation of ϵ/μ to a variable *mass* μ. This implies that we considered the *charge* ϵ as constant. Throughout physics, including nuclear physics, the conservation of electric charge, which here is assumed, is a principle never violated.

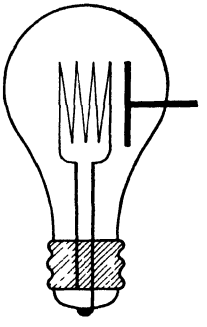


Fig. 8.3. Electron emission from a glowing filament (T. A. Edison).

b. Electric Acceleration and Magnetic Deflection. Next we shall describe a related experiment that leads to an alternative determination of ϵ/μ of free electrons. In 1883, T. A. Edison, during the development of the incandescent lamp, discovered that glowing filaments of carbon or metal give off electricity. This is demonstrated by an incandescent lamp which carries inside the glass bulb a metal plate, insulated from the glowing filament and supported by a wire which is sealed through the glass (Fig. 8.3). When the plate is made positive with respect to the filament, a current flows through the vacuum and is registered on a sensitive meter. There is no current flow when the plate is made negative.

The nature of this current is explored by the following experiment which is easily demonstrated* (Fig. 8.4). A straight glowing filament F is mounted along the axis of a small metal cylinder A, insulated from the cylinder. This cylinder and filament are placed in a large glass bulb which is evacuated except for a very low residual pressure of mercury vapor. When the filament is heated and made negative with respect to the cylinder, a current flows through the gas from the filament to the cylinder. A narrow slit along the wall of the cylinder, parallel to its axis, transmits a narrow ray of electric charges coming from the filament, shooting out in a straight direction. As in Thomson's experiment, the space outside the slit is free of electric fields. The low-pressure mercury vapor has only the function of making this electric ray dimly observable. The whole glass bulb is placed between coils of wire so constructed that the electric current through the wire produces a uniform magnetic field perpendicular to the direction of the ray described. When we turn on this field, we observe that the ray is bent in a circular path of which the radius R is easily measured.

What is the nature of the particles that constitute this ray? They are negatively charged because they are pulled to the positively charged cylin-

*Bainbridge, K. T., *Am. Phys. Teacher*, **6**, 35 (1938).

der. Their specific charge ϵ/μ is determined by the measurement of the accelerating voltage (between filament and cylinder) and the magnetic field.

To begin with, we compute the velocity of the charged particles (charge ϵ, mass μ) coming from the filament and arriving at the plate under the effect of a potential difference V. In order to simplify the computation, we

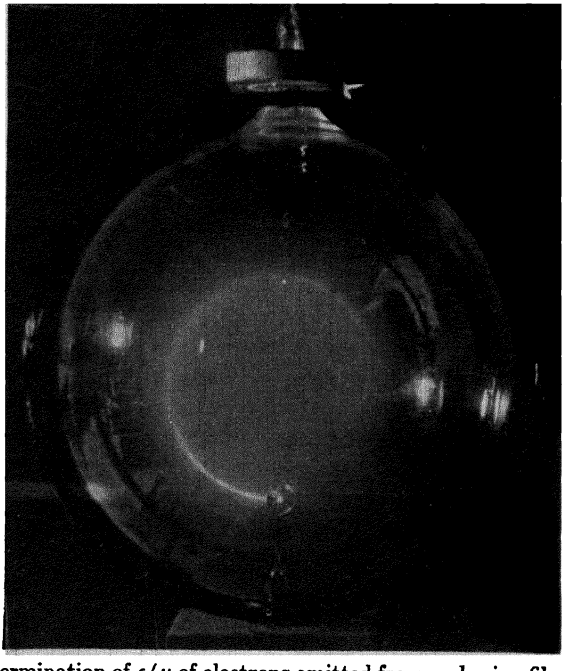


FIG. 8.4. Determination of ϵ/μ of electrons emitted from a glowing filament. (*Courtesy of K. T. Bainbridge.*)

disregard the cylindrical symmetry and rather treat the case of two plane and parallel condenser plates (distance d) one of which emits electrons. (We neglect the inhomogeneity of the field at the edges.) The argument is the same as in the treatment of the free fall in the gravitational field. The electric charges, which are supposed to start from one of the plates with negligible velocity, gain kinetic energy W_k while they lose potential energy which is computed as force $\times$ distance;

$$\text{Force} = E\epsilon = \frac{V}{d}\epsilon$$

$$W_k = \tfrac{1}{2}\mu v^2 = \text{force} \times d$$

or

$$W_k = \tfrac{1}{2}\mu v^2 = V\epsilon \tag{8.8}$$

This result applies as well to *any shape* of the filament and the positive electrode. This follows from the definition of a potential difference as the work per unit charge required to move a test charge from one to another position. More strictly, it follows from the theorem that the electrostatic field has a potential.

Next we represent the effect of the magnetic field H by the same argument as applied to Thomson's experiment:

$$\frac{\mu v^2}{R} = \epsilon v H \tag{8.9}$$

The last two equations contain two unknowns, v and ϵ/μ. These are expressed in terms of measurable quantities as follows:

$$v = \frac{2V}{HR} \tag{8.10}$$

and

$$\frac{\epsilon}{\mu} = \frac{2V}{H^2R^2} \tag{8.11}$$

The numerical result is $\epsilon/\mu = 1.7592 \times 10^7$ emu/g. Here we recognize the same particles identified earlier by Thomson as *free electrons*.

The reader is familiar with the great technical importance of electron emission from glowing filaments, especially as applied in radio tubes. This process will be discussed more in detail in Chap. 10; in the present chapter we are interested only in the determination of ϵ/μ.

The previous statement that glowing filaments give off only *negatively* charged particles is not completely accurate. Occasionally, there is observed also a weak emission of *positively* charged particles which are detected, of course, only when the polarity of the glowing filament with respect to the plate is reversed so that no free electrons can go over. By the determination of ϵ/μ of these positive particles it has been found that they consist of positive ions, usually of sodium and chemically related metals. This emission of positive ions is limited to filaments carrying impurities. As a rule, after a short period of time the supply is exhausted, and the positive current stops — contrary to the current of the opposite polarity, the electron current, which is never exhausted. The emission of positive ions is of minor importance.

Let us compare the two methods for the determination of the specific charge ϵ/μ of electrons. Thomson's original method has the advantage of applyng to any well-defined ray of charged particles, irrespective of its origin. We do not need to discuss the processes in the electric discharge producing the cathode ray. This method is indispensable for the investigation of alpha rays and beta rays which we shall discuss in the section on radioactivity. As these rays are emitted from radium atoms, it is not in our power to accelerate them starting from zero velocity. On the other hand, the acceleration of electrons from a filament combined with the mag-

netic deflection is of great practical importance in numerous laboratory experiments performed with glowing filaments. Furthermore, after having discussed the charge on the electron, we shall see that this method provides us with a new unit of energy, the electron volt, which is commonly used in atomic physics (Sec. 9.3).

c. Helical Method; Electron Microscope. Finally, we shall discuss a third method, the helical method (Busch, 1922) for the determination of ϵ/μ of the charged particles emitted from a glowing filament. Although this method is related to the preceding one, it is of special interest because it introduces the idea of *focusing a divergent electron beam*, the basic idea for

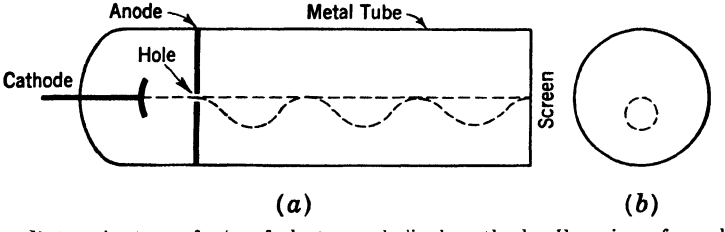


FIG. 8.5. Determination of ϵ/μ of electrons, helical method. Focusing of an electron beam (*a*) Side view; (*b*) front view.

the construction of the electron microscope. In high vacuum a glowing cathode gives off electrons (Fig. 8.5*a*), which are then accelerated by a potential difference of several thousand volts to the anode plate. An auxiliary device, which we need not describe in detail, converges those electrons coming from various directions, within a certain solid angle around the axis, on the center of the anode. Some of these electrons pass through a small hole at the center of the anode plate and emerge from the hole as a divergent beam. Beyond the anode the interior of the metal tube is free of electric fields. Therefore, each charged particle travels in its own straight path, and all of them together produce a blurred fluorescence on the screen. All electrons leave the hole with the same velocity v given to them by the potential difference V between cathode and anode. From Eq. (8.8) we compute this velocity as

$$v = \sqrt{\frac{2\epsilon V}{\mu}} \tag{8.12}$$

Let us consider a particular ray leaving the hole within a small solid angle α measured about the axis of the apparatus. We express its velocity components parallel and normal to the axis as

$$v_a = v \cos \alpha \qquad v_n = v \sin \alpha$$

For small angles α, we replace these expressions by the approximations

$$v_a = v \qquad v_n = v\alpha$$

Next we apply a uniform magnetic field H parallel to the axis of the tube, easily produced by a long solenoid. We treat the effects of this field on the two velocity components separately. The magnetic field does not affect the *axial* component v_a because this is parallel to the field. The effect of the field on the *normal* velocity component v_n has been computed in the preceding section; the field bends this component into a circular path of radius R defined by Eq. (8.9):

$$\frac{\mu v_n^2}{R} = \epsilon v_n H \qquad \text{or} \qquad v_n = \frac{\mu}{\epsilon} HR$$

As before, the field does not affect the absolute value of v_n, only its direction. The time τ required for one full circle is

$$\tau = \frac{2\pi R}{v_n} = \frac{2\pi}{H}\frac{\mu}{\epsilon}$$

This time τ is independent of the radius R since the faster particles travel over correspondingly larger circles.

Both velocity components together form a helix representing the path of this beam leaving the hole within the small solid angle α measured about the axis of the apparatus. Consider, for example, a ray leaving the hole with a normal component v_n perpendicular to the paper toward the observer. Then the magnetic field bends this ray immediately after it leaves the hole. It describes a helical path indicated by the dashed lines in the side view (Fig. 8.5*a*) and the cross section (Fig. 8.5*b*). These particles strike the axis again after performing one full circle during the time τ. Although this particular path shown in Fig. 8.5 is all on one side of the axis of the apparatus, all rays together, representing all directions with respect to the axis, form a symmetrical pattern. During the time τ of one revolution, the particle travels *parallel to the axis* the distance $L = v\tau$ which is easily expressed with the help of Eq. (8.12) in terms of H and ϵ/μ,

$$L = \frac{2\pi}{H}\sqrt{2V\frac{\mu}{\epsilon}} \tag{8.13}$$

We are interested in the fact that the angle α does not enter into this equation because all particles perform the *circular* components of their paths in the same time and, hence, travel meanwhile the same *axial* distance L. Consequently *all rays* passing through the hole, irrespective of this angle, come back to the axis at the same distance L. Hence, under the assumption of small angles of divergence (α) at the hole, all the rays meet at one spot easily viewed if a fluorescent screen is placed in the path at a distance L from the hole. When above the hole considered we drill a second hole through the anode plate and have it exposed to slightly diverging electron rays from the same source, hence incident with the same velocity,

the screen shows a corresponding bright spot above the first. Altogether, the electron rays form an image of the anode on the screen.

The comparison of this effect with the focusing of light by a lens makes the importance of this new device clear. It is true that pictures can be taken without a lens in the pinhole camera. There we rely only on the rectilinear propagation of narrow pencils of light. This compares with the sharp spot of light produced by a sufficiently narrow pencil of cathode rays and is demonstrated by the cathode-ray oscilloscope. But we can build

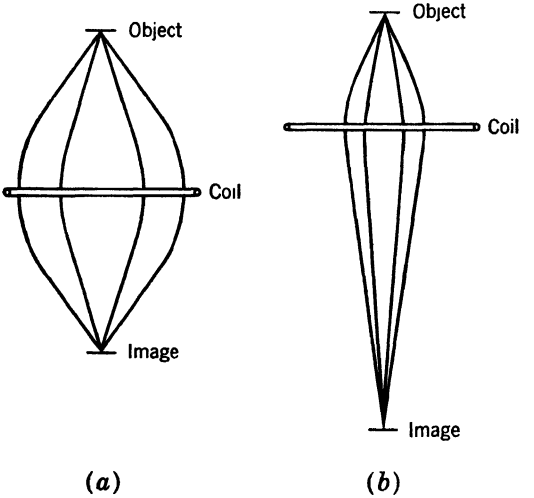


FIG. 8.6. The flat coil as a magnetic lens focusing electrons. (*a*) Full-size image; (*b*) enlarged image. The object, a thin specimen, transmits fast electrons. The diagram does not show that the paths of the electrons are twisted by the magnetic field.

optical instruments of some refinement only when we use a lens to focus on one point of the image a bundle of rays diverging from one point of the object. This is comparable with the apparatus described. Therefore, this application of the magnetic field is called a "magnetic lens."

This apparatus may well serve for the determination of ϵ/μ. The magnetic field H is adjusted until the image on the screen is sharp. Then ϵ/μ is computed from Eq. (8.13) and yields a numerical result in good agreement with those of the preceding methods. The outstanding interest of this method lies in the formation of images by the magnetic lens. Although the long solenoid acting as a magnetic lens furnishes only full-size images, a flat coil is not subject to this restriction. Without further computation this is illustrated by Fig. 8.6*a* in which the uniform field of a solenoid is replaced by the nonuniform field of a flat coil. When the object is placed closer to the coil, this focuses the rays at a greater distance (Fig. 8.6*b*). The analogy with the optical lens indicates that here a *magnified* image is produced. (The figure simplifies the path of the electrons since the helical

path cannot be fully represented by a plane figure. In this respect the magnetic lens focusing electrons is not so simple as the optical lens focusing light.) In the electron microscope (Ruedenberg, 1931) a beam of electrons accelerated by, say, 60,000 volts, traverses a thin specimen; a magnetic lens focuses the electrons so that they form an enlarged image of the specimen; a second lens, in turn, forms another, more enlarged image. A great advantage of the electron microscope over the ordinary optical microscope is evident. It is known that the wave nature of light, because of diffraction,

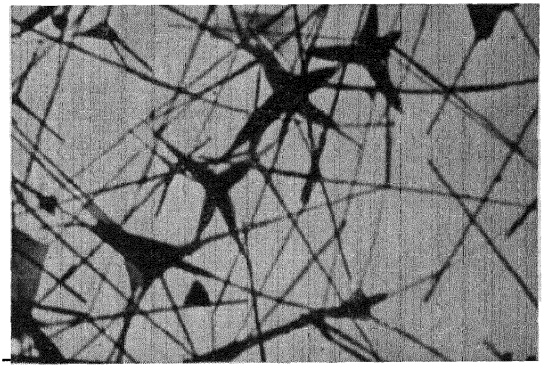


FIG. 8.7. Electron micrograph of zinc oxide smoke particles. Magnification 30,000 ×. The figure shows the superior resolving power of the electron microscope. A micrograph taken through the best optical microscope and enlarged to the same scale would be so blurred that no detail finer than 7 mm could be resolved. The figure is a section from an original that covers an area ten times as large with equally good definition. (*Courtesy of Radio Corporation of America.*)

sets a limit on the resolving power of the optical microscope. This limit is about ½ wave length of light, hence for visible light about 3×10^{-5} cm. Although cathode rays, too, are to a certain extent subject to diffraction, as will be discussed in the chapter on wave mechanics (Chap. 26), this practically does not limit the resolving power of even the best electron microscopes constructed.

The superior resolving power of the electron microscope is evident in Fig. 8.7, which is a picture of zinc oxide smoke particles enlarged 30,000 times. For the sake of comparison we compute the resolving power of the *ideal* optical microscope using, say, yellow light; the picture taken through this instrument, when enlarged to the scale of the figure, would be so badly blurred that no detail finer than 7 mm could be resolved. The wealth of new detail resolved by the electron microscope is striking. Its outstanding drawback is the fact that the specimen under investigation must be placed in high vacuum and, without supporting glass plate, be subjected to a beam of high-energy electrons. There are many objects that cannot stand this

treatment although they can be investigated through the optical microscope.

The electron microscope finds important applications in the investigation of the structures of very small particles. Most important are the medical applications where the structures of bacteria have been investigated. The microscopical study of viruses started with the advent of the electron microscope; thus the viruses of influenza and infantile paralysis have been photographed.

d. Cathode-ray Oscilloscope. The cathode-ray oscilloscope (Fig. 8.8) represents an important application of an electron beam from a glowing filament, accelerated by a potential difference. A small hole in the anode

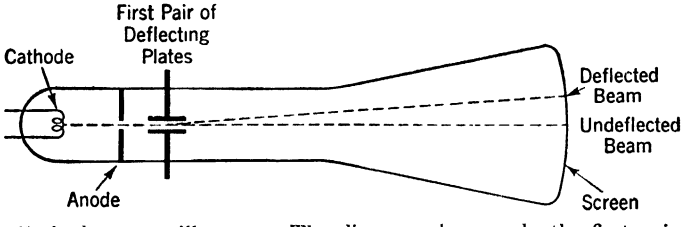


FIG. 8.8. Cathode-ray oscilloscope. The diagram shows only the first pair of plates deflecting the beam up or down. Beyond this pair the beam passes between a second pair causing a deflection normal to the plane of the figure.

transmits a narrow beam which shoots in succession through two small plate condensers, the first pair of plates deflecting the beam up and down in the figure, the second pair (not indicated in the figure) deflecting the beam backward and forward, *i.e.*, in a direction perpendicular to the plane of the figure. When a rapidly variable potential is connected with one or the other pair of plates, the ray follows instantaneously and so, by its deflection, indicates the variable potential. Ordinarily one pair of plates is connected with a "sweep circuit," *i.e.*, a circuit that imposes a deflection proportional to the time, say, in the *horizontal* direction. When the extreme deflection is reached, the ray instantaneously returns to the initial position and repeats the process. The other pair of plates, say, the pair responsible for the *vertical* deflection, is connected to the variable potential difference to be investigated. Then the path of the luminous spot on the screen indicates the potential difference as a function of the time. If, by an auxiliary device, the sweep is repeated in phase with the variable potential difference, the eye perceives a steady curve on the screen representing the potential difference as a function of the time.

The great advantage of this device is its lack of inertia, which makes it applicable to radio frequencies where the mechanical oscillograph built with coils and little mirrors completely fails. Hence, the cathode-ray oscilloscope is one of the most useful and versatile measuring devices for radio-frequency circuits. It is an essential part of radar indicators. It is

indispensable for circuit analysis. In television sets, the scanning in both the pickup device and the viewing tube is carried out by special forms of cathode-ray oscilloscopes. Furthermore, the oscilloscope is extensively used for recording transient phenomena like sparks, explosions in guns, combustion in gas engines. In biology, oscilloscopes are used in studies of heart beats and nerve response.

8.3. ϵ/μ of Positive-ray Particles. As a supplement to the description of the electric discharge (Sec. 8.2, Fig. 8.1) let us consider what happens when an axial canal has been drilled through the cylindrical cathode that fills the narrow neck between the two large spherical bulbs. While in the right bulb the discharge and the cathode ray are in operation as before,

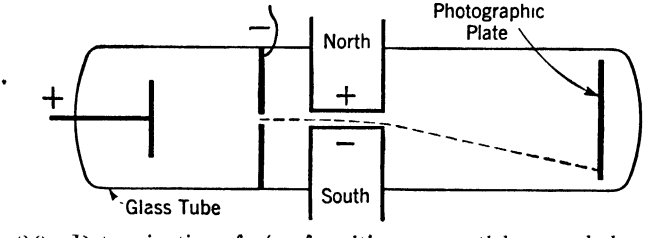


FIG. 8.9. Determination of ϵ/μ of positive-ray particles, parabola method.

in the left bulb a new ray is now observed called the "canal ray" because it comes from the axial canal. If the steel magnet that caused the marked deflection of the *cathode* ray is brought near the left bulb, it fails to affect the *canal* ray, but this is due only to the insufficient field strength. A stronger magnetic field produced by an electromagnet deflects the ray and, by the sense of the deflection, indicates its nature as a stream of *positively* charged particles. The corresponding effect is observed for a strong electrostatic field.

J. J. Thomson determined the specific charges ϵ/μ of positive-ray particles by the parabola method, which represents a modification of the method that he applied to the study of cathode-ray particles (Sec. 8.2*a*). The new method has the advantage that it applies to rays of particles that have a wide velocity range. As in the cathode-ray experiment, the positive ray passes through a combination of electric and magnetic fields, both normal to the velocity of the particles. But here, the deflections produced by these two fields are *normal to each other*. This is accomplished by the arrangement schematically given by Fig. 8.9 in which the ray passes between the pole pieces of an electromagnet whose faces carry insulated plates to be connected to a d-c power supply. Let us assume that the ray consists of particles all of the same value of ϵ/μ and that the electric field deflects the particles downward. If all particles had the same velocity, the trace on the photographic plate would be a sharp spot. Actually it is a line pointing downward, which indicates that the positive ray consists

of particles of a certain velocity range. In the experiment, the ray is simultaneously subjected to the magnetic field which, if acting alone, would deflect it out of the plane of the paper and, hence, would spread it into a band whose trace on the plate would be a horizontal line. Both fields acting together produce a simultaneous deflection downward and out of the plane of the figure which, on the plate, turns out to be a parabola (Fig. 8.10). The theory (see Prob. 8.8) gives the relation between the parameter of the parabola and the specific charge of the particle.

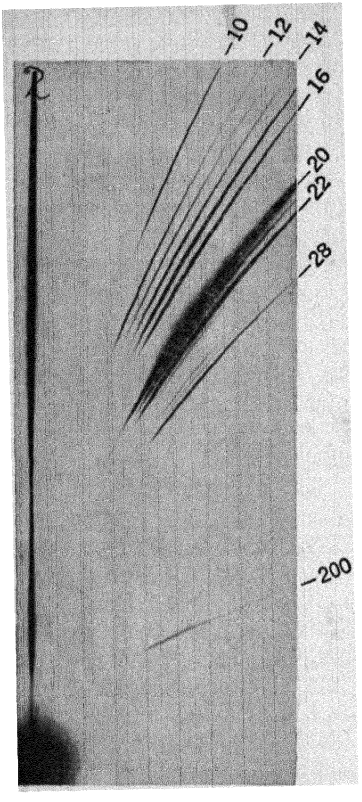


FIG. 8.10. Parabolas. The numbers indicate atomic weights per unit charge (in electronic charges). 10 and 11 are Ne doubly charged; 12 is C; 13 is CH; 14 is CH_2 and N; 15 is CH_3; 16 is CH_4 and O; 20 and 22 are Ne; 28 is N_2; 200 is Hg. (*Courtesy of K. T. Bainbridge.*)

The numerical results depend upon the gas present in the discharge tube. Although the velocities spread over a wide range, the values of ϵ/μ are sharply defined as is evident from the good definition of the parabolas. In hydrogen, for example, the canal ray, or positive ray, splits up into two constituents with the values

$$\frac{\epsilon}{\mu} = 9.58 \times 10^3 \text{ emu/g}$$

and

$$\frac{\epsilon}{\mu} = 4.79 \times 10^3 \text{ emu/g}$$

respectively.

By comparison with the results of electrolysis, we recognize the larger value as belonging to positively charged hydrogen atoms H^+. The smaller value indicates a ray of positively charged hydrogen molecules H_2^+. No other positive rays of comparable intensity are observed in hydrogen. We referred to this observation in our discussion of molecular formulas (Sec. 1.3) when stating that the positive-ray analysis confirms the structure of hydrogen as consisting of diatomic molecules. The presence of charged *atoms* in the positive ray, in addition to the diatomic *molecules*, is explained by the effect of the electric discharge which dissociates some hydrogen molecules into atoms. Corresponding values of

ϵ/μ are obtained by the positive-ray analysis of other gases. In many experiments several types of ion show up by their parabolas. In gases other than hydrogen, ions are observed with two or more positive charges (see the figure).

We shall discuss the origin of the positive ray in the section on electric discharges (Sec. 17.2). In similar experiments, not described here in detail, it has been observed that certain gases form negative ions like atomic chlorine Cl^-, or atomic oxygen O^-, or molecular oxygen O_2^-. Such negative ions, although less important for the understanding of the electric discharge, have great interest for the theory of the periodic system of elements as we shall see below (Sec. 18.4).

For the purpose of the present chapter the outstanding result of positive-ray analysis is the fact that it reveals the *nature of the positive ray* and so indicates the presence in the electric discharge of charged atoms and molecules which, together with the free electrons, are responsible for carrying the electric current. The two neon parabolas evident in Fig. 8.10 (marked 20 and 22) lead to conclusions of a different kind presented in the discussion of nuclear physics (Chap. 20).

8.4. Decrease of ϵ/μ at High Velocities. Throughout the study of atomic physics the reader will become accustomed to the historical fact that over and over again an apparently well-established law has turned out to be only an approximation, valid within a limited range. This is true for the constancy of the specific charge ϵ/μ of electrons, the numerical value of which was given above with five significant figures. Before long (1901) a certain decrease of this value for *high-velocity* electrons was noticed. For example, electrons accelerated by a potential difference of 80,000 volts are observed to have a velocity of about 1.5×10^{10} cm/sec and a specific charge ϵ/μ about one-eighth smaller than the standard value.

Shall we attribute this deviation to a decrease of the charge or an increase of the mass? Such an increase of the mass with the velocity has been predicted by a theory which was not introduced for this purpose but largely for the explanation of Michelson's famous investigation of the velocity of light, *i.e.*, Einstein's theory of relativity. It does not seem advisable here to give a superficial outline of this theory. Instead, we shall first take for granted a certain formula given by Einstein and next explicitly state what we, for the limited purpose of the present book, accept as the fundamental hypothesis.

From his hypothesis of relativity, Einstein derived the statement that the mass m of any body, which at negligible velocity has the "rest mass" m_0, at the velocity v has the larger mass

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}} \tag{8.14}$$

where c = velocity of light. This increase of the mass with the velocity is not noticeable at the velocities observed in daily life. Let us consider higher velocities for which we still may assume that v^2/c^2 is small as compared with unity. Then we may simplify Eq. (8.14) by the binomial theorem, omitting the higher members of the series, and write

$$m = m_0 + \frac{m_0 v^2}{2}\frac{1}{c^2} = m_0 + \frac{W_k}{c^2} \qquad (8.15)$$

(Here we identify $m_0v^2/2$ with the kinetic energy W_k which again, according to Einstein's theory, is only an approximation.) Applying the last equation to our example, *i.e.*, to electrons with the velocity $v = 1.5 \times 10^{10}$ cm/sec, or one-half of the velocity of light, we find

$$m = m_0(1 + \tfrac{1}{8})$$

in sufficient agreement with the observed decrease of ϵ/μ. Einstein's theory applies to all matter, but only with particles of very small mass is it possible to attain high enough velocities to make the effect measurable.

Einstein's theory has led to the more general result that *any energy*, not only kinetic energy, stored in a body is noticeable as an *increase of its mass*. The quantitative relation is a generalization of Eq. (8.15):

$$\text{Change of mass} = \frac{\text{change of energy}}{c^2} \qquad (8.16)$$

Again we do not reproduce Einstein's derivation of this equation from the hypothesis of relativity.* However, for our limited purpose, we could equally well have chosen the last equation (8.16) to be the fundamental hypothesis. This is in accord with the procedure in theoretical physics in which, at the start of the theory, an equation is established, which serves as the fundamental hypothesis. For example, Newton's equations of motion represent the fundamental hypothesis of mechanics; they are proved to be valid (at least for velocities small as compared with the velocity of light) by their power of correctly predicting the observable facts. Likewise we shall test our fundamental hypothesis, the equivalence of mass and energy as stated in the last equation, by comparing conclusions with observed facts. We notice the first success of this hypothesis in that it satisfactorily represents the increase of the mass of cathode-ray particles with the velocity. The velocities of heavy masses, however, are usually too small to produce observable effects (except in the motion of the planet Mercury). In spectroscopy we shall report an observation explained by Einstein's theory (Sec. 15.7). In nuclear physics (Sec. 22.7) we shall deal with energies so large and with determinations of masses so accurate that further tests will become available.

*A simple derivation, which, however, presupposes the hypothesis of light quanta (Sec. 19.1*j*), is given in Appendix 7.

SUMMARY OF CHAPTER 8

In electrolytic conduction the measurable quantities (mass deposited, atomic weight, valence, and quantity of electricity) are correlated by Faraday's law [Eq. (8.1)]. In this law the Faraday constant F, a universal constant, represents the quantity of electricity carried by 1 gram atom of a univalent substance.

From this law it follows that any individual univalent charged atom (ion) carries the same quantity of electricity F/N, each bivalent ion twice this amount, etc. This indicates that electricity can be subdivided only down to this smallest charge F/N. These smallest units of electric charge are called "electrons." The reciprocal of the electrochemical equivalent has the significance of charge to mass (ϵ/μ) of the individual ion. The largest value of ϵ/μ observed in electrolysis is that of the hydrogen ion H^+, *i.e.*, 9.578×10^3 emu/g.

The *cathode ray* is a ray consisting of negatively charged particles leaving the surface of the cathode. The specific charge ϵ/μ of these particles, determined by a combination of electric and magnetic deflections, has the value 1.7595×10^7 emu/g. This far exceeds any value of ϵ/μ known for atoms in electrolysis and has been interpreted by J. J. Thomson as indicating free electrons. The fact that free electrons are always observed with negative charges leads to the conclusion that *positively* charged atoms have *lost* one or several electrons and that *negatively* charged atoms have *gained* electrons.

Glowing filaments give off negative charges which by the determination of ϵ/μ are recognized as free electrons.

A bundle of electrons passing through a hole in a metal plate with uniform velocity but in directions varying within a small solid angle can be focused by a uniform magnetic field placed in the direction of the bundle. The formation of an image by a magnetic lens is the starting point for the construction of the *electron microscope.*

In the *cathode-ray oscilloscope* the electric deflection of the cathode ray indicates rapidly varying potential differences without any noticeable inertia.

The *canal ray* observed behind the cathode through which an axial canal is drilled consists of positive ions of the gas contained in the discharge tube (positive ray).

High-velocity electrons show a decrease of ϵ/μ. This is interpreted on the basis of Einstein's theory of relativity as an increase of their mass μ. This can be represented as a special case of Einstein's law of equivalence of mass and energy.

PROBLEMS

8.1. *Silver plating.* In an electrolytic solution silver is deposited by an electric current of 0.5 amp. Compute the mass deposited upon the negative plate during a 90-min run. Atomic weight of silver = 107.9; valence of silver = 1.

8.2. *Production of electrolytic hydrogen.* In an electrolytic hydrogen generator how long does it take to produce 1 liter hydrogen under standard conditions by a current of 5 amp? How much oxygen is produced during the same time at the other electrode?

8.3. *Force exerted by a magnetic field on an electron.* In the discussion of cathode-ray experiments we started from the familiar expression, force = iLH. (The electromagnetic system of units is assumed.) From this expression derive the force on an electron, charge ϵ, moving with the velocity v through a magnetic field by the following argument: Suppose a current consisting of a stream of electrons, with a density of n electrons *per centimeter length,* and moving with the velocity v, passes through a magnetic field H perpendicular to the velocity v. At any instant the electrons that are about to move within the next time interval Δt through a certain cross section occupy a certain length.

a. What is this length?

b. State the number of electrons passing a cross section during Δt.

c. Express the current as (the number of electrons passing this cross section per second) $\times$ (electronic charge).

d. Introduce this expression into the equation, force = iLH.

e. How large is the force on one individual electron?

8.4. *J. J. Thomson's measurement of* ϵ/μ. In the first experiment the cathode ray passes between condenser plates 1 cm apart, connected with a power supply of 790 volts; the electrostatic deflection is compensated by a magnetic field of 30 oersteds. In the second experiment the same cathode ray is bent by a magnetic field of 12.50 oersteds into a circular path of 12.00-cm radius. Compute ϵ/μ of the cathode-ray particles.

8.5. *Electric acceleration and magnetic deflection.* Electrons are accelerated from a glowing filament toward a plate by a potential difference of 100 volts. After passing through a slit, they enter a space free of electric fields in which they are subjected to a magnetic field of 3 oersteds directed perpendicular to their velocity. Find their linear velocity v behind the slit and the radius R of their path in the magnetic field.

8.6. *Focusing of an electron beam.* Electrons, after being accelerated by 1,200 volts, are diverging from a narrow hole. How large an axial magnetic field is required to focus the beam on a screen placed at a distance of 40 cm from the hole?

8.7. *Positive ions.* Sodium is a univalent electropositive element with the atomic weight 23.0. How large a specific charge ϵ/μ is it expected to show in the positive-ray experiment?

8.8. *Parabola method.* A positive ray is deflected in the vertical direction by an electric field V/d (V = potential difference on the plates, d = distance) and simultaneously in the horizontal direction by a magnetic field H, both fields acting over the same length l of the path (Fig. 8.9). A photographic plate is placed in the path of the ray right behind the deflecting fields. (We disregard the fact that in the actual apparatus the ray, after traversing the fields, continues its path in a straight line and so acquires a larger deflection on a photographic plate that is placed at some distance.) Compute the shape of the trace on the photographic plate made by the ions of a common value of ϵ/μ and different velocities v. Compute the specific charge and identify the type of ion for the following data: l = 8.00 cm; d = 1.00 cm; x = 0.300 cm; y = 0.400 cm; H = 2,000 oersteds; V = 2,380 volts.

HINT: (*a*) Compute the deflection in the vertical direction (y direction) by the same method by which the deflection of a horizontally shot bullet is found. (*b*) Although the magnetic field strictly exerts a force in a direction not fixed in space but turning around with the particle (Sec. 8.2*a*), for small deflections, we assume that the magnetic force is throughout in the direction normal to the figure. Thus we compute the horizontal deflection (deflection in the x direction) by the same method applied under (*a*). (*c*) While under (*a*) and (*b*) the two coordinates of the deflection are computed both

as functions of the velocity v, the trace on the photographic plate, *i.e.*, y as a function of x, is found by eliminating v. (*d*) Which part of the trace is due to fast and which to slow electrons? (*e*) Compute ϵ/μ and find the type of ion for the numerical example.

8.9. *Loss of mass by the sun.* The solar constant (1.96 cal cm^{-2} min^{-1}) gives the energy of solar radiation received per minute per square centimeter at the earth. By radiation the sun is expected to lose mass. How large is this loss of mass per year? (Distance earth to sun = 1.490×10^{13} cm). See related Probs. 9.8 to 9.11.

CHAPTER 9

DETERMINATION OF THE CHARGE ϵ ON THE ELECTRON

9.1. Millikan's Experiment. After the determination of ϵ/μ for free electrons we turn to the next important step, the determination of the charge ϵ on the electron by Millikan's oil-drop experiment (1910). The reader may well approach this subject by forgetting all he has just learned of atoms and electrons. This implies that the new experiment will give entirely *independent* evidence of the structure of electricity.

The first determinations of the electric charges carried by small drops were made by J. J. Thomson and H. A. Wilson. They measured charges carried by water droplets which are formed in a cloud chamber (C. T. R. Wilson, see Sec. 21.2*a*). These preliminary experiments were developed into a high-precision measurement by Millikan who measured the charges on the smallest bodies that can be investigated, ultramicroscopic drops. He used oil because it does not noticeably evaporate. The small drops generated by an atomizer fall under the effect of gravity, the rate of fall being slowed down by friction in air as is the fall of the small water droplets constituting a cloud. Some such oil drops are allowed to fall through a small hole in the upper plate of a horizontal plate condenser (plate distance d), Fig. 9.1. Between the plates, the fall of the drop, carefully shielded from air currents, is observed through a microscope. When a potential difference V is applied to the plates of the condenser, some drops move upward, some downward which indicates that almost all drops carry electric charges. Presumably the charges are produced by friction in the nozzle of the atomizer. The drops, originally falling under the effect of gravity, may be lifted by the application of a sufficiently strong electric field, $E = V/d$.

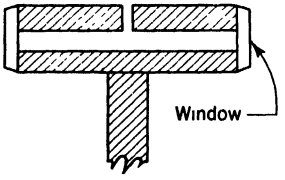


FIG. 9.1. Millikan condenser.

We measure the charge on a drop in either one of two ways. The simpler way consists of adjusting the upward force qE until the drop just stops falling; *i.e.*, until the forces acting upward and downward are equal. Then $qE = mg$ where q and m are the charge and the mass of the oil drop.

The other method is more commonly used although the equation be-

comes more complicated. With a microscope we measure the velocity downward under the effect of gravity and viscosity. A uniform velocity will be attained when these two forces are just equal and opposite. Studies on the effects of viscosity show that there is a force proportional in magnitude and directed opposite to the velocity of the body moving through a viscous medium. The oil drops show a uniform velocity and so give evidence of the fact that the *resulting* force is zero (different from the "free fall"). The fall through a viscous medium, in the absence of an electric field, is described by the equation (writing the forces directed downward as positive) $mg - cv_d = 0$, where c is a constant of proportionality. When the electric field lifts the drop, the force due to the viscosity is directed downward. Now the condition for uniform velocity is $mg - qE + cv_u = 0$. Combining the two equations, we have

$$\frac{v_u}{v_d} = \frac{qE - mg}{mg} \tag{9.1}$$

When the experiment is repeated over and over again, we notice that once in a while the charge q on the oil drop changes spontaneously. A change of charge is likely to occur when we apply X rays or rays from radium to the space between the condenser plates. Whether the charge will increase or decrease, we cannot predict. If we know the mass m of the drop, we can use the last equation for the computation of its charge q since g is known and the velocities and the electric field E are easily measured.

Unfortunately we cannot measure the size of the drop with the microscope whose resolving power is limited by the wave length of the light used to illuminate the drop, since its diameter is of the same order of magnitude as that wave length. However, this does not prevent us from seeing the drop. Under intense illumination from the side against a dark background, it shows up like a star which we can see although we cannot measure its diameter because of the limited resolving power of all optical instruments. Millikan determined the diameter of the drop by observing the rate of fall under the effect of gravity and viscosity and by applying a well-known law that correlates the velocity of fall of a sphere through a viscous medium with its radius. This law, discovered by Stokes (1845) states that

$$v = \frac{2gr^2\delta}{9\eta} \tag{9.2}$$

where v = velocity
g = gravitational acceleration
r = radius of drop
δ = density of the oil
η = coefficient of viscosity of air (Sec. 5.2)

When v, g, δ, and η have been measured, the radius r of the drop may be computed. (According to Stokes' law, the combined effects of gravity

and viscosity cause the body to fall with uniform *velocity* while the effect of gravity alone produces uniform *acceleration*.)

Although we are anxious not to accept any law on authority, we must admit that we are unable to reproduce Stokes' derivation based on hydrodynamics. Instead, we may assume that this law has been established by experiments performed with larger spheres for which the radius r is measurable. Such experiments showing the fall of small steel spheres through glycerin are easily demonstrated. After the determination of the radius r, the mass m of the droplet follows as

$$m = \delta \times \tfrac{4}{3}\pi r^3$$

So far we have measured values of the charge q on an oil drop apart from any preconceived idea regarding the structure of electricity, but this structure becomes directly evident in Millikan's results. He found that the charges on oil drops do not have all possible values within a continuous range, but have only certain discrete values. For example, through a period of several minutes the drop may have a constant charge of 6.40×10^{-20} emu. Then it may change its charge, spontaneously or under the effect of X rays, to 8.00×10^{-20}. After a while it may go to 3.20×10^{-20}, later to 6.40×10^{-20}, *i.e.*, exactly the same value the drop had at the beginning. Such values of charge, in any random order, recur not only for this one drop but also for any other drop. Millikan listed all the values of charge ever observed in the following table, which we limit to the five lowest values:

1.60×10^{-20} emu
3.20×10^{-20} emu
4.80×10^{-20} emu
6.40×10^{-20} emu
8.00×10^{-20} emu

From this table, or still better from Millikan's more extensive table, it is evident that the charges on small oil drops occur only in multiples of a smallest charge whose accurate value is

$$1.6020 \times 10^{-20} \text{ emu}$$

As this result is independent of the conditions of the experiment, in particular the sizes of the drops, Millikan drew the important conclusion that here a fundamental property of electricity is manifest: It cannot be subdivided into smaller charges. This, presumably, is the charge ϵ on the electron of which Thomson had measured the ratio ϵ/μ.

In our brief discussion we failed to do justice to the art of Millikan's experiment. As a matter of fact, only for relatively large drops did he find that the charges are multiples of the fundamental unit, while small drops show systematic deviations. These drops are so small that, under the

microscope, their Brownian motion (Sec. 4.3) is observed as a random motion superimposed on their regular rise or fall. It would be absurd to assume that the structure of electricity depends on the size of the drop. Hence Millikan rather assumed that for the smallest droplets one of the laws on which his method is based becomes invalid. In particular he assumed that Stokes' law, which was tested only for larger spheres, would need a correction factor when applied to spheres so small that their size becomes comparable with the mean free path of the gaseous molecules. Therefore, he used his measurements of the smallest drops for the evaluation of two constants: the charge ϵ on the electron and the correction factor for Stokes' law.

Later Millikan's determination of the charge on the electron was confirmed and improved upon by the independent method of A. H. Compton (1929) who compared X-ray diffraction on crystals and ruled gratings. This will be discussed in the chapter on X Rays (Sec. 19.1*h*).

When performing Millikan's oil-drop experiment in the laboratory, the student is impressed by the fact that the structure of electricity becomes evident from the data collected within a few hours. For this purpose the student need only measure several different values of charge on the same drop. More difficult is the accurate evaluation of ϵ which includes the correction to Stokes' law.*

9.2. Masses of Atoms and Molecules. Now we know Millikan's value of the absolute charge ϵ of the electron, Thomson's value of its specific charge ϵ/μ, furthermore the specific charges of atoms, derived from electrolysis or positive-ray analysis. On this basis we compute the absolute masses of electrons and atoms with a high degree of accuracy. Also Avogadro's number N, the number of molecules per mole, follows from Eq. (8.3) based on Faraday's law $F = N\epsilon$. The best numerical values† known are given in the following table; the last decimal place of each figure is uncertain. The masses of other atoms and of molecules are easily computed with the help of their atomic or molecular weights.

a. The Electron:

$$\epsilon = 1.6020 \times 10^{-20} \text{ emu}$$
$$\epsilon/\mu = 1.7592 \times 10^{7} \text{ emu/g}$$
$$\mu = 9.106 \times 10^{-28} \text{ g}$$

b. The Hydrogen Ion H^+:

$$\epsilon/\mu = 9.579 \times 10^{3} \text{ emu/g}$$

*A detailed account of this procedure is given by R. A. Millikan, in "Electrons, Protons, Photons, Neutrons, Mesotrons, and Cosmic Rays," University of Chicago Press, Chicago, 1947.

†Birge, R. T., *Am. J. Phys.*, **13**, 63 (1945). See the recent comprehensive survey by J. W. M. DuMont and E. R. Cohen, *Revs. Modern Phys.*, **20**, 82 (1948).

c. The Neutral Hydrogen Atom:

$$\mu = 1.6734 \times 10^{-24} \text{ g}$$

d. The Oxygen Atom:

$$\mu = 26.56 \times 10^{-24} \text{ g}$$

e. Avogadro's Number:

$$N = 6.023 \times 10^{23} \text{ mole}^{-1}$$

The *sizes* of atoms and molecules can be given only with much lower accuracy, not because our method is inferior but because they are not so sharply defined as the *masses*. We shall consider this further in our discussion of atomic structure. Since the atoms are described as consisting of electric charges, they do not form sharply defined, smooth surfaces but are surrounded by electric fields. Various methods for the determination of the sizes lead to results that only approximately agree. The simplest argument is as follows: The density of a liquid may be expressed in terms of the molecular mass and volume since in the liquid the molecules are supposed to be in touch with one another. Hence,

$$\text{Density} = \frac{\text{mass of 1 molecule}}{\text{volume of 1 molecule}}$$

The volume of 1 molecule of water results as 29.9×10^{-24} cm^3. The common result of all such determinations is that the diameters of atoms and the simpler molecules are a little larger than 10^{-8} cm.

How do the molecular dimensions compare with what we can see through a microscope or weigh on a balance? The smallest length resolved under the optical microscope, 3×10^{-5} cm, contains about 1,000 water molecules; hence molecular dimensions are far below the wave length of light. But the electron microscope (Sec. 8.2*c*) is able to resolve lengths of the order of magnitude of the size of the largest protein molecules. The smallest mass we can weigh, about 10^{-7} g, would contain approximately 10^{16} water molecules.

9.3. The Electron Volt. In Sec. 8.2*b* we discussed the acceleration of electrons (or, in rare cases, positive ions) emitted from a glowing filament. Now we know the charge ϵ of these particles and apply the experiment mentioned to the definition of a new unit of energy commonly used in atomic physics. The kinetic energy W_k of particles of charge ϵ having fallen through a potential difference V is computed above [Eq. (8.8)] as $W_k = V\epsilon$. The mass μ does not enter into this equation. Hence the energy W_k is independent of the mass and completely defined by the potential difference and the charge. Since in many modern experiments electrons and ions are observed that have been accelerated through a measured potential difference, a convenient unit of energy is the "electron volt,"

(abbreviated ev) *i.e.*, the kinetic energy of any particle carrying the electronic charge ϵ which has been accelerated through a potential difference of 1 volt. In equations correlating various electric and magnetic quantities and their energies, the absolute unit erg remains indispensable. The electron volt is only an abbreviation for an energy of

$$10^8 \text{ emu of potential difference} \times 1.602 \times 10^{-20} \text{ emu of charge} = 1.602 \times 10^{-12} \text{ erg}$$

The energy given to the electron in high vacuum by a potential difference is fully available when the electron hits the anode and its kinetic energy is there changed into heat. This is a commonly used method for baking out metal plates in high vacuum. The various energy exchanges will become clear by a comparison with familiar mechanical processes. Water stored in a reservoir at a high altitude above a valley represents potential energy. We convert this energy into heat by either one of two ways. Either the water is allowed to flow down to the valley through pipes so narrow that by friction all the potential energy changes into heat and no kinetic energy is formed, in a manner comparable with the flow of electricity through an ohmic resistance; or in a waterfall the potential energy is all changed into kinetic energy which is converted into heat when the water hits the ground, in a manner comparable to the heating of a metal in high vacuum by electron bombardment.

SUMMARY OF CHAPTER 9

In the oil-drop experiment Millikan measured the electric charge on submicroscopic oil drops by observing their velocity of fall through air under the effect of gravity and their velocity of rise under the effect of an electric field against gravity. He measured the masses of the oil drops with the help of Stokes' law describing the velocity of fall of a spherical body through a viscous medium. His outstanding result is that the charges on small drops occur only as multiples of a smallest charge 1.602×10^{-20} emu. As this charge is entirely independent of the special conditions of the experiment, he concluded that this is a fundamental property of electricity and this charge is identical with the charge ϵ on the electron.

On this basis and with the help of the results of the preceding chapters, the masses of electrons and atoms and Avogadro's number can be computed.

A convenient unit of energy, the electron volt, is defined as the energy given to a particle carrying the charge of 1 electron when it is accelerated through a potential difference of 1 volt; 1 ev = 1.602×10^{-12} erg.

PROBLEMS

9.1. *Oil-drop experiment.* In the oil-drop experiment a condenser is used with a plate separation of 2.50 mm. A droplet is observed *falling* without electric field through a distance of 1.00 mm in 25.3 sec. When a potential difference of 154.8 volts *raises* the same droplet, it travels a distance of 1.00 mm in 18.0 sec. The density of the oil is given as $\delta = 0.920$ g/cm^3, the viscosity of air as $\eta = 1.82 \times 10^{-4}$ cm^{-1} g sec^{-1}. How large is the electric charge on the droplet expressed in emu?

9.2. *Balancing a droplet* In the oil-drop experiment we want to balance a droplet carrying a charge of one single electron. Using a condenser with its plates 3 mm apart and a potential difference of 110 volts, we must select a suitable size of the droplet by watching its velocity of fall under the influence of gravity alone. How large a velocity must we select? For the density of oil and the viscosity of air see the preceding problem.

9.3. *Acceleration of electrons.* Suppose that the negative plate of an evacuated plate condenser is red hot and emitting electrons. Compute the time required for electrons to cross from the negative to the positive plate and the velocity and kinetic energy with which they arrive. Treat the electrons like freely falling bodies. Plate distance $d = 0.600$ cm; potential difference $V = 120$ volts (see Sec. 10.1).

9.4. *Kinetic energy of electrons and ions.* Starting from the principle of conservation of energy, compute the velocities v and kinetic energies W_k (in ergs and ev) of the following particles, all accelerated by 110 volts: (*a*) an electron, (*b*) a singly charged H ion, (*c*) a singly charged Na ion, (*d*) a doubly charged Ca ion. Neglect the correction due to the theory of relativity.

HINT: Equate W_k with the potential energy lost by the charged particle during acceleration.

9.5. *Thermal kinetic energy of molecules.* For comparison with the result of the preceding problem compute the velocity (in cm/sec) and the kinetic energy (in ergs and ev) of *hydrogen molecules* at room temperature (293° abs). The density δ of molecular hydrogen at room temperature and 1 atm pressure is 8.99×10^{-5} g/cm^3. One atmosphere pressure is exerted by a mercury column of 76 cm height (density of mercury = 13.55 g/cm^3).

9.6. *Comparison of units.* In a chemical reaction, for example the combination of two H atoms forming a H_2 molecule, each molecule formed liberates a certain energy, which we may measure in the fundamental unit, ergs. Practically, the reaction is allowed to take place in a calorimeter, and the heat liberated measured in kilocalories per mole of gas. What is the factor of proportionality between this new unit and each of the other units, erg and electron volt? Two H atoms have an energy of combination of 4.45 ev. Express this energy in kcal/mole.

COMMENT: Apparently, there can be no relation between 1 ev (a unit of energy) and 1 kcal/mole (a unit of energy/mass). In this case, however, ev always means electron volts per molecule; correspondingly here erg always means erg per molecule.

9.7. *Force exerted by positive-ion current.* Cesium ions Cs^+ emitted from a glowing filament form an electric current of 10^{-10} amp. After being accelerated by a potential difference of 110.0 volts, they strike a target, giving off all their momentum (*inelastic* collisions, see Prob. 3.5). How large is the force on the target?

9.8. *Change of mass of mercury atoms.* In the electric discharge through mercury vapor, atoms are being excited to an energy of 4.9 ev (see Sec. 17.1). Express the increase in mass given to the mercury atom in terms of percentage of its original mass.

COMMENT: Notice that this increase is far below the observable limit.

9.9. *Gain of mass by dissociation.* When dissociating a hydrogen molecule H_2 we *spend* the energy of dissociation $D = 4.4$ *eV*. The two free atoms so produced contain

this amount of energy more than the molecule. Hence, according to Einstein's principle, they have a larger mass. Compute this increase of mass. What per cent of its mass does each atom gain by the process described? Is this increase of mass within the accuracy of the mass spectrograph which is evident in Appendix 5? This process will be compared with nuclear disintegrations in the next problem. Note that the same amount of energy spent in the dissociation of a molecule is liberated in the combination of two atoms

9.10. *Disintegration of* He *into* 4 H. Four hydrogen atoms H are slightly heavier than 1 helium atom He (see Appendix 5). We interpret the slight difference between these masses as a difference in energy. (This energy is independent of the special process or sequence of processes by which 1 hydrogen atoms may combine to form 1 helium atom. In particular, we do not claim that in one process 4 hydrogen nuclei and 2 electrons join to form a helium nucleus.) How much energy, expressed in ergs and electron volts, must be imparted to the helium atom in order to split it up into 4 hydrogen atoms? (Similar processes will be discussed in more detail in Sec. 20.4.)

9.11. *Energy content of hydrogen.* First we separate all the hydrogen contained in a glass of water (250 g water) from the oxygen. Then suppose we succeed in combining each 4 hydrogen atoms to form 1 helium atom. Compute the total energy liberated (in ergs and kwhr). Compute the cost of this energy, assuming 2 cents for 1 kwhr. (Disregard the presence of rare isotopes, Sec. 20.5.)

Comment to Probs. 10 and 11: Later, in the discussion of the nuclear atom, we shall study a more detailed picture of transmutation of elements (see Sec. 20.3 and Probs. 20.1, 22.4, 22.6, and 22.8) where only the nuclei and not the external electrons enter. The simple calculation given here, in which nuclei and external electrons are lumped together, is historically important since the enormous energy liberated by the hypothetical combination of 4 hydrogen atoms represents the earliest indication of the fact that the heat radiated from the sun is generated by this process (see Sec. 23.3).

CHAPTER 10

ELECTRONS IN METALS

10.1. Richardson's Equation. After the explanation of electrolysis, cathode rays, and positive rays on the basis of the electron theory, we shall give a report of the theoretical picture of electrons *in metals* omitting the mathematical detail.

The conduction of electricity through metals is fundamentally different from the phenomenon of electrolytic conduction where ions, electrically charged atoms or molecules, are transported through the solution as evidenced by the visible effects on the electrodes. When a copper wire has carried an electric current even for many years, no chemical change can be detected in, or at the ends of, the copper. More than a century ago it was first postulated that electricity is an agent that can flow freely through a metal. The sign of this agent, flowing in one direction or the other, was unknown, but it was assumed to flow from the arbitrarily defined "positive" terminal to the opposite or "negative" terminal. At present we have reason to believe that this agent is identical with the electrons discovered by Thomson, thereby reversing the above sign convention. Although electrons can freely move through the *body* of the metal, its *surface* presents an obstacle. This is demonstrated by the well-known ability of a metal, when supported by an insulator, to keep an electric charge.

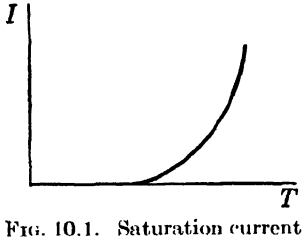


FIG. 10.1. Saturation current from glowing filament plotted against absolute temperature.

This theoretical picture of electrons in metals has been refined in order to include electron emission from a glowing metal (Sec. 8.2*b*). Suppose that in high vacuum a glowing filament is surrounded by a metal cylinder. This simple apparatus is called a "diode." We easily determine the total number of electrons per second given off by the filament when we connect the filament and cylinder to the negative and positive terminals of a power supply. The current produced by a sufficiently strong electric field is due to all the electrons given off (Fig. 10.1). The reason why a strong field is needed for this process will be explained later. When the filament is at low temperature, the current is not noticeable; at red heat, depending on the properties of the material, it starts, and with further increasing tem-

perature the current rapidly increases, described approximately by an exponential function of the temperature.

This observation has led to a much more detailed picture of electrons in metals (Richardson, 1901). It is assumed that electrons take part in the thermal motion of the matter. The electrons, however, are not bound to fixed positions but are free to move like the atoms of a gas. The surface of the metal represents a fence preventing the electrons from leaving the metal. The kinetic energies of the electrons are distributed over an unlimited range, as described by Maxwell's velocity distribution (Sec. 7.1), such, however, that their mean energy is represented by the expression we derived for gaseous molecules (Sec. 3.2). Thus, a few electrons have a kinetic energy far exceeding the average. If such a fast electron shoots against the wall with a velocity component perpendicular to the wall exceeding a certain limit, the electron escapes and is registered as part of the current reaching the anode.

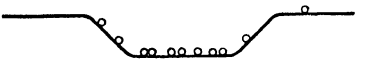


FIG. 10.2. Mechanical model of electrons in a metal.

This process is illustrated by the following mechanical model (Fig. 10.2). Suppose that on the flat bottom of a washbasin that has a sloping rim there are many small steel spheres violently shaken by some mechanism. They will roll all over the bottom. When a sphere runs against the rim, it climbs part of the slope. If the component of its velocity perpendicular to the rim exceeds a certain well-defined value, the sphere will climb over the top and escape. This process compares with the escape of an electron from the metal. This mechanical picture indicates that we must characterize each metal by the energy required to liberate an electron from the metal. This energy is called the "work function" of the metal. In our mechanical picture it compares with the work required to lift a steel sphere from the bottom to the edge of the basin. It is of practical interest that the work function of a metal is strongly affected by impurities at the surface.

This is a general outline of the idea that Richardson carried through mathematically. He derived an expression for the electron current in terms of the temperature in good agreement with the measurements. In recent years the theoretical background has been fundamentally modified in order to include the explanation of other phenomena like the specific heats of metals (Sommerfeld, 1927).

Here we must meet an obvious objection to our determination of ϵ/μ of electrons emitted from a glowing filament (Sec. 8.2*b*). We assume that the electrons take part in the thermal motion in the interior of the glowing filament. Therefore, they are expected to leave the metal with a certain initial velocity, which should be higher at a higher temperature. Does this not affect the kinetic energy of the electrons outside the metal, which we simply expressed in terms of the accelerating potential as $V\epsilon$? As a matter

of fact, in most experiments the thermal velocities are negligible. This is evident from a numerical example. It is a convenient standard that at room temperature the kinetic energy of a particle, irrespective of its mass, equals $\frac{1}{30}$ ev (Sec. 3.2). Then in a glowing filament of, say, 2100°K the thermal energy would be only $\frac{7}{30}$ ev. This is negligible unless the accelerating potential is low. However, for high-precision determinations of ϵ/μ it must be considered that not all electrons emitted from a filament have the same velocity.

10.2. Saturation Current and Space-charge Current. Finally, we must explain why, in the experiment described above, a considerable potential difference is needed to pull all the electrons from the glowing filament to the anode, although apparently an electron leaving the filament would be free to cross the highly evacuated space to the surrounding cylinder. A more detailed experimental investigation will lead to the explanation. In Fig. 10.3 the electron current I leaving the filament is plotted against the potential difference V between filament and plate for constant filament temperature. The electron current is increasing with the potential difference and reaches a limiting value at a potential of, say, 100 volts (depending on the filament temperature and the geometry of the apparatus). This current is called the "saturation" current. It is supposed to represent all electrons emanating per second from the glowing filament. This is the current we plotted in Fig. 10.1 against the temperature.

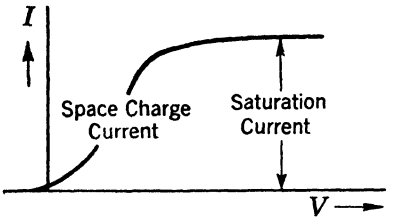


FIG. 10.3. Current-potential curve of a diode at constant filament temperature.

Why is the current smaller for the lower voltages although in high vacuum there are apparently no obstacles to prevent the passage of electrons? The electrons themselves form such an obstacle. At low potential difference the electrons travel slowly enough so that a certain accumulation in space occurs, known as a "space charge." The electrons are accelerated by the electric field on their way from the filament to the anode. As the accumulation is largest where the velocity is smallest, the space charge has the greatest value immediately in front of the filament where the electrons have not yet picked up an appreciable velocity. The effect of the space charge is that an electron just leaving the filament has a good chance of colliding on its way to the anode with other electrons. They may deflect the newcomer back into the filament. On the other hand, a high accelerating potential speeds up all electrons to such an extent that no appreciable space charge is formed, and all electrons leaving the filament reach the plate. Space-charge effects are of outstanding importance in electron tubes.

SUMMARY OF CHAPTER 10

The electric conductivity of metals is explained by electrons which are free to move like atoms of a gas within the metal but are prevented by the surface from leaving the metal. In order to explain electron emission from a glowing metal, Richardson assumed that a well-defined energy, characteristic for the metal with a clean surface, called the "work function," is required to liberate an electron from the metal. Any electron that approaches the surface with a sufficiently high velocity component escapes from the metal.

It requires a considerable potential difference to pull all electrons so liberated from the filament to the anode (saturation current). At low potential difference the electrons travel so slowly that in the vacuum near the surface of the filament a space charge is formed, which bends some newly emitted electrons back into the filament (space-charge current).

PART IV

STRUCTURE OF LIGHT

Our next aim is to introduce the quantum theory of light. Historically, the quantum theory had its origin in the explanation of black-body radiation but, in order to avoid the more advanced mathematical treatment indispensable for this theory, we shall introduce instead the quantum structure of light on the basis of the photoelectric effect. We shall discuss first the experimental facts concerned with this effect, next the attempt to explain them on the basis of the electromagnetic theory of light, and, finally, Einstein's quantum theory of this effect. In the following two chapters we shall discuss further evidence supporting the quantum theory of light.

CHAPTER 11

PHOTOELECTRIC EFFECT AND THE QUANTUM OF LIGHT

11.1. Experimental Facts. Heinrich Hertz discovered that an electric spark starts more readily when the electrodes are exposed to ultraviolet light (1890). The underlying phenomenon is investigated by means of the apparatus shown in Fig. 11.1. In a highly evacuated quartz bulb the metal plate M is exposed to light, quartz being used because it transmits ultraviolet as well as visible light. Between this plate and another metal

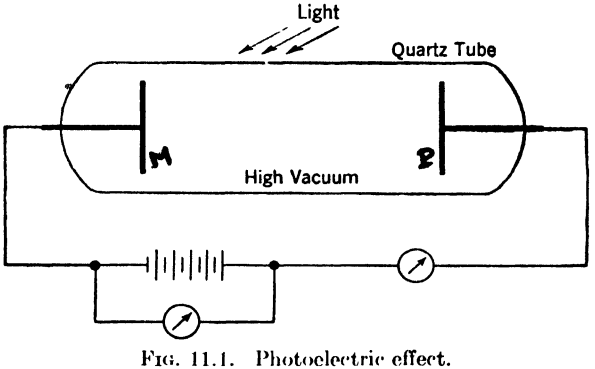


FIG. 11.1. Photoelectric effect.

plate P which is shielded from the light, a potential difference, V, of about 50 volts is applied. When the plate M is exposed to the light from a quartz mercury arc a current flows, but only if the plate P is made positive with respect to M. This indicates that negatively charged particles are liberated by the light from the metal M and pulled by the potential difference to the plate P.

For the further investigation of the nature of these particles we apply the same method of electric acceleration and magnetic deflection by which we tested the nature of the particles emanating from a glowing filament (Sec. 8.2*b*). Omitting the construction of the apparatus, we record only the result, stating that the specific charge of the liberated particles is the same as that characteristic of electrons, thereby proving that light liberates *electrons* from a metal surface.

The current-potential curve of the photoelectric cell of Fig. 11.1, for

constant illumination, is given by Fig. 11.2. With increasing potential difference the current reaches a limiting value, called the "saturation" current, presumably due to the limited number of electrons liberated per second by the light. (This is comparable with the saturation current from a glowing filament, Fig. 10.3.) For small *negative* values of potential difference (retarding the electrons), the current flows *in the same direction* as for positive values, diminishing, however, for increasing negative values until, at a sharply defined potential difference, the current goes down to zero. This value is called the "stopping" potential. The current never reverses its direction, unless some stray light reaches the other plate P and there produces photoelectric effect.

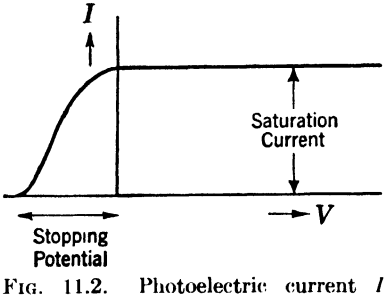


FIG. 11.2. Photoelectric current I plotted against the accelerating potential difference V for constant illumination.

We shall understand the significance of the stopping potential by a comparison with an experiment in mechanics. A stone thrown vertically upward will climb until its initial kinetic energy is completely changed into potential energy; hence, knowing the maximum height reached we can calculate the magnitude of the initial kinetic energy. Correspondingly, the value of the stopping potential enables us to compute the maximum kinetic energy W_m of the electrons liberated from the metal plate M by the light. The conservation of energy is expressed as

$$W_m = \tfrac{1}{2}\mu v_m^2 = \epsilon V_s$$

where V_s = stopping potential, ϵ, μ, and v_m = charge, mass, and maximum velocity, respectively, of the electrons liberated. In Sec. 8.2*b* we used the same equation in order to compute the kinetic energy W_k of a particle carrying the charge ϵ accelerated by the potential difference V [Eq. (8.8)].

In the systematic study of the photoelectric effect we vary at will the light and the metal illuminated. In order to have well-defined conditions, we use monochromatic light described by its intensity and wave length* λ (or, instead, its frequency ν in the unit sec^{-1}). We measure the saturation current and the stopping potential as functions of these independent variables and so obtain results described as follows. Using the same metal and the same frequency of the light, varying its *intensity*, we obtain a family of current-potential curves given in Fig. 11.3. They indicate that the

*The wave length of light is conventionally expressed in angstrom units, abbreviated A; $1\text{A} = 10^{-8}$ cm. However, in equations like $\nu = c/\lambda$ all quantities must be expressed in the same system of units, conveniently the cgs system.

stopping potential is independent of the light intensity, and the saturation current is proportional to the intensity.

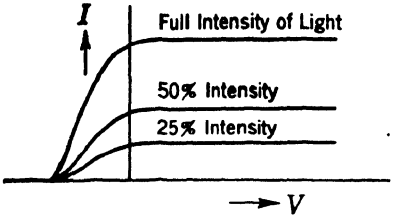


FIG. 11.3. Photoelectric current I plotted against the accelerating potential difference V for various intensities of illumination on the same metal by the same source of light.

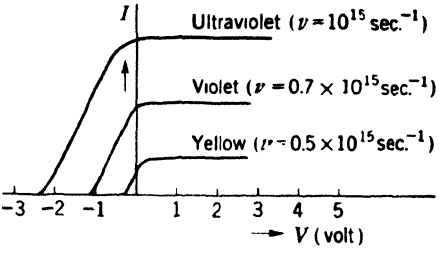


FIG. 11.4. Photoelectric current I plotted against the accelerating potential difference V for three different frequencies of light incident on a potassium surface.

This last result makes the photoelectric cell a very convenient photometer.

Photographic exposure meters are photometers based on a different effect. In the exposure meter the light produces an electromotive force in a thin film of a semiconductor like cuprous oxide placed between copper and another metal. Without the light this combination acts as a rectifier, *i.e.*, transmits current in a preferred direction. When the cell is illuminated, a current, which is nearly proportional to the intensity of the light, flows in a direction opposite to the preferred one mentioned above. We are not concerned with the theory of this effect which is of importance for the theory of electric conduction in solids.

Numerous other applications of the photoelectric effect may be mentioned. For example, light and dark cigars are sorted by an electrical device containing a photoelectric cell which puts the cigars into different boxes according to the intensity of the light scattered by the cigars. More important is the use of photoelectric cells for television.

For the understanding of the nature of light we are concerned with the measurement of the stopping potential V_s as a function of the frequency ν of the light. Again we observe the current-potential curves for, say, a sodium surface, this time varying the *frequency*, say, from $\nu = 10^{15}$ sec^{-1} (ultraviolet) to $\nu = 0.7 \times 10^{15}$ (violet), and $\nu = 0.5 \times 10^{15}$ (yellow) and, finally, $\nu = 0.4 \times 10^{15}$ (red). The curves are plotted in Fig. 11.4. The red light fails to produce any photoelectric current.

For each frequency only one representative curve is drawn, disregarding the fact that for varying intensity we should obtain families of curves, for each frequency a family with the same stopping potential as in Fig. 11.3. Hence in Fig. 11.4 we pay attention only to the stopping potentials, not to the saturation currents.

The curves show a relation between the *stopping potential* V_s (the limiting value of V) and the *frequency* ν of the light. How simple this relation is,

is evident when we plot V_s against ν; instead of V_s, we may as well plot the maximum kinetic energy $W_m = \frac{1}{2}\mu v_m^2$ of the photoelectrons, which is proportional to V_s. For this new diagram we do not need new measurements; we simply take the corresponding values of V_s and ν from the preceding diagram (Fig. 11.4) and so plot Fig. 11.5, representing $W_m = \epsilon V_s$ as a function of ν. The diagram shows a linear relation between these variables. We may express the same relationship by a linear equation between the maximum kinetic energy ϵV_s and ν

$$\epsilon V_s = h\nu - P \quad (11.1)$$

Here h and P represent constants characteristic of the straight line the numerical values of which may be computed from the measurements plotted in Fig. 11.4. The diagram as well as the equation indicate that the kinetic energy W_m becomes zero for a sharply defined frequency limit $\nu_l = P/h$. This is called the "threshold frequency" of the photoelectric effect; there is no effect whatever observed for lower frequencies.

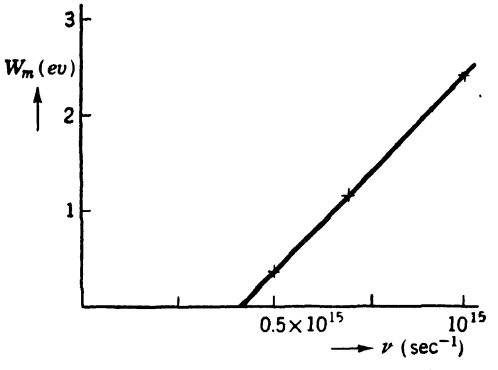


FIG. 11.5. Derived from Fig. 11.4. Maximum kinetic energy W_m of the photoelectrons from a potassium surface (measured by the stopping potential) as a function of the frequency ν of light.

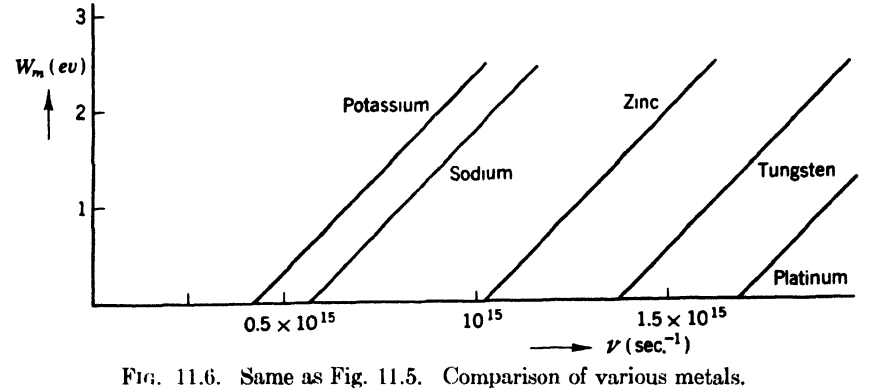


FIG. 11.6. Same as Fig. 11.5. Comparison of various metals.

In our last set of experiments we vary the *metal* exposed to light. Plotting the straight line just described for sodium, zinc, platinum, and tungsten, we obtain another family of curves given in Fig. 11.6. We notice the fact that all these lines have the same slope but that their intersections with the ν axis, indicating the threshold frequencies, differ. This same fact is expressed in terms of Eq. (11.1) by stating that h is a constant common

to all metals, in other words a universal constant, while P is a constant characteristic for the metal.

It is evident from Eq. (11.1) that P and $h\nu$ both have the dimension of energy; hence h has the dimension of energy/frequency and is measured in erg sec. The numerical values are: $h = 6.61 \times 10^{-27}$ erg sec; P between 0.7×10^{-12} and 4×10^{-12} erg (or between 1 and 6 ev) depending upon the metal.

So far we have strictly reported experiments and represented their results by diagrams and a simple equation. We summarize these results in so far as they are important for the theory. The maximum kinetic energy W_m of the photoelectrons is independent of the *intensity* of the light. It depends on the *frequency* of the light by the relation $W_m = h\nu - P$, where h is a universal constant and P a constant characteristic for the metal.

11.2. Failure of the Electromagnetic Theory. To begin with, we try to explain the observed facts described in the preceding section on the basis of the electromagnetic theory of light which, at the end of the last century, seemed to be established beyond any doubt. Here we shall briefly review the background of this theory. The old controversy between the wave theory of light (Huygens, 1678) and the corpuscular theory (Newton, 1775) had been decided in favor of the wave theory by the work of Fresnel and Young (between 1800 and 1820). The main arguments in favor of the wave theory are given by the phenomena of interference and diffraction. The dark interference fringes, observed, for example, in Newton's rings, prove that light superimposed on light may produce darkness. This is a strong argument for the idea that light consists of a wave motion because, by the superposition of two wave trains, standing waves may be produced that contain spots without any motion whatever. On the other hand, the corpuscular theory of light seems incompatible with the dark interference fringes because corpuscles of light superimposed on other corpuscles cannot produce darkness. Another argument for the wave nature of light is given by diffraction. A knife-edge placed in the path of parallel light does not cast an absolutely sharp shadow; some of the light enters into the geometrical shadow and so shows a certain, although very small, deviation from rectilinear propagation. This is a well-known property of waves, in this case of very short length. Corpuscular rays, however, would not show diffraction.

These two arguments for the wave theory leave the nature of the light waves unknown. Their nature was discovered much later by Maxwell (1873). He started from a mathematical investigation of electricity and magnetism which, to begin with, did not seem to be concerned with light. He represented the relations between electric and magnetic fields by a set of differential equations not to be discussed here. On the basis of this investigation he was able to predict the existence of *electromagnetic* waves

with the following properties. In vacuum they should propagate with a constant velocity, which Maxwell computed on the basis of electric and magnetic data to be 3×10^{10} cm/sec. On the surface of insulators (glass, water) they should be partly reflected, partly refracted with a certain change in their polarization. These properties—and additional properties theoretically predicted—agree so completely with the properties of light, known from experiments, that the conclusion is inevitable that light consists of electromagnetic waves.

Maxwell's theoretical argument was strongly supported by the experiments of Hertz (1890). With electrical apparatus (wires, spark gaps, induction coil) Hertz produced an effect that was propagated by a wave motion from one loop of wire to another. The wave nature could be demonstrated by the production of standing waves. The order of magnitude of their wave lengths was measured as decimeters. These electromagnetic waves could be reflected, refracted, and polarized in the same way as the electromagnetic waves predicted by Maxwell. Thus Hertz's experiments confirm Maxwell's theory. At the same time they make it plausible that light waves are electromagnetic waves differing from those explored by Hertz only by their wave lengths, which are between 4 and 8×10^{-5} cm.

It is a strange coincidence that, in the same experimental work that seemed firmly to establish the electromagnetic theory of light, Hertz discovered the photoelectric effect, which turned out to be incompatible with this theory and led to its profound modification. Is the electromagnetic theory of light capable of explaining the photoelectric effect? At the first glance this seems possible. In this theory electric and magnetic fields are attributed to the light waves, which may well exert forces on the electrons contained in the metal and so liberate them from the metal surface. However, on this basis we should predict that light of high intensity, *i.e.*, consisting of strong fields, would give high kinetic energy to the electrons liberated. This is not the case; on the contrary, the experiments show that the kinetic energy is independent of the light intensity. Furthermore, according to the theory we should expect that light of low frequency (infrared), if sufficiently intense, would be as effective as high-frequency light (ultraviolet). Again this prediction of the electromagnetic theory contradicts the experiments, which show that light of a frequency below a sharply defined threshold is entirely ineffective. So we are forced to conclude that the electromagnetic theory of light fails to explain the photoelectric effect.

11.3. Quantum Theory. In order to appreciate Einstein's quantum theory of the photoelectric effect we must briefly survey the earlier development. Planck, in 1900, introduced the quantum theory in his discussion of the radiation emitted from a black body. He assumed that the black body consists of atoms able to radiate and absorb light, each atom being a vibrator of a well-defined frequency ν. The blackness of the body he explained by the presence

of radiators of all possible frequencies. In order to create a theory agreeing with the experiments, Planck introduced a new hypothesis of fundamental importance which we here only report. He assumed that the energy contained in each vibrating atom cannot have values covering a continuous range but only sharply defined, "quantized" values. For each atom, characterized by its frequency ν, Planck assumed a quantum of energy proportional to ν or of the value $h\nu$ where h is a constant of proportionality. Each atom can contain an integral number of such quanta, that is an energy $nh\nu$ where $n = 0, 1, 2, 3, \ldots$. Here h is a new universal constant which, on the basis of the measurements of black-body radiation, is determined to be $h = 6.61 \times 10^{-27}$ erg sec. (We notice that this is the same figure that we found when representing certain straight lines describing the photoelectric effect by an equation.) The new law discovered by Planck cannot be derived from the older laws of physics, frequently called "classical physics" as contrasted with "quantum physics." It is as foreign to these older laws as, for example, the atomic hypothesis is to the laws of Newtonian mechanics.

We shall not apply Planck's argument but have to mention it in order to point out the background of Einstein's theory of the photoelectric effect. In order to explain the photoelectric effect, essentially described by Eq. (11.1) Einstein (1905) introduced the bold assumption that the energy of light is not uniformly distributed over the wave front, as the energy of water waves is. Instead, it is concentrated in packages of the energy content $h\nu$ where ν is the frequency of light and h a new universal constant determined on the basis of the photoelectric measurements. Hence the individual packages, called *quanta of light* or *photons*, are small for light of low frequency and large for light of high frequency. All we know is that each package $h\nu$ must be so concentrated that it can transfer its whole energy content to 1 electron. Applying the principle of conservation of energy to this transfer, Einstein postulated that the energy of the quantum $h\nu$ when hitting the metal surface goes into two parts, one part P being used for the liberation of the electron from the metal and the balance for kinetic energy or, written as an equation,

$$h\nu = P + \text{kinetic energy}$$

This is essentially the same as the empirical Eq. (11.1). Thus the theory predicts the observed fact that P is a constant characteristic for the metal while h is a universal constant, characterizing the property of light as consisting of energy quanta $h\nu$. Here it becomes evident that the constant h, introduced above in the description of a very special phenomenon, the slope of certain straight lines concerned with the photoelectric effect, has a much more general importance in the theory of the quantum structure of light. This transfer of the energy of light to the electrons by no means

takes place for all the quanta incident on the metal. It is a fact that most metal surfaces are good reflectors of light. Therefore, we must assume that only a small fraction of all quanta incident on the metal suffer the change described above.

In this theory, high intensity of visible light is described not as due to very large quanta or strong electric and magnetic fields but, instead, as a very large number of quanta per second traveling as a light ray. Thus light of high intensity is expected to liberate many electrons per second and so cause a relatively large photoelectric current without, however, giving to each electron a larger energy than low-intensity light of the same frequency does. This agrees entirely with the observation.

This theory seems to predict that light of the frequency ν must give the *same kinetic energy* $h\nu - P$ to *all electrons* liberated. Experimentally this is not the case as is evident from the slope of the curve of Fig. 11.2. Actually, the current I gradually vanishes when the retarding potential V increases and approaches the value of the stopping potential V_s. This means that the number of electrons endowed with the full theoretical energy content is vanishingly small. The increase of the current for decreasing retarding voltages indicates that many electrons are liberated with less than the full energy content. This is theoretically explained by the well-known fact that light is not absorbed at the metal surface proper but is able to penetrate thin layers of metal. Therefore, the photoelectric effect, which is a special process of absorption of light, may well take place at a certain depth below the metal surface. In this case the liberated electron has to traverse several molecular layers before it escapes; under way it may lose a part of the energy given to it by the quantum. Furthermore, the electron liberated from the surface with the full kinetic energy given by Eq. (11.1) can overcome the full stopping potential only if it happens to leave the metal plate in a direction perpendicular to the surface. Therefore, in agreement with the observation, only a vanishing part of all photoelectrons is expected to reach the plate P when the full theoretical stopping potential is approached.

The significance of the quantity P as the energy required for the liberation of a photoelectron from the metal suggests an experimental test of Einstein's theory. The same quantity was mentioned in our discussion of the liberation of thermoelectrons from glowing metals. There it was given the name "work function" of the metal. We may obtain its value for the same metal from both thermoelectric and photoelectric measurements. The results obtained by the two methods agree, although it must be admitted that this comparison can be carried out for only a few metals like tungsten and platinum, which stand white heat and can be prepared with very clean surfaces. This is necessary since impurities of the surfaces are liable to affect the energy of liberation P.

The student is by no means asked to discard the old electromagnetic wave

theory of light and instead accept the more recent quantum theory. The wave theory is so firmly founded on experiments as outlined above and, on the other hand, the quantum theory fails so conspicuously to explain interference and diffraction that, for the time being, we can only state the dilemma: The wave theory is indispensable for the explanation of interference and diffraction, the quantum theory for the explanation of the photoelectric effect. Einstein himself, when introducing the new theory in 1905, did not claim that it represents an absolute truth. He only suggested it as a tentative new principle that might lead to new discoveries. Although the two theories are apparently incompatible with one another, for twenty years this dilemma remained unsolved until in 1925 wave mechanics showed the way to a reconciliation of the two opposed ideas. This will be discussed in Chap. 26.

Einstein's quantum theory of light is frequently called the "corpuscular theory of light." The word "corpuscular," however, overstates the case. The theory does not claim that the quanta of light have the same properties as, for example, atoms. Outstanding differences are as follows: The quantum of light always travels with the velocity 3×10^{10} cm/sec. Matter, however, is observed to travel with any lower velocity; the theory of relativity even claims that matter can never reach the velocity of light. Light is easily *absorbed*, *e.g.*, by a black body, and its energy changed into heat; furthermore light is easily *created*, *e.g.*, when heating a metal filament by an electric current. These facts are not at all true for matter.

Our discussion of the quantum theory, based on the experimental investigation of the photoelectric effect, does not follow the historical development. It has been mentioned already that the constant h was discovered by Planck in his theory of black-body radiation. Universally it is called "Planck's constant." In our discussion, h first appears as an empirical constant describing photoelectric measurements. Actually, Einstein in 1905 postulated the quantum of light and established his fundamental equation of the photoelectric effect [Eq. (11.1)] long before the difficult experiments were performed. Eleven years later the theory was confirmed by Millikan's measurements and determination of Planck's constant h from the photoelectric effect. Only the simple principle of his apparatus is described by Fig. 11.1 while the actual apparatus, constructed for the preparation of clean metal surfaces, was so complicated that he called it a "machine shop in high vacuum."

It is striking how thoroughly the theory affects our judgment of the importance of one field or another. Strictly from the experimental point of view, the photoelectric effect seems to be a rather remote corner of physics with technical applications of no great significance. However, Einstein's theory makes it clear that the photoelectric effect gives evidence of the nature of light, one of the greatest problems of physics.

A summary of this discussion will be found at the end of Chap. 13.

PROBLEMS

11.1. *Determination of Planck's constant.* An experiment on the photoelectric effect on potassium leads to the following data: irradiations with yellow light from a sodium arc and ultraviolet light from a mercury arc (5,890 and 2,537A) liberate electrons with the stopping potentials 0.36 and 3.14 volts, respectively. Given the charge on the electron (Sec. 9.9), derive (*a*) Planck's constant h; (*b*) the work function P of potassium; (*c*) the long wave-length limit of the photoelectric effect on potassium.

11.2. *Number of quanta required for heating.* . Green light ($\lambda = 5{,}000 \times 10^{-8}$ cm) is completely absorbed by the mercury bulb of a thermometer. This bulb contains 2.00 g of mercury. How many quanta of light must be absorbed in order to heat the bulb 3.00°? Neglect all losses of heat.

11.3. *Number of quanta received by the eye.* Suppose that a source of yellow light ($\lambda = 5{,}900$A) has an intensity of 1 candlepower. With a bolometer it is observed that, at a distance of 1 m from the source, the energy passing 1 cm^2 in 1 min is 1.162×10^{-5} cal. How many light quanta are passing 1 cm^2/sec?

11.4. *Number of quanta per sec barely visible.* The human eye is able to see a star of 6th magnitude, equivalent to 10^{-8} candlepower at a distance of 1 m. How many quanta are passing per second through the pupil of the eye? (Diameter of pupil = 3 mm.) Assume the same λ as in Prob. 11.3.

CHAPTER 12

FUNDAMENTAL LAW OF PHOTOCHEMISTRY

Simultaneously with the fundamental equation of the photoelectric effect, Einstein proposed the fundamental law of photochemistry as another consequence of the quantum theory of light. In photochemistry chemical reactions produced by light are investigated. In most cases the reaction progresses in several steps. The absorption of light causes a primary reaction which is followed by secondary reactions of the atoms and radicals produced. Einstein's fundamental law is the consistent application of the idea of the light quantum. It states: *Each quantum of light absorbed causes one molecule to react in the primary reaction.*

The relation of this statement to the observations will become clear when we consider an example. It is observed that hydrogen iodide, HI, is decomposed by light into hydrogen H_2 and iodine I_2. The "yield" of the reaction is defined as the number of HI molecules decomposed divided by the number of quanta absorbed. The yield has been measured as 2 molecules decomposed for each quantum absorbed, which seems twice the amount predicted by Einstein's fundamental law. In order to explain this yield, secondary reactions are assumed as follows. First each quantum $h\nu$ absorbed decomposes 1 molecule, schematically written

$$HI + h\nu \rightarrow H + I$$

(How dissociation by light shows up in a continuous absorption spectrum will be discussed in Sec. 17.5*b*.) The free H atom so produced has such a strong affinity for another H atom that it decomposes a second HI molecule and so forms an H_2 molecule by the reaction

$$H + HI \rightarrow H_2 + I$$

The two free I atoms produced by these two steps cannot decompose HI molecules; instead, each migrates through the gas until it meets another free I atom with which it forms a molecule:

$$I + I \rightarrow I_2$$

This theoretical scheme explains the observed yield of 2 molecules per quantum since each photochemical decomposition of 1 molecule is automatically followed by one and only one additional decomposition. In the exposure of a photographic plate the primary process is the dissociation by light of silver bromide, AgBr.

The quantum theory of light makes a fact that has been known for a long time understandable. Ultraviolet light is ever so much more effective in producing chemical reactions than visible light; on the other hand, for most reactions infrared light is completely ineffective. For example, the human skin feels red, and infrared, light only as producing *heat;* however, it is *chemically* affected by ultraviolet light. The theory explains this fact by the idea that each chemical change in a molecule, *e.g.*, dissociation, requires a certain minimum energy to be supplied by the quantum. If the quantum has energy in excess of the minimum required, as may be the case for ultraviolet light, this excess goes into kinetic energy of the products. If, however, the energy of the quantum is insufficient, the process cannot take place. For example, the lowest frequency of light sufficient for the dissociation of HI molecules is about $\nu = 7.5 \times 10^{14}$ sec^{-1} ($\lambda = 4{,}000$A). The energy of this quantum $h\nu$ follows as 5.0×10^{-12} erg, or 3.1 ev, or 72,000 cal mole.

It is not safe to assume that this limit represents the energy of dissociation of the HI molecule since it has been found that some molecules do not respond to certain ranges of frequency although the energy of the quantum would be sufficient to produce the chemical reaction. This is explained in detail in the theory of molecular spectra with which we are not concerned here. We shall discuss experimental evidence for it in Sec. 17.9. All we can safely conclude from the fact mentioned is that the energy of dissociation of HI is *equal to or smaller than* 5.0×10^{-12} erg.

Photochemical reactions play a part in living organisms. The process of visual excitation seems to be connected with a photochemical reaction in the retina. The quantum of light enters into the question: How many quanta are required to produce the faintest sensation of light? One quantum is not sufficient, but it seems that as few as five to seven quanta absorbed by the retina may produce a sensation. The light flash incident on the eye must contain more quanta since by no means all quanta incident on the eye reach the retina.

Our examples make it clear that photochemical reactions give evidence supporting the quantum theory of light although, because of the secondary reactions, the evidence is not so clear cut as that based on the photoelectric effect.

A summary of this discussion will be found at the end of Chap. 13.

CHAPTER 13
COMPTON EFFECT

In our endeavor to find experimental tests of the quantum theory of light we must mention the Compton effect although we shall be able to discuss it in detail only after having investigated X-ray spectra (Sec. 19.1*j*). We shall find evidence that X rays are essentially of the same nature as light, except that their wave lengths are 1,000 or 10,000 times smaller than those of visible light. We can measure the wave lengths or frequencies of X rays, observing diffraction by a ruled grating or, preferably, a crystal grating (Sec. 19.1*f*). Furthermore, for any frequency ν so determined, we can compute the energy of the quanta $h\nu$.

A. H. Compton (1923) discovered that X rays of a sharply defined frequency incident on material of low atomic weight, like carbon or paraffin, may suffer a change of frequency when scattered. While the spectrum of the scattered X rays still contains the original frequency, in addition X rays of smaller frequency are produced, the shift of frequency depending on the angle between incident and scattered rays. Compton also discovered that this shift of frequency can be predicted by a bold application of the quantum theory of light. He assumed that each quantum of X rays, as well as a moving body, may be characterized by its energy and its momentum. This enabled him to apply the laws of mechanical impacts, governing the collisions between billiard balls or between atoms (Chap. 5), to the impacts of X-ray quanta on matter. We have learned already that atoms and molecules contain electrons in their structure (Sec. 8.2*a*). At the impact of an X-ray quantum on an electron contained in the carbon or paraffin a part of the energy of the incident quantum is transferred to the electron. The mathematical analysis of this process, to be discussed later, leads to the prediction that the X-ray quantum loses a part of its energy, hence the scattered X ray shows a *shift toward low frequencies* in good agreement with the observed shift. In addition, the magnitude of the *energy transferred to the electron* is theoretically predicted; it has been measured with a technique to be discussed later (Wilson's cloud chamber, Sec. 21.2), again in agreement with the theory. Thus the Compton effect supplies another confirmation of the quantum theory of light.

SUMMARY OF CHAPTERS 11–13

Here we finish our discussion of the structure of matter as consisting of atoms, of electricity as consisting of electrons, and of light or X rays as consisting of quanta. Looking back, we compare the evidence on which these various statements are founded.

The *atomic structure of matter* is inferred from the vast array of the facts of chemistry. There is hardly a discussion in chemistry in which atoms and molecules are not mentioned. Their existence is confirmed by the positive-ray analysis in which atomic weights are found bearing the same proportions as those determined by chemical methods.

Ever so much simpler is the evidence of the *atomic structure of electricity.* The smallest electric charges accessible to measurements, those carried by tiny oil drops, have values represented by multiples of a certain charge. As this charge is independent of all special properties of the experiment, we are forced to conclude that it is a fundamental property of electricity.

Most involved, it seems to us, is the argument that leads to the *quantum structure of light.* The fundamental law of the photoelectric effect correlates the maximum kinetic energy W_m given to the photoelectrons with the frequency ν of the light: $W_m = h\nu - P$. This equation, which describes the observed facts, seems incompatible with the wave theory of light. Einstein anticipated this equation long before the experiments were performed by assuming that light waves contain, instead of energy uniformly distributed over the wave front, quanta of energy $h\nu$ so concentrated that one incident quantum may liberate one electron if the quantum is large enough. The principle of the conservation of energy and the experiments lead to the same equation. This idea explains in particular the threshold frequency characteristic for a metal by the minimum size of the quantum just able to supply the energy of liberation P. Although the wave theory of light is well supported by interference and diffraction of light, the quantum theory of light seems indispensable for the explanation of the photoelectric effect. It is confirmed by its applications to photochemistry and the Compton effect.

PART V

ELECTRONIC STRUCTURE OF ATOMS

In the kinetic theory of gases we describe the individual atom as a body of a certain mass and size and a shape presumably approximated by a sphere. In the next two parts we shall discuss the detail of the structure of individual atoms. We shall start from Rutherford's observation of the scattering of alpha particles which leads to the picture of an atom consisting of a small nucleus surrounded by electrons. Here we shall carry the exploration of the nuclei only so far as it is needed for the understanding of spectra and the periodic table of elements. The picture of the nuclear atom so arrived at justifies the subdivision of the further discussion into that of the *electronic* structure (Part V) and that of the *nuclear* structure (Part VI).

CHAPTER 14

NUCLEAR ATOM AS REVEALED BY ALPHA-RAY SCATTERING

14.1. Discovery of the Nuclear Atom. Rutherford and his collaborators, in 1911, investigated the scattering of alpha rays by thin metal foils. By this time alpha rays were known as one of the radiations emanating from radium and some other radioactive elements. For the present purpose it is sufficient to record some of their outstanding properties, which give evidence of their nature. Alpha rays, when hitting certain substances, for example zinc sulfide crystals, produce flashes of light called "scintillations." When a zinc sulfide screen is irradiated by rays from a weak radium sample, a well-rested eye using a magnifying lens resolves the light emitted from the screen into local, short flashes. These scintillations show that the alpha ray is emitted discontinuously and might be composed of a stream of particles. The student may see such flashes when viewing the luminous paint of a watch through a magnifying lens in a dark room; this paint contains a very weak radioactive material embedded in a fluorescent screen.

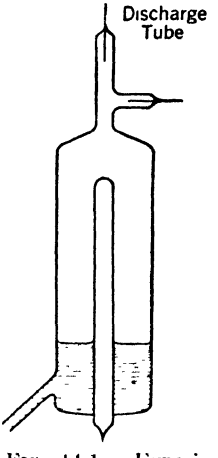


FIG. 14.1. Experiment showing the identity of alpha particles and helium nuclei.

Alpha rays have a *penetrating power* which enables them to pass through metal foils or thin glass walls. This is demonstrated by the observation that such thin films do not prevent the alpha rays from causing the discharge of an electroscope.

The nature of the alpha rays becomes evident when they accumulate in a glass tube and are made to exhibit their optical spectrum. This experiment was performed by Rutherford in an apparatus shown in Fig. 14.1. A quantity of a radioactive gas (radon, see Sec. 21.4) was introduced into a very thin-walled glass tube. This was surrounded by a wider, highly evacuated glass tube which was connected with a small electric-discharge tube. For the spectroscopic investigation all gas that accumulated in the wider tube was compressed into the small discharge tube by the raising of a mercury level. After a few days the accumulated gases when excited by an electric discharge exhibited the spectrum of helium. A

control experiment showed that helium gas could not have leaked through the thin-walled tube. Rutherford concluded that the alpha rays are composed of particles which are essentially the same as helium atoms but which can penetrate the thin glass wall while helium atoms cannot. This result immediately gives information as to the mass of the alpha particle. If we assume that the alpha particle has the same mass as the helium atom it resembles, the mass of the alpha particle is larger than the mass of hydrogen in the ratio of their atomic weights. Hence the mass is $\mu = 6.64 \times 10^{-24}$ g.

What distinguishes the alpha particle from the helium atom? Alpha particles are deflected by strong electric or magnetic fields in the direction characteristic of *positively* charged particles. Their specific charge ϵ/μ and speed v are measured by the method discussed in detail in Sec. 8.2*a*. The result is $\epsilon/\mu = 4.82 \times 10^3$ emu/g. This figure combined with the mass μ given above leads to a charge $\epsilon = 3.20 \times 10^{-20}$ emu. This is just twice the well-known electronic charge (Sec. 9.1). This measurement of the charge carried by each alpha particle is confirmed by another pair of experiments. First, the number of alpha particles coming from a certain emitter is measured by counting the scintillations produced on a zinc sulfide screen. (A more convenient counting device, the Geiger counter, will be described in Sec. 21.2.) Next, the total electric charge carried by the particles emitted from the same source is measured by allowing them to charge an electroscope. A simple computation yields the positive charge carried by the individual particle, the result agreeing with the value just given. In the experiment described above, alpha particles, although *doubly charged*, are identified by their spectrum with *neutral* helium atoms. Here we must assume that each alpha particle picks up 2 electrons either from the glass wall or the mercury surface. The speed v of the particles is characteristic for the specific radioactive element; *e.g.*, radium emits alpha particles of a speed $v = 1.519 \times 10^9$ cm/sec.

We summarize the properties of alpha rays that were known before Rutherford's work on their scattering: The rays consist of individual particles which are identical with *doubly positively charged helium ions;* they are able to produce scintillations and pass through metal foils.

Rutherford and his collaborators investigated the scattering of alpha particles by observing what happens to a beam of such particles when penetrating thin gold foil (Fig. 14.2). Their apparatus was in principle constructed as follows: A radium sample is placed at the bottom of a metal capsule whose wall absorbs all alpha particles except those which pass through a narrow hole. This capsule, in turn, is placed at the bottom of a glass bulb which is highly evacuated so that collisions of alpha particles with air molecules are negligible. The inside surface of the bulb is covered with a thin zinc sulfide screen so that the narrow pencil of alpha particles shooting upward through the hole in the metal capsule produces intense

scintillations at the top of the bulb. Rutherford investigated how these scintillations are affected when a gold foil is placed in the path of the rays. Let us try to predict what should happen. A thin gold foil of 6×10^{-5} cm

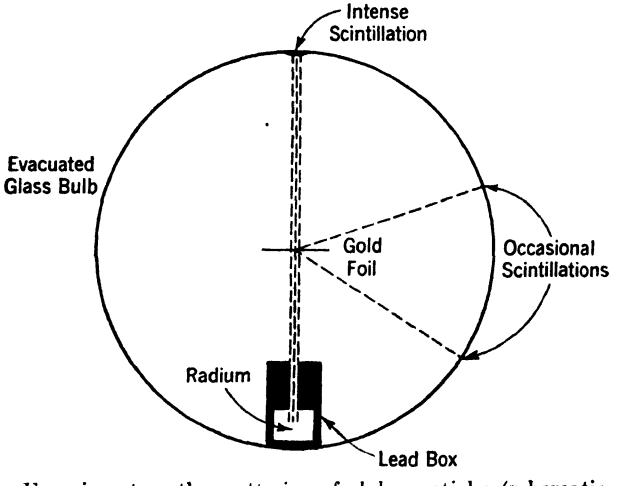


FIG. 14.2. Experiment on the scattering of alpha particles (schematic diagram).

thickness is experimentally proved airtight and hence has no holes. Each gold atom has a diameter (estimated by the methods discussed in Sec. 9.2) of 3×10^{-8} cm. Therefore, the foil toward which we shoot alpha particles contains as many as 2,000 molecules lined up along its thickness. We may compare the gold foil with an array of billiard balls, closely placed on a large table, 2,000 balls thick, and represent the alpha particle by another, much lighter ball which we try to shoot through the thickness of 2,000 balls (Fig. 14.3). We feel safe in predicting that we shall be unable to shoot this lighter ball through the vast array of billiard balls or, by analogy, to shoot the alpha particles through the gold foil.

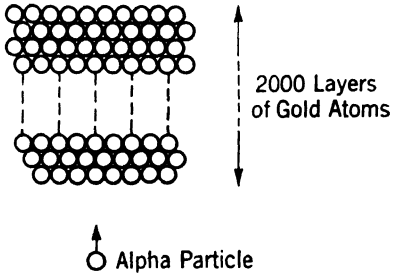


FIG. 14.3. Alpha particle incident on gold foil; atoms pictured as solid balls.

This plausible prediction turned out to be wrong. Rutherford observed that the alpha particles are hardly affected by the gold foil. Most of them still produce scintillations at the same spot as before the foil was placed in the beam. The main effect of the gold foil is to deflect a small percentage of the particles, which now show up by scintillations all over the glass bulb and hence have been deflected through angles of any size, some angles being larger than 90 deg. The deflection is a rare event, but once it occurs it may be strong.

For the explanation of this unexpectedly high transmission of alpha particles, Rutherford introduced a new picture of the structure of atoms. He assumed that the mass of the atom is concentrated in a nucleus which is exceedingly small as compared to the total size of the atom, measured for example by the methods of the kinetic theory. From the experiments of J. J. Thomson (Sec. 8.2) we know already that electrons may be knocked out of an atom and leave it positively ionized. Hence Rutherford assumed that the external structure of the atom consists of electrons. In order to provide a force binding the electrons to the nucleus, he attributed a positive charge to the nucleus. In the neutral atom the nuclear charge has to be as large as the total charge of the surrounding electrons. The Coulomb force binding the electrons and the nucleus together has the same mathematical form as the gravitational force, both being inverse square laws. Hence, to a certain extent, Rutherford's atom is similar to the solar system; the electrons circle around the nucleus just as the planets circle around the sun.

To a limited extent Rutherford's idea of circling electrons was anticipated by Ampère (1823) in a much earlier period when nothing was known of the structure of individual atoms. In order to explain the magnetism of iron, Ampère assumed that each atom contains a small circular current which may be oriented by an external magnetic field.

In applying Rutherford's picture of the atom to the passage of alpha particles through gold foil, we keep in mind the law of elastic collisions derived in mechanics (see Prob. 14.1). The results of this important problem will be applied to several other arguments. There it is proved that a light body hitting a heavy body simply bounces back or is deflected sideways without an appreciable transfer of kinetic energy. Everybody knows that a ball hitting the earth bounces back and changes only its direction, not its kinetic energy. In the opposite case of a heavy body striking a light object, the heavy body continues on its straight path with negligible loss of kinetic energy, while the light object is thrown aside. An example is given by the collision of a heavy truck with a pedestrian, in so far as we are allowed to treat this collision as elastic. After the collision, the truck continues its straight path. In the intermediate case, the elastic collision of two bodies of equal mass, the maximum transfer of kinetic energy takes place as between two billiard balls; in the head-on collision the initially moving body loses all of its kinetic energy to the body first at rest.

On the basis of the theory of the nuclear atom, Rutherford's observation is understandable. As seen from the incoming ray, all the nuclei contained in the thin gold foil by no means appear to fill the whole surface area uniformly, but are only little specks which, like the stars in the sky, are very small as compared to their mutual distances. While most alpha particles shoot straight through the array of nuclei, a few approach close enough to a gold nucleus to be strongly deflected although without trans-

ferring any appreciable kinetic energy, the alpha particle being much lighter than the gold nucleus. More frequently the alpha particles collide with the numerous electrons contained in the gold. Here the alpha particle is much the heavier body and shoots straight ahead, throwing the light electrons away from its path. This prediction of two types of collision processes suffered by alpha particles, rare collisions with nuclei and frequent collisions with electrons, will be strikingly confirmed by observations with the cloud chamber to be described in Sec. 21.2.

In order to explain the free passage of the alpha particle through the spaces between the nuclei, the alpha particle itself must be assumed to be a very small body, presumably a nucleus. This completes our picture of the alpha particle, which we found at first to be a helium atom that had lost 2 electrons. Now, by its penetrating power, we recognize it as an atom stripped of *all* electrons. We draw the conclusion, important for our later discussion of chemistry, that the alpha particle is a helium nucleus carrying two positive electronic charges. This complicated argument will be confirmed by the spectrum emitted from helium ions (Sec. 15.6). We shall explore further the properties of alpha particles in Secs. 20.3 and 21.2.

The effective size of the atom is entirely different in the kinetic theory of gases and in the case discussed here, the passage of alpha particles. In the kinetic theory we are dealing with mutual collisions between atoms or molecules; their electronic structure is responsible for their cross section. The alpha particle, however, is deflected not by electrons but only by nuclei. Here the effective size of a gold atom is represented only by the small space in which the Coulomb field surrounding the nucleus is strong enough to produce a noticeable deflection of the alpha particle.

Considering the great complication of many modern experiments in nuclear physics that require a staff of experts and extra buildings, it is striking how simple the technique is in Rutherford's experiment on the scattering of alpha particles. A radon sample behind a gold foil, a fluorescent screen attached to a microscope that can be rotated in an airtight metal box—these are the essential parts required for an experiment that has led to one of the most important new ideas on atomic structure.

14.2. Charge of the Nucleus. Rutherford and his collaborators developed the qualitative observations just discussed into a measurement of nuclear charges. Suppose we compare two foils, silver and platinum, both with the same number of atoms per square centimeter of the foil. Then the alpha ray suffers *equal numbers of deflections* in both foils, but the nuclei with *larger nuclear charge*, producing larger Coulomb forces, cause *deflection by larger angles*. Thus the number of particles transmitted by a foil expressed as a function of their deflection angles serves to determine the charges on the nuclei. The theoretical treatment, which requires calculus, is given in Appendix 6.

Table 14.1 gives the nuclear charges (in multiples of the electronic charge) measured in this way by Chadwick for three elements. They are compared with the atomic numbers of the elements.

The atomic number of an element, familiar to the chemist, is defined as follows: When writing all elements in the order of their atomic weights, we count the lightest element, hydrogen, as 1, the second lightest, helium, as 2, etc. These numbers are called the "atomic numbers" of the elements. Some minor adjustments of the numbers so defined will be mentioned in the chapter on the Periodic Table of Elements, Sec. 18.3.

Table 14.1. *Atomic Numbers and Nuclear Charges*

(In multiples of the electronic charge)

Element	Atomic No.	Nuclear charge
Copper....	29	29.3 ± 0.5
Silver.....	47	46.3 ± 0.8
Platinum..	78	77.4 ± 0.8

The table shows the striking and simple result that, within the accuracy of the measurement, *the nuclear charge equals the atomic number.* In our discussion of spectroscopy we shall find more evidence confirming this important relation.

14.3. Size of the Nucleus. Beyond the vague result that the nucleus is very small as compared with the size of the atom, the scattering of alpha particles leads to an estimate of the size of the nucleus. In most cases the theoretical picture of point charges mutually repelled by the Coulomb force adequately describes the scattering observed. This picture leads to the simple theory of scattering (Appendix 6). From the kinetic energy of the impinging alpha particle we can compute the distance of the closest possible approach that takes place in a head-on collision (see Prob. 14.2). The good agreement between the theory and the observation proves that the Coulomb law correctly describes the repulsive force down to this distance; hence it gives an upper limit for the size of the nucleus. For uranium this has been determined to 3×10^{-12} cm, for copper 10^{-12} cm.

It has been found, however, that the agreement between the theory and the experiment is good only for heavy elements but that the picture of point charges fails for the bombardment of lighter elements like aluminum by high-energy alpha particles. (Here the theory is refined by taking into account the recoil of the target nucleus.) Alpha particles which, if subjected only to the Coulomb repulsion, would approach the aluminum nucleus to a distance as short as 0.6×10^{-12} cm do not follow the theory outlined and so make it evident that for such close approaches the size of the nucleus makes itself felt. This figure then is an estimate of the size of the aluminum nucleus. When in a model the nucleus is given a diameter of 1 cm, the whole atom has a diameter of about 400 m.

The present chapter gives us the knowledge of the nuclei needed in t next chapters, which are devoted to spectra and the periodic table of el ments. The systematic discussion of nuclei will be given in Part VI.

SUMMARY OF CHAPTER 14

The nature of alpha rays is inferred from the following observation The rays produce short, local scintillations on certain screens indicatin that they consist of individual particles, which are able to penetrate met foils When collected in a small glass tube, they show by their optic spectrum that they are essentially the same as helium. This gives th individual particle a mass of nearly 4 hydrogen atoms. The measuremen of ϵ/μ (combined with this mass) shows that each alpha particle carri the charge of 2 electrons but with the positive sign, in other words, tha it is a doubly charged helium ion.

Rutherford discovered that alpha particles penetrate thin gold foil without an appreciable deflection with the exception of a few particles tha are scattered through large angles. Rutherford explained this observatio by the picture of the nuclear atom. He assumed that the mass of th gold atom is concentrated in a small nucleus carrying a large positive charge which attracts electrons and holds them in stable orbits around the nucleu just as the sun holds the planets in their paths by gravitation. At the same time he assumed that each alpha particle is a very small bullet, presumably itself a nucleus. This last assumption, combined with the above result that the alpha particle carries two positive electronic charges, attributes to the helium nucleus the positive charge 2, giving the neutral helium atom 2 external electrons.

The deflections of alpha particles by films of various metals have been studied quantitatively. In this way the nuclear charges of various atoms have been measured, with the result that the nuclear charge equals the atomic number.

The order of magnitude of the nuclear size is 10^{-12} cm.

PROBLEMS

14.1. *Elastic collisions.* Elastic collisions are of great importance in atomic physics describing, for example, collisions between gaseous atoms or collisions of electrons with atoms or of alpha particles with nuclei or, in the theory of the Compton effect, of X-ray quanta with electrons. In the text we shall repeatedly refer to the results of the present problem (see Prob. 21.6).

Elastic collisions are collisions in which the kinetic energy present before the collision is completely conserved as kinetic energy, and no other kind of energy is produced. This is true, to a good approximation, for collisions between billiard balls. After the collision, the bodies in general proceed in two separate directions, both different from their original directions. We restrict ourselves to the special case of the head-on colli-

sion, *i.e.*, the case in which all motion before and after the collision takes place in the same straight line.

Suppose that the mass m_1 (velocity u_1) collides head on with the mass m_2 which, before the collision, is at rest (velocity $u_2 = 0$). Compute the velocities v_1 and v_2 after the collision on the basis of the laws of conservation of energy and momentum. Write the result for three special cases: (*a*) $m_1 = m_2$, (*b*) m_1 negligible compared with m_2, and (*c*) m_2 negligible as compared with m_1.

HINT: (*a*) Write the principle of conservation of energy stating that before and after the collision the total kinetic energy is the same. (*b*) Write the law of conservation of momentum making the corresponding statement for the linear momentum. Since the momentum of a body may be positive or negative, you must define a direction as positive, *e.g.*, the direction of the velocity u_1. (*c*) Express the unknowns, v_1 and v_2, in terms of the known quantities m_1, m_2, u_1. (*d*) Write this result for the three special cases mentioned above.

COMMENT: The complete transfer of energy resulting for equal masses may be seen in the head-on collision between billiard balls. On the other hand, a light body bounces back from a heavy body as a rubber ball from the earth, or an electron from an atom, or an alpha particle from a gold nucleus. The present problem deals with *elastic* collisions; *inelastic* collisions are treated in the Probs. 17.4 and 22.7.

14.2. *Size of the nucleus.* Suppose that the fastest alpha particles occurring in nature (those emitted from thorium C″, energy 8.8 Mev) are scattered by uranium. Compute the distance of the closest possible approach assuming that the force acting between the alpha particle and the uranium nucleus is given by the Coulomb repulsion.

COMMENT: In Sec. 14.3 observations are discussed that indicate that the radius of the uranium nucleus is smaller than the distance of closest approach for 8.8 Mev alpha particles.

SPECTRUM OF THE HYDROGEN ATOM AND BOHR'S THEORY

Rutherford's theory of the nuclear atom, further developed by Bohr, has led to a detailed explanation of atomic spectra, in particular the spectrum of the hydrogen atom. This is the subject of the present chapter. We shall start from the discussion of the spectrum observed and shall find that the electromagnetic theory of light fails to explain it. Next we shall discuss Bohr's theory of the hydrogen atom and its application to the helium ion. Finally, in order to judge the validity of Bohr's theory, we shall give a brief report of further comparisons between the advanced development of the theory and experiments.

15.1. Spectrum of Hydrogen Atoms. We begin the study of spectra with a brief historical outline of spectroscopy. Newton, in 1666, was the first to analyze white light into its spectral colors by observing the dispersion of sunlight passing through a prism. Later (around 1800) the spectrum was extended on both sides of the visible region into the ranges called "infrared" and "ultraviolet." Fraunhofer (1814) improved the observation of the solar spectrum and found many narrow, black lines on the bright, colored background. Kirchhoff and Bunsen (1859) discovered that any given spectral line defined by its wave length (or frequency) is characteristic of a type of atom; *e.g.*, a prominent pair of yellow lines at 5,890 and 5,896A, emitted from a bunsen burner or electric arc between carbon electrodes, indicates the presence of sodium atoms. Furthermore, they found that certain spectral lines observed in absorption, *i.e.*, as black lines on the background of a white spectrum, exactly coincide in wave length with well-known emission lines. This is true for the yellow pair of lines just mentioned. Hence the absorption lines as well as the emission lines serve for the identification of sodium atoms. This discovery explained the dark lines observed by Fraunhofer in the solar spectrum. Kirchhoff and Bunsen interpreted them as absorption lines produced by the solar atmosphere on the white background emitted from the body of the sun. Since they were able to identify many of the Fraunhofer lines with spectral lines observed at the laboratory, *e.g.*, those of sodium, calcium, and iron, they accomplished the equivalent of a chemical analysis of the solar atmosphere. Since then almost all the lines observed in emission or absorption

in the spectra from the sun and stars have been so identified. This is the basis of astrophysics. The progress that has been made in the study of the cosmos using this discovery would have seemed unthinkable before the time of Kirchhoff and Bunsen.

The analysis of atomic spectra began in 1885 when Balmer represented, by a simple formula, a series of spectral lines observed in an electric discharge through hydrogen. In 1906 Lyman discovered a hydrogen series in the extreme ultraviolet related to the Balmer series. The analysis of spectra, atomic and molecular, has been continued up to the present time.

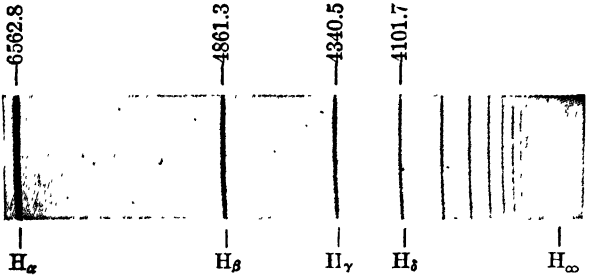


FIG. 15.1. Balmer series of atomic hydrogen emitted by an electric discharge (photographic negative). H_∞ marks the computed position of the series limit. (*Courtesy of G. Herzberg and Dover Publications. Reprinted from G. Herzberg, "Atomic Spectra and Atomic Structure,"* 1927.)

On the basis of Rutherford's discovery of the nuclear atom (1911), Bohr in 1913 introduced his theory explaining the hydrogen spectrum, which was the starting point of a vast development of atomic theory.

When an electric discharge is maintained in hydrogen, a very complicated spectrum is observed. This spectrum is seen to consist of two parts: a well-ordered series of a few brilliant lines superimposed on a mess of very many weaker ones. It is plausible to attribute the few bright lines to hydrogen *atoms* and the many background lines to hydrogen *molecules*, for the atoms, being simpler, might be expected to emit the simpler spectrum. Although ordinary hydrogen gas consists of diatomic molecules, in the electric discharge one may well assume that the current dissociates some molecules into atoms. This idea is confirmed by the fact that with increasing current the few brilliant lines gain in relative intensity, thus indicating increasing dissociation by the current. We are interested only in the lines attributed to hydrogen atoms. The visible part of the atomic spectrum consists of four lines, but a photographic investigation of the near ultraviolet region shows that these four are followed by many more lines, all converging toward a limit (Fig. 15.1). The first line of this series, called H_α, has a wave length in vacuum of 6,562.80A. (Since experiments with gratings or interferometers yield measurements of *wave lengths*, it is

conventional to use wave lengths for the description of experiment results; *frequencies* are more important for the theory.)

This is the series of lines, which Balmer represented by the simple formul

$$\nu = cR\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, \ldots$$

Here ν is the frequency in sec^{-1}; c = velocity of light. (We introduce th factor c in order to represent the spectral lines by their *frequencies* in sec^{-1} without the factor c the formula would give *wave numbers* = reciproca wave lengths in cm^{-1}). For $n = 3$ the formula gives the first line, the conspicuous red line of the series, for $n = 4$ the second line, etc.; finally, as n approaches infinity, the convergence limit $\nu_c = cR$ 4. R is a constant computed so that the formula represents the observed frequencies and is called the "Rydberg constant" after the distinguished Swedish spectroscopist. Its numerical value is

$$R = 109{,}677.76 \pm 0.05 \text{ cm}^{-1}$$

This figure gives evidence of the high accuracy of spectroscopic measurements.

In the extreme ultraviolet Lyman (1906) discovered a similar series with its first line at 1,215.7A. He represented this series by the similar formula

$$\nu = cR\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, \ldots$$

Here the constants c and R have the same significance as before. This series converges at the frequency $\nu_c = cR$. The theoretical significance of the Lyman series which becomes manifest in Bohr's theory justifies its designation as the prototype of all spectral series. Later Paschen found another similar series in the infrared represented by

$$\nu = cR\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \qquad n = 4, 5, 6, \ldots$$

With improved experimental technique more such hydrogen series have been discovered in the infrared, but no other series are found in the ultraviolet at frequencies higher than those of the Lyman series.

All these series are represented by one comprehensive formula

$$\nu_{\text{obs}} = cR\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right) \tag{15.1}$$

The subscript "obs" emphasizes that this formula describes observed frequencies which later will be compared with those resulting from the theory. The formula [Eq. (15.1)] gives the Lyman series when $n'' = 1$ and $n' = 2, 3, 4, \ldots$. Furthermore, it gives the Balmer series for $n'' = 2$ and $n' = 3, 4, 5, \ldots$. Several such series are schematically given by Fig. 15.2. Although our experimental knowledge of the infrared is limited, we infer

that there are infinitely many such series, described by the same formula with larger integers n''. We shall call this the "Balmer formula."

In applying this formula, it is easy to change from the Lyman series to the Balmer series, *e.g.*, by exchanging $n'' = 1$ for $n'' = 2$. But the formula fails to say how difficult it is for the experimental physicist to observe the various series. The Balmer series is the one most easily found. Its visible

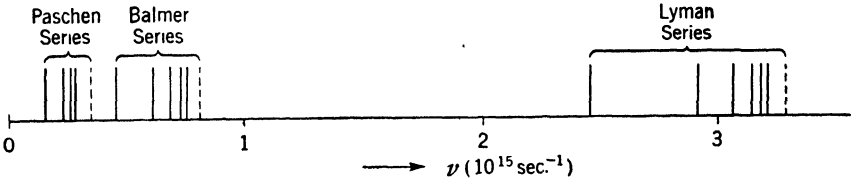


FIG. 15.2. First three series of atomic hydrogen. Broken lines indicate series limits. More infrared series appear at frequencies lower than those of the Paschen series.

lines may be seen with any spectroscope, and the higher lines in the beginning ultraviolet are photographed with a quartz spectrograph.

The Lyman series, however, does not show up in the quartz spectrograph, in spite of the fact that quartz transmits ultraviolet light down to 2,000A, a much shorter wave length than the transmission limit of glass. Beyond this range three difficulties are encountered concurrently: (1) The quartz becomes opaque and must be replaced by one of the rare crystals like fluorite which transmits light of still shorter wave lengths. (2) Ordi-

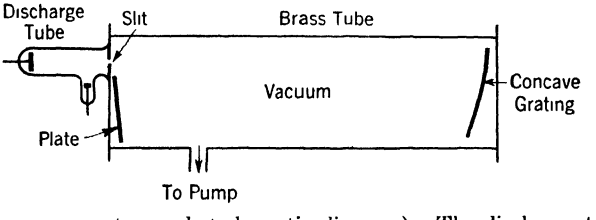


FIG. 15.3. Vacuum spectrograph (schematic diagram). The discharge tube is sealed to the wall of the spectrograph in front of the slit.

nary photographic plates fail to respond, because the gelatine absorbs the light so strongly that it does not penetrate into the emulsion; special photographic plates must be prepared. (3) Since the air becomes opaque, the whole apparatus must be evacuated. Great progress has been made with fluorite vacuum spectrographs, but they fail to record the Lyman series because even fluorite crystals are opaque at the extremely short wave length range of this series. For the range beyond that of fluorite, Lyman used a concave grating since this does not require any transparent substance and relies solely on the reflecting power of the metal on which the grating is ruled. In the extreme ultraviolet, this power, although weak, is still high enough. This explains the construction of Lyman's spectrograph (Fig. 15.3). A highly evacuated wide brass tube contains the grat-

ing, the plate of special type, and the slit; the electric discharge tube with hydrogen is cemented on in front of the slit.

Other difficulties are encountered in the investigation of the infrared spectrum. There a glass prism is opaque and must be replaced by a rock-salt prism or a grating. Photographic plates fail completely for reasons discussed in the chapter on photochemistry (Chap. 12). Instead, a bolometer or thermocouple records the incident radiation.

15.2. Failure of Electromagnetic Theory of Radiation. The electromagnetic theory of radiation (Sec. 11.2), based on the work of Maxwell and Hertz, has been so eminently successful that we must try to apply it to the spectrum just described. In this theory the atom is supposed to be similar to the antenna of a radio transmitter, although much smaller, of course, and radiating a much higher frequency. At first glance such a transmitter seems to emit light with some of the properties of the spectrum described. A transmitting antenna made of a straight piece of wire has a fundamental frequency of vibration and a series of harmonics of higher frequency, much like the characteristic frequencies of a violin string. But this series cannot be compared quantitatively to the series spectrum of hydrogen because the higher antenna harmonics are multiples of the fundamental frequency ν; *i.e.*, their frequencies are 2ν, 3ν, 4ν, etc. Hence this series predicted by the electromagnetic theory fails to show the finite convergence limit characteristic of the hydrogen spectrum observed. Furthermore, the transmitter fails to show more than one such series, while the hydrogen atom exhibits many.

We may try to modify our theory by discarding the straight-wire picture and replacing it by Rutherford's nuclear atom, which, in the simplest case, would be 1 electron revolving about the nucleus. But here the electromagnetic theory leads to another difficulty. From the laws of planetary motion we know that the electron may revolve about the nucleus in circular or elliptic orbits. Suppose that energy is given to this system, *e.g.*, in the discharge tube by the impact of a *free* electron, so that the *revolving* electron is thrown into a distant orbit, which we assume as circular for the sake of convenience. If the electron would stay there, it would have a well-defined frequency of revolution. But the electromagnetic theory tells us that the electron would perform differently from a planet. While the planet, as a *neutral* body, continues indefinitely on the same orbit, the electron, being a *charged* body, loses energy continuously by radiation at a rate predicted by the theory. This energy is radiated at the expense of the energy stored in the revolving motion. Thus the electron must gradually spiral in toward the nucleus and thereby increase its frequency of revolution. (The relation between the radius and the frequency of revolution is easily computed on the basis of elementary mechanics.) Since this process would go on continually, the spectrum would not consist of sharp lines but would be

continuous. This prediction based on the electromagnetic theory contradicts the observed facts and makes the failure of this theory when applied to sharp spectral lines evident.

15.3. Review of Gravitational Motion. In Bohr's theory we shall study the simplest aspect of Rutherford's nuclear atom, the case of only 1 electron circling about a nucleus. In the present section we shall review some formulas of elementary mechanics that are applied in Bohr's theory. Since the Coulomb force keeping the electron to the nucleus has the same mathematical form as the law of gravitation, we take over the results of the theory of planetary motion, for simplicity restricting ourselves to circular orbits. In order to make the calculation applicable to more highly charged nuclei, we write the nuclear charge as Ze where Z = atomic number (see Sec. 14.2).

Notation and Units:

μ = mass of electron, g
ϵ = absolute value of the charge on electron, esu
Ze = absolute value of the charge on nucleus, esu
r = radius of circular orbit, cm
v = linear velocity, cm sec
ω = angular velocity, sec^{-1}
$v = r\omega$

We define the *moment of inertia* of the revolving mass μ as $I = \mu r^2$ (unit: g cm^2). Furthermore, we define its *angular* momentum as $I\omega = \mu r^2\omega = \mu vr$ (unit: g cm^2 sec^{-1}).

The force of attraction is given by the Coulomb force: force $= Ze^2/r^2$. Here it is supposed that ϵ is expressed in electrostatic units. (If we should use electromagnetic units, Coulomb's law would contain the factor c^2.) In circular motion a centripetal acceleration $= v^2/r$ occurs all the time. Hence this motion requires for its maintenance a centripetal force $= \mu v^2/r$. When we whirl a stone around on a string, this force is given by the tension of the string. In our case, this force is supplied by the Coulomb force. Therefore, the condition for the circular motion is

$$\frac{Ze^2}{r^2} = \frac{\mu v^2}{r} \qquad \text{or} \qquad \frac{Ze^2}{r} = \mu v^2 \tag{15.2}$$

As ϵ, Z, and μ are constants, this is an equation between two variables, r and v. The two variables have values covering a *continuous range* with the restriction that for any value of r the equation prescribes the corresponding value of v.

Next we compute the total energy W, composed of kinetic energy W_k and potential energy W_p. The kinetic energy W_k is easily expressed as $W_k = \mu v^2/2 = Ze^2/2r$. Finding the expression for the potential energy W_p is more difficult. The potential energy, or energy of position, of the elec-

tron with respect to the nucleus depends only on the relative distance r. We are interested only in the difference between the potential energies of two positions. This difference is *defined* as the work required to lift the electron against the Coulomb attraction from the smaller radius r_1 to the larger radius r_2. It is easily computed if we restrict ourselves to a change of radius $\Delta r = r_2 - r_1$ very small as compared to each of these radii. Then the Coulomb force $Z\epsilon^2/r^2$ may be treated as constant or, still better, may be expressed by writing the geometrical mean of the radii r_1 and r_2, *i.e.*, by replacing r^2 by $r_1 \times r_2$. So we obtain

$$\Delta W_p = \frac{Z\epsilon^2}{r_1 r_2}(r_2 - r_1) = Z\epsilon^2\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

When computing ΔW_p over a larger distance, we subdivide this distance into many small steps, apply the approximate formula to each step, and compute the total energy ΔW_p as the sum of these small contributions. Since all these intermediate values of $1/r$ cancel out, our final result

$$\Delta W_p = Z\epsilon^2\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{15.3}$$

is the same as derived above for each small step. (For students familiar with calculus the computation is given as Prob. 15.1.) The energy ΔW_p is positive if $r_2 > r_1$.

Although we are interested only in differences of potential energies, it will be convenient to define an arbitrary zero point of potential energy in order to simplify our expressions. For example, as zero point we might define the potential energy at 1 cm or 10^{-9} cm distance from the nucleus (not at zero distance because that would lead to infinitely large energies). The mathematical expression for W_p will be a little simpler when as a zero point we select the *infinitely large* distance, $r_1 = \infty$. Equation (15.3) shows that in this case the energy difference computed is still finite: $\Delta W_p = -Z\epsilon^2/r_2$. The negative sign indicates that energy will be *released* when moving the electron from $r_1 = \infty$ to $r_2 =$ finite. (Our definition of the zero point amounts to the same as if we should measure the gravitational potential energy within a laboratory room by defining $W_p = 0$ at the ceiling.) For any definition of the zero point the essential property of the potential energy, its *increase* with *increasing* radius, is preserved. A potential energy of -1 unit is *higher* than that of -100 units. Now we may drop the subscript 2 because we got rid of r_1

$$W_p = -\frac{Z\epsilon^2}{r}$$

The total energy of the revolving electron becomes

$$W = W_k + W_p = \frac{Z\epsilon^2}{2r} - \frac{Z\epsilon^2}{r} = -\frac{Z\epsilon^2}{2r} \tag{15.4}$$

Here again the negative sign has no physical significance since it is based on the arbitrary definition of the zero point of W_p.

15.4. Bohr's Theory. The hydrogen atom was the object of the first theoretical attack, because as the lightest of all atoms it is assumed to have the simplest structure. This is confirmed by the fact that its spectrum, described above, is by far the simplest of all atomic spectra ever observed. Bohr's *starting point* was Rutherford's theory of the nuclear atom, Planck's quantum theory ascribing to each vibrating atom a quantized energy content $nh\nu$ (see Sec. 11.3), and Einstein's theory attributing energy quanta $h\nu$ to light of the frequency ν. Bohr's *aim* was to establish a theory from which he could derive the observed hydrogen spectrum as given by the Balmer formula

$$\nu_{\text{obs}} = cR\left(\frac{1}{n'^2} - \frac{1}{n''^2}\right) \tag{15.1}$$

As the simplest atom contains presumably only 1 revolving electron, its nucleus has a positive charge of the same value. This charge is experimentally confirmed by positive ray analysis (Sec. 8.3) in which a great abundance of *singly* charged hydrogen atomic ions H^+, but no *doubly* charged ions H^{++} are observed. In the preceding section we found that, for a revolving electron, the electromagnetic theory would predict a continuous spectrum, in contrast to the sharp-line spectrum actually observed. Bohr's first, far-reaching hypothesis states that the electromagnetic theory has to be discarded in the description of the radiation from atoms. It is true that the electromagnetic theory is thoroughly confirmed by experiments in the macroscopic realm of physics, in particular for the radiation from antennas. But this success does not force us to assume that the same theory will apply to processes in individual atoms, for atoms are so very much smaller than any of our laboratory tools that conditions are entirely different.

This is a general consideration that had been applied before in other fields of physics. For example, Newton's mechanics had been confirmed by laboratory experiments and astronomical observations to such an extent that it was thought to represent an absolute truth. Now we know that it is only an approximation which fails for velocities comparable to that of light. Therefore, it is not unusual that an apparently well-established law of physics is changed under conditions that are vastly different from those under which the law originally had been discovered.

This repudiation of the electromagnetic theory gave Bohr a wide field for new hypotheses to describe the radiation from the electron revolving about the nucleus. We shall first discuss Bohr's general idea and next the mathematical development.

Einstein's quantum theory of light suggests the hypothesis that an atom,

when emitting light of the frequency ν, loses by radiation the energy $h\nu$ by going down from a state endowed with high energy W' to another with lower energy W''. Under this assumption the sharp spectral lines observed indicate that the atom can exist only in states of sharply defined energy content and emits a quantum $h\nu$ when going from an upper to a lower energy level.

How are these sharply defined energy levels to be predicted? Planck's hypothesis, which was mentioned in the historical survey, fails to lead to the desired result. It only suggests the guess that Planck's constant h somehow determines the energy levels. A more specific suggestion is given by noticing that the dimensions of Planck's constant are the same as the dimensions of an angular momentum. Hence Bohr may have guessed that the quantized orbits are defined by the condition that the angular momentum of the revolving electron is proportional to a multiple of Planck's constant h. Bohr found that the desired result is actually reached when the following quantum condition is introduced: The revolving electron exists only in "quantized" energy levels defined by the condition that the angular momentum $= nh/2\pi$. The factor $1/2\pi$ is solely justified by the success of the theory.

This factor has no profound significance because, instead of Planck's constant h, one may as well define a fundamental constant of the value $h/2\pi$; then the factor $1/2\pi$ would disappear in our hypothesis, although the factor 2π would show up somewhere else.

No claim is made that the reasoning just presented constitutes a convincing argument that these assumptions are the best ones and will lead to the correct answer. The reasoning only serves to indicate a way that may lead to the fundamental hypothesis. Its validity is tested only by the comparison of the resulting *theoretically derived* spectrum with the *observed* spectrum given by the Balmer formula. We restrict the treatment to circular orbits. The results of the more elaborate theory of elliptic orbits will be briefly reported in Sec. 15.7.

a. Orbits Given by Classical Physics. As discussed in the review of gravitational motion, classical physics supplies the condition: centripetal force = Coulomb force, or

$$\mu v^2 r = Z\epsilon^2$$

b. Quantized Orbits. From the continuum of orbits given by this equation, the quantum condition (angular momentum $= nh/2\pi$) selects certain sharply defined orbits

$$\mu v r = \frac{nh}{2\pi} \qquad n = 1, 2, 3, \ldots \tag{15.5}$$

For any quantum number n the orbit is defined, because now we have two equations with the two unknowns r and v. These are easily evaluated in terms of n, and the constants ϵ, Z, μ, and h as follows:

$$r = n^2 \frac{h^2}{4\pi^2 \mu Z \epsilon^2} \tag{15.6}$$

and

$$v = \frac{1}{n} \frac{2\pi Z \epsilon^2}{h} \tag{15.7}$$

Furthermore the total energy W of the electron with respect to the nucleus is

$$W = -\frac{Z\epsilon^2}{2r} = -\frac{1}{n^2} \frac{2\pi^2 \mu Z^2 \epsilon^4}{h^2} \tag{15.8}$$

We shall distinguish W' and n' for the upper level from W'' and n'' for the lower level by the single and double primes.

c. Spectrum Theoretically Derived. The frequencies of the spectral lines are theoretically derived by Einstein's equation $h\nu_{\text{th}} = W' - W''$, or

$$\nu_{\text{th}} = \frac{W' - W''}{h} = \frac{2\pi^2 \mu Z^2 \epsilon^4}{h^3} \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right) \tag{15.9}$$

d. Comparison with the Observation. We are satisfied that this equation for ν_{th} has the same mathematical form as Balmer's equation for ν_{obs} [Eq. (15.1)], since the quotient in front of the bracket contains only constants. But beyond this general resemblance between the two equations, Bohr is able to predict the numerical value of the factor cR which is found experimentally in the Balmer formula. For the hydrogen atom Bohr assumes a nuclear charge of the same absolute value as the electronic charge ϵ. The numerical value for ϵ is taken from the oil-drop experiment, that for ϵ/μ from the cathode-ray experiment, and that for h from the photoelectric effect. In this way Bohr derives the numerical value of the factor

$$\frac{2\pi^2 \mu Z^2 \epsilon^4}{h^3} = 3 \times 10^{10} \times 109{,}700 \text{ sec}^{-1}$$

This is compared with the factor of the Balmer formula

$$cR = 3 \times 10^{10} \times 109{,}677 \text{ sec}^{-1}$$

The quantitative agreement is as good as the limited accuracy of the experiments permits. Since, at present, the fundamental constants ϵ, ϵ/μ, and h are known with only four significant figures, the factor can be theoretically predicted only within this limit. This is the first outstanding success of the theory.

In spite of this great success, the student is not urged to accept Bohr's theory right away, as it certainly was not generally accepted at the time of its discovery in 1913. One may judge that the success is heavily paid for by discarding classical physics and replacing it by arbitrary assumptions; hence there is no mathematical way of saying whether these assumptions are necessary or may be replaced by something different. In order

to arrive at a judgment of Bohr's theory, through all the following arguments we must keep in mind these questions: How do more detailed observations compare with the conclusions of Bohr's theory? How great is the fertility of Bohr's theory in stimulating new experiments?

When studying the foundation of Bohr's theory, the student may be disappointed by the fact that the fundamental hypothesis is by no means a revelation that immediately impresses him as a new truth. This difficulty is inherent in the quantum theory. Our feeling for processes in nature is based on daily experience well described by classical physics, as contrasted with quantum theory. But we must not approach processes in atoms with the naïve expectation that we may feel what is bound to happen. Here our only criterion for the validity of the theory is the comparison of the theoretical prediction with the observed facts.

Bohr's theory is an example of the method of research in theoretical physics. Here the theoretical physicist has at hand experimental facts (such as the Balmer formula) which are unexplained by any known theory. He attempts to construct a new theory that will give the desired empirical result by trying out various hypotheses. The theory is then checked by investigating experimentally the predictions of the theory which result from the new hypotheses. The theory is then substantiated until a new more refined experiment once more reveals a discrepancy, requiring an alteration of the theory. This process is still going on in modern quantum mechanics.

15.5. Conclusions. *a. Numerical Values of r and v.* The radius r of the orbit has its smallest value for $n = 1$. The state of the atom so described is called the "normal" state. This implies that all atoms are in this state unless they are brought to an *excited state* ($n > 1$), *e.g.*, in the electric discharge by the impact of free electrons. After a short lifetime the excited atoms emit radiation. For the normal state ($n = 1$) we compute the radius r from Eq. (15.6) and find $r_1 = 0.53 \times 10^{-8}$ cm. Here Bohr's theory, although primarily designed to give account of the spectrum, unexpectedly predicts the diameter of the atom. The prediction is in satisfactory agreement with other evidence (Sec. 6.1) although the usual measurements are obviously concerned with hydrogen molecules instead of atoms.

Why does the electron revolving in the "normal" orbit just computed not fall into the nucleus to which it is attracted by the Coulomb force? All we can say is that normal atoms are observed to have a diameter of the order of magnitude 10^{-8} cm. Therefore, we select $n = 1$ as the smallest quantum number, excluding $n = 0$. We admit that this does not answer the question. All we can do is adjust the quantum hypothesis so that it fits the observed facts.

We computed the orbits as given by classical physics on the basis of the centripetal force expressed in terms of Newtonian mechanics. Are we right

in disregarding the relativity correction? This is not obvious, for the ability of electrons to attain velocities comparable to the velocity of light has been found in cathode-ray investigations. In order to judge our approximation, we must compute the linear velocities of the revolving electrons from Eq. (15.7). The highest velocity, occurring for $n = 1$, is computed in terms of the velocity of light c as $v_1/c = 7.29 \times 10^{-3}$. This leads to an exceedingly small relativity correction. [On the basis of Eq. (8.14), which we did not derive, at this velocity the mass μ is expressed in terms of the "rest mass" μ_0 as $\mu = \mu_0 \times 1.000027$.] However, observations made with powerful spectrographs are so exceedingly accurate that a small relativity effect has been observed. This will be reported later in Sec. 15.7.

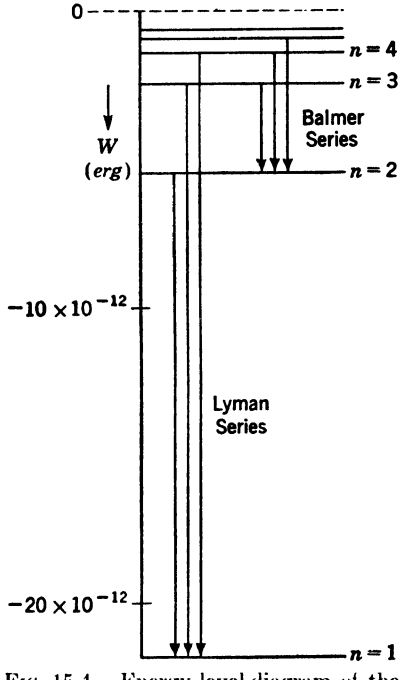


FIG. 15.4. Energy-level diagram of the hydrogen atom. The energy of the level $n = \infty$ is arbitrarily counted as zero. The vertical arrows indicate the first three lines of the Lyman series and those of the Balmer series.

b. Energy-level Diagram. The energies of the various quantized orbits are computed as

$$W = -\frac{1}{n^2}\frac{2\pi^2\mu Z^2\epsilon^4}{h^2}$$

and plotted in Fig. 15.4. The negative energies given by the equation are plotted downward starting from $W = 0$. This "energy-level diagram" well represents the theoretical idea that the electron may be lifted upward from the lowest level, the normal state, to the higher levels, the excited states, from which it spontaneously falls down emitting light. A spectral line is attributed not to the individual level but to a difference between any two levels, the upper level being the *initial* level of the emission process, the lower level the *final* level.

Since the frequency of each spectral line is given by $\nu_{th} = (W' - W'')/h$, it is proportional to the distance between two energy levels. The *Lyman* series, characterized by the quantum number of the lower level $n'' = 1$, is represented by all transitions (indicated by arrows) ending at the normal state of the atom. The convergence limit of this series is the highest frequency that can be emitted by a transition between any two quantized hydrogen levels. The *Balmer* series, characterized by $n'' = 2$, is due to all transitions ending at $n'' = 2$; its very conspicuous red line, which gives the

red color to the electric discharge through hydrogen, is given by the transition from $n' = 3$ to $n'' = 2$. The transitions between the higher levels, from $n'' = 3$ upward, are responsible for the various infrared series.

There is one question that the Bohr theory fails to answer. Suppose the hydrogen atom is excited to the level $n = 3$. Then it has two alternative ways of going down and emitting light. Either it goes down directly to the normal level, $n = 1$, and so emits the second line of the Lyman series, or it goes down in two steps, first to $n = 2$, emitting the first line of the Balmer series, next to $n = 1$, emitting the first line of the Lyman series. Bohr's theory fails to predict the relative probabilities of these two processes, which would determine the relative intensities of the various lines originating from $n = 3$. For the higher levels of the atom there are many more different ways, more or less direct, for "cascading down" to the normal level. It is a limitation of the theory that only *frequencies*, not *intensities*, of spectral lines can be derived. This deficiency is remedied by wave mechanics (Chap. 26) which predicts intensities as well as frequencies.

The energy-level diagram effectively simplifies the description of the spectrum. Originally (Sec. 15.1) we described each series as an aggregate of infinitely many lines, and the whole spectrum as containing infinitely many such series. The same situation is much more simply described by the energy-level diagram which consists of only one aggregate of infinitely many levels from which all lines of all series are to be derived.

c. Energies of Excitation and Ionization. The energy-level diagram directly represents two important quantities characteristic of the atom, which will be discussed later in more detail: the *energies of excitation* and *ionization*. From the diagram we infer that the excitation of the hydrogen atom requires as a minimum the energy needed to lift the atom from the *normal* state $n = 1$ to the *lowest excited* state $n = 2$. This energy difference, called the "excitation energy," is computed from Bohr's theory as $W_2 - W_1 = 16.31 \times 10^{-12}$ erg $= 10.19$ ev. It may equally well be computed from the frequency of the first line of the Lyman series.

The other energy difference of outstanding importance is the one between the normal state ($n = 1$) and the convergence limit ($n = \infty$). For $n = \infty$, the revolving electron is lifted to an infinitely distant orbit which is another way of saying that it is separated from the nucleus. Therefore, the energy difference described is the ionization energy of the atom. It is computed from the theory (or from the convergence limit of the Lyman series) as $W_\infty - W_1 = 21.76 \times 10^{-12}$ erg $= 13.58$ ev. Later we shall discuss another method, independent of the spectrum and Bohr's theory, for the measurement of these two characteristic energies (Sec. 17.1).

d. Combination Rule. It has been known for a long time that many combinations exist between the observed frequencies of the various lines

emitted from the same atom. When we write the frequency of the first line of the Lyman series as L_1 and other frequencies of the Lyman series and Balmer series correspondingly, the empirical relation holds

$$L_1 + B_1 = L_2$$

This relation, called the "combination rule," and numerous similar ones follow directly from the energy-level diagram. Notice that you can add frequencies, or quantities directly proportional to frequencies (like energies or wave numbers), but it makes no sense to add wave lengths, because the justification of the combination rule lies in the energy-level diagram.

c. Bohr Magneton. According to Bohr's theory, each hydrogen atom represents a circular current, hence is equivalent to a small magnet. For any quantized orbit, the magnetic moment M is computed from the relation given by electrodynamics

$$M = \text{area of orbit} \times \text{current}$$

The current equals the charge on the circling electron $\times$ number of circles described per second. On the basis of Bohr's theory the result is easily obtained:

$$M = \frac{\epsilon}{\mu} \frac{nh}{4\pi c}$$

where ϵ = charge on the electron in esu. Hence all orbital magnetic moments are multiples of a fundamental magnetic moment

$$\frac{\epsilon}{\mu} \frac{h}{4\pi c} = 9.27 \times 10^{-21} \text{ erg/oersted.}$$

This result is of importance in the theory of magnetism, since other atoms and molecules have magnetic moments that can be expressed as multiples of the same value. This value of the magnetic moment is called a "Bohr magneton." Although the electron is one of the *fundamental* entities of physics, *i.e.*, not to be predicted on the basis of other data, our argument shows that the magneton is a *derived* constant.

15.6. Application to the Helium Ion. *a. Approximate Treatment.* The first success of Bohr's theory beyond the interpretation of the hydrogen spectrum was the application of the theory to the helium ion. Helium gas ordinarily emits a much more complicated spectrum than that of hydrogen atoms. However, under very violent conditions in an electric discharge, an additional spectrum appears with a simple structure closely resembling the hydrogen spectrum. The unusual conditions required for its excitation make it plausible to attribute this spectrum to *ionized* helium atoms He^+, while the complicated more easily excited spectrum is attributed to *neutral* helium atoms.

In the visible range the new helium ion spectrum shows a series described by the formula

$$\nu_{\text{obs}} = 4cR\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \qquad n = 5, 6, 7, \ldots$$

Here c = velocity of light as before and R is a constant very nearly identical with the Rydberg constant which enters into the Balmer formula for the hydrogen spectrum. For the time being we shall consider the two constants as identical and postpone the discussion of the slight difference between them. The last formula describes a helium series of which every second line (for $n = 6, 8, 10, \ldots$) coincides with a line of the Balmer series; but the helium series has additional lines (for $n = 5, 7, 9, \ldots$), one of them

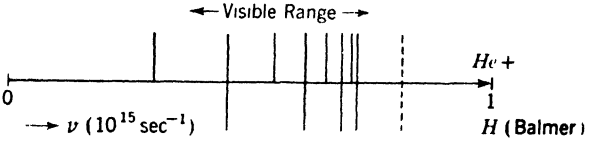


FIG. 15.5 Balmer series of hydrogen ($n'' = 2$) compared with series of ionized helium ($n'' = 4$). The small frequency difference between corresponding lines is not noticeable on the scale of the figure

between any two successive lines of the Balmer series (Fig. 15.5). In the ultraviolet and infrared, the helium ion has still other series described by similar formulas. All of them are given by the following comprehensive formula, which differs from the Balmer formula by only the factor 4:

$$\nu_{\text{obs}} = 4cR\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$$

What prediction does Bohr's theory make regarding this spectrum? On the basis of an elaborate argument based on the investigation of alpha particles (their nuclear charge, specific charge, and scattering, Sec. 14.1) we attributed the nuclear charge + 2 to helium thus giving 2 external electrons to the neutral helium atom. This leaves only 1 external electron in the singly charged helium ion He^+, which we have assumed to be the carrier of the spectrum just described. As the presence of only 1 revolving electron is one of the essential assumptions of Bohr's theory, we should be able to predict the spectrum of the He^+ ion as well as that of the neutral H atom. Bohr's final equation contains the factor Z^2 (Z = atomic number). Hence for He^+ it predicts the factor 4 while the formula for the hydrogen spectrum carries only the factor 1. This prediction agrees with the observed fact and thus strengthens our confidence in Bohr's theory.

This success of Bohr's theory extends farther than just to the spectrum of He^+. It has been found that the third element of the periodic table, lithium, when under violent excitation (by a spark discharge at low pressure and high voltage), emits a spectrum described by the formula

$\nu_{obs} = 9cR(1/n''^2 - 1/n'^2)$, differing from the spectra treated above by the factor 9. Correspondingly, this spectrum is explained as emitted from a lithium atom that has lost all external electrons but one. The factor 9 requires the additional assumption that the lithium nucleus has the charge 3. Next for beryllium, the fourth element in the period table, an analogous spectrum has been observed differing only by the factor 16. Again the same idea applies with the additional special assumption that beryllium has the nuclear charge 4. The corresponding observations have been carried out for the next heavier elements in the periodic table up to oxygen. Thus the nuclear charges are experimentally determined for the next elements, namely, boron, carbon, nitrogen, and oxygen, as 5, 6, 7, and 8, respectively.

We are interested in finding cross checks connecting one line of argument with another. The quantitative treatment of the scattering of alpha particles led to the rule: atomic number = nuclear charge (Sec. 14.2). This relation has been well established in particular for the heavier elements. Here, by a completely independent line of reasoning, based on Bohr's interpretation of the simplest spectra, we find the same rule confirmed for the eight lightest elements.

b. Relative Motion of the Nucleus. We mentioned the observed fact that the numerical values of the Rydberg constant R describing the spectra of He^+ and H, respectively, are nearly but not completely identical. The two constants, computed from the observed spectra, are found to be $R_H = 109{,}677.8\ cm^{-1}$ and $R_{He} = 109{,}722.4\ cm^{-1}$.

Does the theory predict such a difference? The answer was given by Bohr, who pointed out that his original theory contained an approximation. He had assumed that the electron circles about the nucleus as a planet about the sun. As a matter of fact, the planet and the sun both circle about their common center of gravity. The error introduced by the approximation is small because the mass of the sun (or nucleus) is very much larger than the mass of the planet (or electron), so the center of mass is very nearly coincident with the position of the larger body. Bohr applied the same refinement of the theory to the motion of electron and nucleus. The details of this computation, which strictly follows Bohr's original theory, are relegated to a problem (Prob. 15.4). The result is

$$\nu_{th} = \frac{2\pi^2 \mu M Z^2 \epsilon^4}{h^3(\mu + M)} \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right)$$

This formula contains the "reduced mass" $\mu M/(\mu + M)$ instead of the electronic mass μ appearing in the approximate formula. [Notice that for very large values of M this formula becomes identical with the simpler old formula, Eq. (15.9).] The theoretical result quantitatively agrees with the experimental values of R.

The effect of the relative motion of the nucleus is noticeable in the spectrum of heavy hydrogen, called "deuterium." This is a rare form of hydrogen, which has the same nuclear charge as ordinary hydrogen but twice as heavy a nucleus. For deuterium Bohr's theory predicts all the same spectral lines as for ordinary hydrogen, except that all of them should be slightly shifted because the relative motion of the heavier nucleus is less noticeable. The wave-length shifts so predicted agree quantitatively with the observed spectrum. As a matter of fact, the predicted spectrum played a decisive part in Urey's discovery of heavy hydrogen (see Sec. 20.5).

This theory of the spectrum of He^+ constituted an amazing success of the Bohr theory. First, it predicted the approximate position of all He^+ series, interlocking with the hydrogen series, by the idea that the nuclear charge of helium is twice that of hydrogen. Next, it even predicted the value of the small difference between adjacent lines of He^+ and H by the relative motion of the nuclei. Finally it predicted the spectra of highly ionized lithium and heavier elements and led to the discovery of heavy hydrogen.

15.7. Report on Further Developments. We have witnessed two great successes of Bohr's theory, the theoretical derivation of the spectra of hydrogen atoms and those of the next heavier ions. It seems hardly possible that this agreement between observation and theoretical derivation is only accidental and that the processes in these atoms and ions are inconsistent with Bohr's hypothesis. In order to arrive at a more thorough valuation of Bohr's theory, we shall give a report on the further comparison of experiment and theory. Since we shall deal with a development requiring a more advanced mathematical treatment, we shall report only results and omit the derivations.

Considering the great importance of Bohr's theory, Paschen measured the spectra of hydrogen atoms and helium ions with the highest precision, applying a large concave grating spectrograph. His results were perplexing. He found that all lines, originally described as single, when photographed with high resolution show more or less elaborate fine structures. For example, all "lines" of the Balmer series are doublets; that means, each one of them consists of two lines very close together with nearly the same frequency difference between the components of each doublet. Much more complicated structures are seen upon close examination of all "lines" of ionized helium.

Sommerfeld succeeded in adapting Bohr's theory to this very complex observation. While our outline of Bohr's theory simplifies the problem by considering *circular* orbits, Bohr, in his first paper, had already considered the more general case of *elliptic* orbits. They lead to exactly the same spectral lines as the circular orbits. However, Sommerfeld success-

fully generalized Bohr's quantum condition and took into account the theory of relativity. We have estimated (Sec. 15.5*a*) that the linear velocities of the electrons are so small, smaller than one-hundredth of the velocity of light, that this correction amounts to very little. But the "fine structure" splitting of the spectral lines into components is just such a small effect. On this basis Sommerfeld was able to predict the fine structure described, *i.e.*, the doublet structure of all Balmer lines of hydrogen and the very elaborate structures, different for each "line," of ionized helium. It is true that many of the components predicted by the theory are so close together that they cannot be resolved even by the most powerful spectrographs (Fig. 15.6). Furthermore, this theory predicts only the *frequencies*,

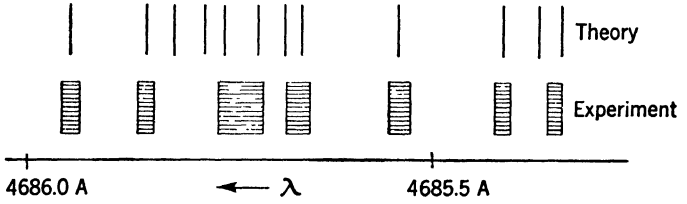


FIG. 15.6. Fine structure of the line 4,686A of He^+, comparing theory and experiment. Intensities are not represented. The structure covers only about 0.8A.

not the *intensities*, of the various components. But within these limitations the very complex material supplied by experiments turned out to be theoretically predictable. This success confirms our belief in the Bohr and Sommerfeld theories of spectra. However, a small deviation between the modern, greatly refined theory and the observations must be mentioned. The red hydrogen line consists of components that are slightly closer together than predicted. This discrepancy has recently been confirmed by experiments applying the modern microwave technique. This result may lead to a revision of the fundamental assumptions (Lamb and Retherford, 1947).

The next successes of Bohr's theory are connected with the effects of magnetic and electric fields on spectral lines. When the source of light is placed into a strong *magnetic* field, all spectral lines of hydrogen split up into three components with mutual distances proportional to the magnetic field. (Here we disregard the fine structure just discussed.) This is called the "Zeeman effect" after the discoverer. Again, this effect has been derived from Bohr's theory as generalized by Sommerfeld. But we do not dare list this success as a criterion confirming the *quantum* theory of radiation as against the classical *electromagnetic* theory, because, strangely enough, this effect has been quantitatively derived from the old electromagnetic theory by H. A. Lorentz. The situation is different in the case of the *electric* field. This, too, causes a splitting up of all spectral lines of hydrogen but in much more complicated patterns, each original

line having its characteristic pattern. This is called the "Stark effect." From the quantum theory of Bohr and Sommerfeld all these elaborate Stark patterns have been derived, while the classical electromagnetic theory completely fails.

We summarize the successes of Bohr's theory and Sommerfeld's generalization by listing the observations that are predicted by the theory:

The line spectrum of hydrogen atoms

The diameter of the hydrogen atom

The line spectra of helium ions and certain ions of the next heavier elements

The small wave-length shift explained by the relative motion of the nucleus and the center of mass

The fine structure of all lines explained by the elliptic orbit treated with the relativity correction

The Zeeman effect

The Stark effect

One cannot doubt that the theory represents a great step forward toward the truth. But it has been recognized that its validity is limited. It fails to predict the spectra of atoms with more than 1 electron, like the neutral helium atom. Here the application of Bohr's theory has not led to an agreement with the experiments.

SUMMARY OF CHAPTER 15

The spectrum emitted from atomic hydrogen is described by the Balmer formula $\nu_{\text{obs}} = cR(1/n''^2 - 1/n'^2)$ where c = velocity of light, R an empirical constant, $n'' = 1$ for the Lyman series, 2 for the Balmer series, etc., and n' an integer larger than n''.

This spectrum is theoretically derived by Bohr on the basis of the following hypotheses: The hydrogen atom consists of a stationary nucleus carrying a positive electronic charge and only 1 revolving electron. From classical physics the idea is taken that the centripetal force is given by the Coulomb force. From the continuum of orbits so described, quantized orbits are selected by the quantum condition: angular momentum $= nh/2\pi$. The frequencies of spectral lines are derived from the equation: $h\nu_{\text{th}} = W' - W''$ where W' and W'' are energies of quantized orbits. These hypotheses lead to the theoretical formula

$$\nu_{\text{th}} = \frac{2\pi^2\mu Z^2\epsilon^4}{h^3}\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$$

which quantitatively agrees with the formula describing the observation.

Bohr's theory predicts the diameter of the hydrogen atom in its normal state to 1.06×10^{-8}, which is in satisfactory agreement with observations.

The energy-level diagram greatly simplifies the description of the spec-

trum. It gives evidence of the energies of excitation and ionization and the combination rule.

The spectrum of He^+ is approximately described by a formula differing from the Balmer formula by only the factor 4. This is predicted by Bohr's theory by considering the nuclear charge 2 of helium. Similarly, the spectra of Li^{++} and Be^{+++} and heavier ions are predicted, attributing nuclear charges 3 to Li, 4 to Be, etc. A very small difference between the two Rydberg constants, observed for H and He^+, is predicted in agreement with the observation, by taking into account the relative motion of the nucleus about the center of mass.

PROBLEMS

15.1. *Potential energy.* (*a*) State the difference of potential energy ΔW_p of a stone (mass m) moved from the initial height h_1 to the final height h_2. The resulting equation holds only near the surface of the earth ($h_2 - h_1$ small as compared to radius of earth). It is convenient to define $W_p = 0$ at an arbitrarily chosen initial height h_1 so that one talks of the potential energy, $W_p = mgh$, without mentioning the arbitrary zero point. We can choose the zero point arbitrarily since we shall be interested only in certain differences of W_p which are not affected by the position of the zero point. Obvious zero points are the surface of the earth or the table of the laboratory. (*b*) Can a mass have a negative potential energy? Can a mass have a negative kinetic energy? (*c*) Suppose a giant moves a mass m from the distance r_1 to r_2 (distances from center of earth, possibly large as compared to the radius of the earth). He must spend the energy $\Delta W_p = -GmM/r_2 + GmM/r_1$ (see Sec. 15.3 and Prob. 15.3; G = gravitational constant, M = mass of earth). Derive the expression for W_p given under (*a*) as an approximation from the last equation. Express the gravitational acceleration g by the gravitational constant G, the mass M and the radius r_e of the earth. (*d*) Again it is convenient to define $W_p = 0$ at an arbitrarily chosen initial distance r_1. (We cannot use $r_1 = 0$ as a zero point, since that would lead to infinitely large energies.) Express W_p with the radius of the earth r_e as zero point. How large an energy is required to lift the mass m to an infinitely large height, *i.e.*, to separate it entirely from the earth? (*e*) Express W_p choosing this infinitely large height as an arbitrary zero point.

15.2. *Velocity of escape from the earth.* A body (mass m) with a negligible initial velocity falls from an infinitely large distance to the surface of the earth. Disregarding air friction, compute the velocity v with which it strikes the earth (radius 6.37×10^8 cm; mass 6.00×10^{27} g; the force outside of the earth is the same as if its total mass were concentrated at its center.) A mass thrown upward with a velocity smaller than this value will fall back but, when thrown upward with a larger velocity, it will leave the earth altogether. Compare the velocity computed here with the average thermal velocity of hydrogen atoms and hydrogen molecules, at 0°C.

COMMENT: The result is that hydrogen atoms with a velocity somewhat exceeding the average have a good chance to leave the upper atmosphere for good.

15.3. *Potential energy of gravitational force (calculus method, to Sec. 15.3).* On the basis of Newton's law of gravitation compute the work required to increase the separation of the masses m and M from r_1 to r_2, in particular from r_1 to ∞.

HINT: (*a*) Subdivide the distance $r_2 - r_1$ into elements Δr so small that within each element the force $F = GmM/r^2$ is approximately constant. Express the element of work ΔW required to carry m over this distance Δr. (*b*) Express the total work required

to carry m from r_1 to r_2 as the sum of all these elements. (*c*) While these are approximations, the total work is rigorously expressed by going to the limit for $\Delta r \to 0$, *i.e.*, by replacing the sum by the integral. Evaluate this definite integral between the limits r_1 and r_2. (*d*) Express the total work for the special case $r_2 = \infty$.

15.4. *Relative motion of the nucleus* (*difficult problem*). In this problem the student is asked to introduce a more refined mechanical picture, taking into account the relative motion of the nucleus, into Bohr's theory of the emission of light from hydrogen atoms (Sec. 15.4). In any orbit, the electron and the nucleus circle about their common center of gravity always keeping in opposite directions as seen from this center. Hence, the theory will be simplified by introducing their common angular velocity into the expressions for the centripetal forces and angular momenta.

Additional notation:

M = mass of nucleus
r = radius of orbit of electron
R = radius of orbit of nucleus
V = linear velocity of nucleus
ω = angular velocity

HINT: *a*. State the fundamental equations: Eq. (I) states that centripetal force of electron = Coulomb force = $\epsilon E/(r + R)^2$; Eq. (II) states the same for the nucleus; Eq. (III) states that the total angular momentum of the system of both particles = $\mu r^2\omega + MR^2\omega = nh/2\pi$. This system of three equations contains the three unknowns r, R, and ω.

b. Equations (I) and (II) furnish the well-known condition for the center of gravity. This serves for eliminating R. What is left is a pair of equations with the unknowns r and ω.

c. From this pair eliminate ω. Thus one equation is obtained for r in terms of n and the fundamental constants.

d. ω and $v = \omega r$ are expressed in terms of n and the fundamental constants. (It is advantageous to introduce v instead of ω for the simplest expression of the kinetic energy W_k.)

e. The total energy $W = W_k + W_p$ is expressed in terms of r, v, R, and V.

f. Since under (*c*) and (*d*) we derived only the expressions for r and v, we must replace R and V by r and v in the expression for the total energy W.

g. The last step, the computation of the frequency ν_{th}, is the same as in Bohr's theory. Introduce the "reduced mass" $\mu M/(\mu + M)$ of the system.

h. Compute the ratio of the Rydberg constants for hydrogen and ionized helium R_H/R_{He} on the basis of the atomic weights: 5.48×10^{-4} for the electron, 1.008 for hydrogen, and 4.00 for helium. Compare your result with the empirical data given in Sec. 15.6*b*. You will be able to use your slide rule when you introduce approximations, *e.g.*, $A/(A + \alpha) = 1/(1 + \alpha/A) = 1 - \alpha/A$ for α small as compared with A.

15.5. *Spectrum of* He^+. The series spectrum of He^+ is represented by the formula

$$\nu = 4cR\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$$

Which series of He^+ is observed in the extreme ultraviolet partly coinciding with the Lyman series of hydrogen? Compute the wave lengths (in A) of the first four lines of this series and compare them with lines of the Lyman series. Assume the same value of R for H and He^+.

15.6. *Effect of gravitational force.* In Bohr's theory we assumed that the electron and the proton are kept together by the Coulomb force. In addition, there is the gravitational force. Compute how large this is as compared to the Coulomb force.

15.7. *Excited energy levels.* How far above the normal level are the four lowest excited energy levels of the hydrogen atom? Compute the energies (expressed in ev) on the basis of the series formula.

15.8. *Ionization energy.* Compute the ionization energy of the hydrogen atom (in erg and ev) from the series formula

$$\nu = 3.000 \times 10^{10} \times 109{,}700\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)\text{sec}^{-1}$$

15.9 *Hydrogen of mass number three.* Assuming that an amount of hydrogen of mass number three (see Chap. 20) sufficient for spectroscopic examination can be put into a tube containing ordinary hydrogen, determine the separation of the H_α lines that would be observed.

15.10. *Excitation by heat.* Compute the temperature of atomic hydrogen gas at which the average kinetic energy of the atoms would be sufficient to excite H atoms to their first excited level ($n = 2$). Why is thermal radiation observed at much lower temperatures?

to carry m from r_1 to r_2 as the sum of all these elements. (*c*) While these are approximations, the total work is rigorously expressed by going to the limit for $\Delta r \to 0$, *i.e.*, by replacing the sum by the integral. Evaluate this definite integral between the limits r_1 and r_2. (*d*) Express the total work for the special case $r_2 = \infty$.

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e. The total energy $W = W_k + W_p$ is expressed in terms of r, v, R, and V.

f. Since under (*c*) and (*d*) we derived only the expressions for r and v, we must replace R and V by r and v in the expression for the total energy W.

g. The last step, the computation of the frequency ν_{ik}, is the same as in Bohr's theory. Introduce the "reduced mass" $\mu M/(\mu + M)$ of the system.

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CHAPTER 16

MORE COMPLICATED SPECTRA

16.1. Spectra of Heavier Atoms. *a. Term Diagram.* The spectra of the heavier atoms have led to detailed information on atomic structure which culminated in the interpretation of the periodic table of elements. The greater complexity of these spectra is due to the presence of several electrons. The spectra of the various elements belonging to the same chemical group, like the alkalies or the halogens, are closely related, the alkalies exhibiting the simplest spectra. As typical of these spectra we shall describe the sodium spectrum (Fig. 16.1). At first glance the numerous lines seem to be completely disarranged; no orderly series are obvious.

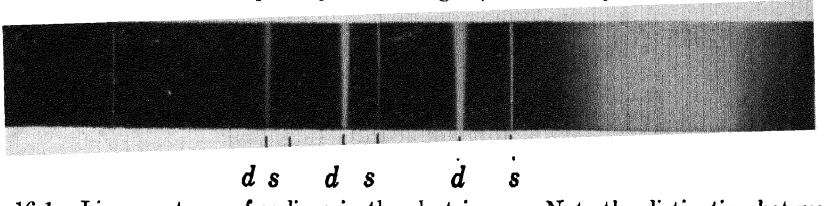


FIG. 16.1. Line spectrum of sodium in the electric arc. Note the distinction between diffuse series *d* and sharp series *s*. The yellow line is strongly broadened.

Closer inspection, however, shows that certain lines of strikingly high intensity belong together as a series, called the "principal series," which converges like any hydrogen series. Among the weaker lines those of very sharp appearance and those of more diffuse character form separate series.

Although we cannot theoretically predict an energy-level diagram (as we did for hydrogen), we can *invent* a diagram from which we can derive the observed series using Bohr's frequency condition (Fig. 16.2). While the energy-level diagram for hydrogen contains only one column of levels, we notice that the sodium diagram contains several. Within the same diagram all columns of levels converge toward the same limit. The levels of the first vertical column are called "S levels," those of the second column "P levels," and those of the third, "D levels." These letters are taken from the descriptive names (sharp, principal, diffuse) attached to the observed series which correspond on the diagram to transitions from the levels marked S, P, D. The investigation of the infrared spectrum reveals many such columns of levels with which we are not concerned.

Not all possible transitions between any two energy levels on the diagram lead to spectral lines. Only combinations of two levels that belong

to adjacent vertical columns are "allowed." This rule is called a "selection" rule. For example, the principal series is represented in the diagram as a transition of any level of the *second* vertical column (any P level) to the lowest level of the *first* vertical column (the lowest S level). This latter level, the lowest of all the energy levels, represents the "normal state" of the sodium atom. The first line of this series is the prominent yellow line of sodium, which makes the light from sodium lamps yellow. The selection rule says that the atom whose energy is described by a high P level may emit light by radiating an amount of energy equal to the difference between the atom's initial energy and the final energy corresponding to any lower S level or D level. This gives a great multitude of different series, most of them located in the infrared. Only a few of these series, those with the *lowest* S level or P level or D level as the final state of the emission process, are to be found in the *visible* or *ultraviolet*. The lines of the principal, sharp, and diffuse series are indicated on the diagram. The selection rule limits only the transitions taking place with emission of light or, as we shall see later, with absorption of light; it does not restrict the excitation by electron impact.

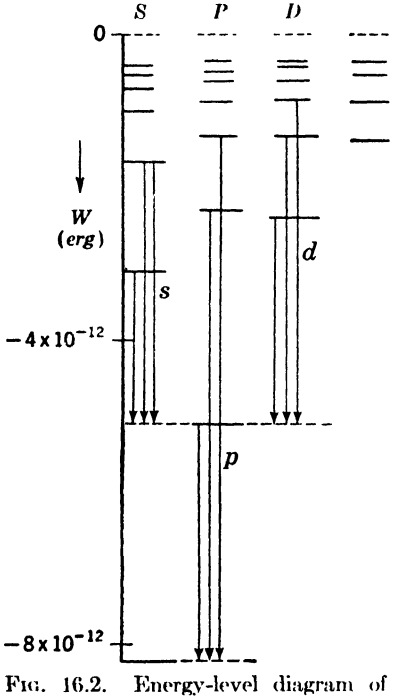


FIG. 16.2. Energy-level diagram of sodium atoms; p = principal series, s = sharp series; d = diffuse series. The smallest frequency of the principal series belongs to the prominent yellow line.

This diagram fulfills the same purpose as that of hydrogen: A large number of spectral lines are described in the most economical way. One may wonder whether the diagram of Fig. 16.2 describes the energies of the atom before and after emission uniquely, or whether it might be replaced by a different arrangement that would also yield the correct wave lengths for the emitted lines. Actually it is much better founded than the argument just presented may seem to indicate. Only an example will be given of the additional evidence. With a spectrograph of higher resolving power it is observed that each line described above actually consists of a pair of closely adjacent components. For example, the yellow line of sodium has two such components differing in frequency by 51.54×10^{10} sec^{-1}. This indicates that either the upper or the lower level of this line consists of two closely adjacent "sublevels." This alterna-

tive is solved by the observation that exactly the same frequency difference is found for all pairs of lines of both the sharp and the diffuse series. This fact proves that all these lines mentioned have one energy level in common, which when high resolving power is applied, is revealed as consisting of a pair of sublevels. This conclusion agrees with the [illegible]sed

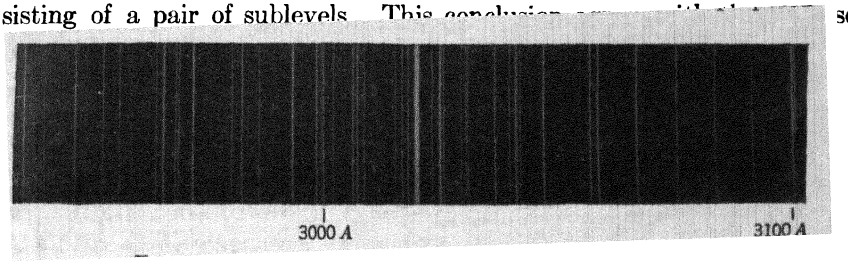


FIG. 16.3. Small section of iron spectrum from electric arc.

diagram: The lowest P level is the one common to the whole sharp and diffuse series and the first line of the principal series.

The spectra of other alkali atoms are strictly analogous so that for any line of sodium one can point out the corresponding line of any other alkali. The elements of the other groups of the periodic table have different, in most cases vastly more complicated, spectra. As an example we reproduce

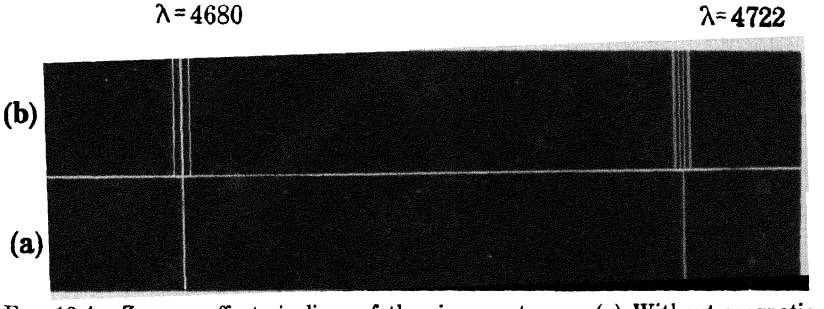


FIG. 16.4. Zeeman effects in lines of the zinc spectrum. (*a*) Without magnetic field; (*b*) with magnetic field. (*Courtesy of J. B. Green.*)

a small section of the iron spectrum, which illustrates how difficult a problem the analysis may be (Fig. 16.3).

When a beam of light is passed between the poles of a powerful magnet, no change in the resulting spectrum is observed. But when we put the emitting source in a strong magnetic field, we find that each spectral line is split up into several components with small frequency differences which are proportional to the field strength. This phenomenon is called the "Zeeman effect." For most lines, the patterns so obtained are more complicated than the group of three components into which the hydrogen lines split. An example is given in Fig. 16.4. Even for the powerful fields of

large electromagnets, these patterns are so narrow that their investigation requires spectrographs of high resolving power.

The Zeeman effect contributes to the exploration of the sun. Hale (1908) discovered that the spectral lines emitted from a sunspot show the splitting characteristic of the Zeeman effect. He assumed that this splitting is due to a magnetic field caused by ionized gases whirling about the spot and so representing a circular electric current. This observation led to a measurement of these fields, which are of the order of magnitude 3,000 oersteds and of an extension in space several times the volume of the earth.

b. Displacement Law. In our discussion of Bohr's theory we found that the spectra of neutral hydrogen and ionized helium contain closely related series, the helium series being shifted toward the ultraviolet by the factor 4 in the formula for the frequency because of the larger nuclear charge of helium.

This is a special case of the spectroscopic displacement law, discovered by Sommerfeld. This law is based on the general rule that the nuclear charge equals the atomic number. (This rule we derived from alpha-ray scattering and confirmed by applying Bohr's theory to the lightest atoms.) The element magnesium, for example, has 12 external electrons, one more than its predecessor in the periodic table, sodium. Consequently, the singly charged magnesium ion Mg^+ has only 11 external electrons, just as many as neutral Na. This relation explains why Mg^+ and Na have spectra of the same type. Just as with H and He^+, the lines of Na and Mg^+ can individually be correlated, although the lines of the magnesium ion, because of the higher charge of the magnesium nucleus, are located at higher frequencies. This example leads to the displacement law: Any singly charged ion has the same type of spectrum as the neutral atom of the preceding element in the periodic table but shifted to higher frequencies.

One can extend this law to ions that have lost several electrons. We have studied the simplest case, comparing H, He^+, Li^{++}, etc., all spectra being described by Bohr's theory. Correspondingly the spectra of Na, Mg^+, Al^{++}, etc., are all of the simple, easily identified type of an alkali spectrum; but the spectra of the higher ions are increasingly shifted to the extreme ultraviolet (to high frequencies). Hence their investigation requires the difficult technique of the vacuum spectrograph. Such a group of atoms and ions, which all have the same number of external electrons but differ by their nuclear charges, is called an "isoelectronic sequence."

These experimental results described by the spectroscopic displacement law confirm the rule stating that the atomic number equals the nuclear charge, because this rule is needed to explain that any singly charged ion has the same number of external electrons as the neutral atom preceding it in the periodic table.

c. Energies of Excitation and Ionization. One can derive the *excitation*

energy and *ionization* energy of an atom from its energy-level diagram, following the argument applied to hydrogen (Sec. 15.5*c*). For example, the theory predicts that the first line of the principal series (the yellow line of sodium, $\lambda = 5{,}896\text{A}$; $\nu = 5.083 \times 10^{14}$ sec $^{-1}$) is excited only if the energy $h\nu = 3.36 \times 10^{-12}$ erg = 2.10 ev is imparted to sodium atoms in the normal state. Furthermore, the convergence limit of the energy-level diagram is interpreted as the energy (above the lowest, normal level) which, when absorbed by an electron in the normal state, will allow the electron to escape from the atom, hence represents the energy of ionization. The height of this convergence limit above the normal state of the atom is computed from the observed (or extrapolated) convergence limit of the principal series, *i.e.*, 2,412A. The computation of $h\nu$ leads to an energy of ionization of 8.22×10^{-12} erg = 5.14 ev. (The unit electron volt should not obscure the fact that our computation of the energies is based on spectroscopic observations; see Sec. 17.1.)

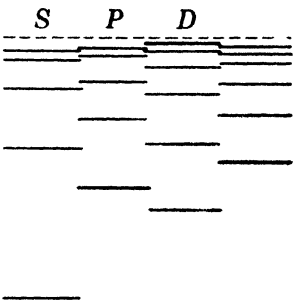


Fig. 16.5. Schematic energy-level diagram containing a metastable level (the lowest *D* level).

d. Metastable Levels. The selection rule mentioned above states that emission of light takes place only by transitions between levels that belong to adjacent vertical columns. This leads to a curious prediction in the case of certain exceptional energy-level diagrams in which the location of the levels is somewhat different from the arrangement for sodium atoms. For example, in the energy-level diagram of Fig. 16.5 it happens that the third vertical column has its lowest level a little below those of both adjacent columns. In the electric discharge, all possible levels may be excited by impacts or reached, after the excitation process, by emission of light. Thus some atoms finally arrive at the lowest D level. Here, although they contain energy stored up, the atoms are "forbidden" to radiate by the selection rule, because the adjacent vertical columns have no levels with lower energy. This situation gives to these levels much longer lives than the ordinary excited atoms have. These special levels are called "metastable" in contrast to the common unstable levels and the one and only stable level, the normal state of the atom. The analysis of the line spectrum furnishes the metastable levels with the same accuracy as all other levels because they show up as *final* levels in the emission of certain spectral lines whose initial levels are known.

As good a picture of a metastable level as mechanics has to offer is given by a rock placed high up on a slope, resting in a shallow hole from which it may easily be pushed out. While any other position on the slope is *unstable* and the position at the bottom of the valley is *stable*,

the hole gives some *inferior stability* to a position high above the stable state.

The prediction of metastable levels presented here on the basis of the diagram Fig. 16.5 is only a special case. The complete treatment of atomic spectra describes the fine structure levels with additional quantum numbers which necessitate more selection rules and present other chances of metastable levels. Such levels occur in mercury, helium, oxygen, and other atoms. We shall come back to them in the discussion of absorption spectra and impacts of the second kind (Sec. 17.5 and 17.10).

It is an overstatement that metastable levels are entirely unable to radiate. It is more accurate to say that their probability of radiation is exceedingly small. Hence they have theoretical lifetimes a great deal longer than the common, unstable levels, possibly a million times longer. But in an electric discharge, the metastable levels, exposed to a permanent bombardment by electrons and ions, hardly ever reach the old age that would lead to their natural death by radiation. Instead they suffer many collisions with other particles, one of which may give the metastable atom enough energy to raise it to an unstable level, after which it radiates and so goes down to the ground state. The situation is different in nebulae and the solar corona. Here no walls are present as in a discharge tube, and the density is only about 10^{-15} that of our atmosphere. Therefore, collisions are much rarer in nebulae and the corona, and the chances of survival of metastable atoms so much greater that intense spectral lines due to forbidden transitions, *i.e.*, transitions from metastable levels, are observed. The spectra of planetary nebulae show lines which, decades ago, were attributed to a mysterious element called "nebulium." At present, we are sure that there is no place for more elements in the periodic table as will be discussed in the section on X rays (Sec. 19.2*a*). Now these nebulium lines are attributed to forbidden transitions in ionized oxygen and nitrogen atoms. Recently lines in the solar corona have been explained as forbidden lines in highly ionized iron, nickel, and calcium atoms.

A forbidden transition is prominent in the northern lights. These lights are explained by charged particles ejected from sunspots during an eruption, which, in many cases, is observed as a brilliant light flaring up in the spot. These particles on approaching the earth have two effects. They are the equivalent of an electric current, affecting compass needles and causing a magnetic storm. In addition, when entering the upper atmosphere, they represent an electric discharge through a gas. Because of the very low pressure, a forbidden transition within oxygen atoms can take place. This is responsible for the greenish color of the northern lights.

e. Report on Further Developments. In the further development of our knowledge of atomic spectra, experiment and theory are closely interlinked. The spectra of the alkali atoms (Figs. 16.1 and 16.2) occupy an intermedi-

ate position between the simple hydrogen spectrum and the other much more complex atomic spectra. An alkali atom is assumed to consist of a nucleus surrounded by "shells" of electrons, which remain in their very stable positions, and one particular electron, called the "series electron," which can readily be excited. When returning to a position of lower energy, the series electron is responsible for the radiation emitted. (This structure will be discussed further in the chapter on the periodic table, Chap. 18.) When the series electron is in a large circular orbit around the nucleus and the other electrons, which lie in more closely packed shells, it is affected by the nucleus and the other electrons as if all their charges were concentrated at the nucleus. Thus, in the case of sodium, the nucleus has a charge of + 11, but this is masked by shells of altogether 10 electrons, so that the series electron is influenced by a charge of only + 1 at the nucleus. This picture explains the fact that in any alkali atom the high-energy levels have nearly the same relative positions as in the hydrogen atom. On the other hand, the *lower* energy levels differ from those of the hydrogen atom since here the series electron closely approaches the shells of the more stable electrons or may even penetrate into them.

The more recent development of wave mechanics (starting 1925, see Chap. 26) essentially confirms the quantum numbers introduced by Bohr, but slightly changes their numerical values. For example, it attributes zero orbital angular momentum and zero orbital magnetic moment to the first column of levels designated above as S levels. (This column has a particular importance since, for the atoms of many elements, *e.g.*, the alkalies, it includes the normal states.) The following columns (the P levels, D levels, etc.) have the orbital angular momenta 1, 2, etc., respectively.

It has been mentioned above that the alkali spectral lines show a doublet structure. This fact leads us to a new hypothesis, which is of great importance for spectroscopy as well as for nuclear theory. It is assumed that each electron, in addition to its orbital motion considered by Bohr and Sommerfeld, performs a *spin* motion about its own axis (Goudsmit and Uhlenbeck, 1925). Obviously, the starting point for this hypothesis was the planetary motion. But in quantum theory the spin is restricted by a quantum condition which is adjusted so that the conclusions agree with the observed facts. In this case the condition is strikingly simple: The angular momentum of the spin is once and for all $\frac{1}{2} \times h/2\pi$ (without a variable quantum number).

In order to justify the further assumption regarding the positions of the spin, we must go back to an older result derived from Sommerfeld's general quantum conditions dealing with the orbits of the electron. This theory predicts that, when the atom is subjected to an external magnetic field, the orbits take up discrete orientations with respect to the direction of the field, the allowed orientations being described by certain quantum numbers.

This is called "space quantization." In the theory of the alkali atom the same idea is applied to the electron *spin*, which is subjected to the magnetic field caused by the *orbital* motion of the electron. Here space quantization implies that the spin is either parallel or antiparallel to this magnetic field. These two positions of the spin represent energies that differ only slightly. They are responsible for the splitting up of the energy levels into close pairs, and thus for the doublet structure observed.

At the same time the hypothesis of the electron spin explains the complicated Zeeman patterns characteristic for one or the other spectral line. Here for each energy level, space quantization of the *total* angular momentum (the vector sum of the *orbital* and *spin* momenta) is assumed. This leads to the prediction that the magnetic field causes each level to split up into a group of sublevels. For a quantitative prediction of these sublevels, an assumption must be made regarding the magnetic moment associated with the spinning electron. Considering the *orbital* motion, we were able to *compute* the magnetic moment (see Sec. 15.5*c*), since there the electric charge obviously travels along the same orbit as the mass. For the spin, however, no such prediction can be made. All we can do is *invent an extra hypothesis* such that the observed facts can be derived from the theory. When we assume that the magnetic moment of the spin equals one magneton, the observed Zeeman effects are quantitatively predicted.

The elements of the second vertical column of the periodic table, the alkaline earths, are interpreted as having 2 series electrons. Here a new hypothesis is needed regarding their mutual interaction. It is assumed that their respective orbital angular momenta are oriented with reference to one another according to the rules of space quantization, that the same is true for the two spin momenta, and, finally, that space quantization governs the relation between the *resulting* orbital and spin momenta so produced. Again the Zeeman effects are predicted by the quantized orientations of the *total* angular momentum in an external magnetic field. Thus a few consistent rules lead to the theoretical interpretation of a vast material of spectral lines and their Zeeman effects. We shall come back to the same system of quantum numbers when reporting on the theory of the periodic table of elements (Sec. 18.9).

The same basic idea is applied to the interpretation of more refined observations. With spectrographs of very high resolving power, a very narrow "hyperfine structure" of many spectral lines has been discovered. This is explained by attributing angular momenta and magnetic moments to the *nuclei* and assuming similar rules for their orientations with respect to the *total electronic* angular momentum. This is one of the few connecting links between spectroscopy and nuclear physics. The exploration of the hyperfine structure of spectral lines has led to the determination of many nuclear angular momenta and the magnetic moments associated with

them. They have been confirmed by entirely different experiments (see Sec. 20.7).

f. Quantitative Spectral Analysis. It has been known for a long time that in an electric discharge the relative intensities of the spectra of several gases in a mixture fail to indicate their relative concentrations. The reason is that there are other factors affecting the intensities, partly inherent in the atomic structure as probabilities of transition, partly depending on the velocity distribution of the electrons in the discharge. The many unknown factors involved prevented *quantitative* spectroscopic analysis for a long time.

Only in the last two decades has progress been made. This success is

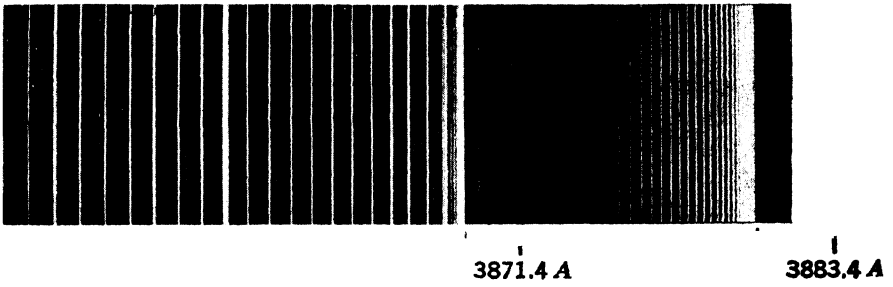


FIG. 16.6. Part of a molecular spectrum; cyanogen bands.

directly based on experience and is independent of atomic theory. Suppose that in the manufacturing process of steel we want to test the concentration of manganese in iron. To begin with, for the purpose of calibration, we prepare a set of mixtures of iron with small percentages of manganese, say, 0.3, 0.4, 0.5, etc., per cent. The spectra of these samples, excited by an electric spark, are photographed, and the relative intensities of some representative lines of iron and manganese are measured. Next, a sample with an unknown concentration of manganese is investigated in the same way, and by comparison with the set of calibration spectra the concentration of manganese is determined. This method of testing, although of limited application, has practical importance because it is more rapid than many chemical tests. In particular it is suitable for small impurities.

16.2. Molecular Spectra. A typical molecular spectrum is given by Fig. 16.6. It is more complicated than an atomic spectrum by the appearance of broad bands. For this reason molecular spectra are frequently called "band spectra" as contrasting to "line spectra" emitted by atoms. In most cases these bands can be resolved into individual sharp lines, which by their crowded arrangement give the impression of bands. Typical of most bands are the sharp and intense edges. Superficially, they look very much like series converging limits. But this impression is misleading, since in some cases the lines near the edge can be completely resolved and in other cases the law describing the individual lines is so well known that

there is no question about the fact that the edge represents only a finite number of lines crowded together in a peculiar arrangement.

Only a brief report of the theory of band spectra will be given. These spectra, which for decades defied analysis, were interpreted soon after the discovery of the Bohr theory. Here both vibration and rotation of the atoms constituting the molecule take place and must be taken into account in addition to the electronic excitation. For both these motions, quantum theory predicts quantized energy levels.

The energy levels of the *rotation* have a very narrow spacing of the order of hundredths of an electron volt. Quantum transitions between such levels lead to radiation in the *extreme infrared*. The energy levels of *vibration* have a wider spacing of the order of tenths of an electron volt. Quantum transitions between vibrational levels produce a radiation in the *near infrared*. (Ordinarily a change of a *vibrational* quantum is accompanied by a simultaneous change of a *rotational* quantum. The various combinations lead to the "vibration-rotation bands" in the near infrared.) Finally, a quantum change of the *electronic* state of the molecule, which causes *visible* or *ultraviolet* radiation, ordinarily takes place with simultaneous changes of vibration and rotation. These combinations are responsible for the complicated band spectrum of Fig. 16.6.

A whole band system, covering many hundred angstrom units, may be due to one definite change of electronic orbit, hence correspond to one single line in an atomic spectrum. In the molecule the simultaneous changes of *vibration* and *electronic energy* cause the *coarse structure*, this means that any one *single band* with its sharp edge is due to a simultaneous change of electronic orbit, one well-defined change of vibration, and all possible changes of rotation. Finally, any *one single sharp line* within this band is attributed to a well-defined change of *rotation*.

Fine structures of the individual rotational lines belonging to a band are interpreted by the electron spin (see Sec. 16.1*c*) which proves as important in the interpretation of molecular spectra as in atomic spectra.

Recent new discoveries in spectroscopy are due to the extensive development of *microwave techniques* during the Second World War. Developed for the purpose of radar, microwave transmitters of great constancy make possible the investigation of important new absorption spectra of molecules in the range between the extreme infrared and radio wave lengths.

The interpretation of molecular spectra may well be listed among the great successes of the quantum theory. The analysis of these spectra led to a better understanding of molecular structure. Molecular spectroscopy is a wide field in which no border line exists between physics and chemistry.

SUMMARY OF CHAPTER 16

As an example of *a spectrum of an atom heavier than hydrogen*, the spectrum of sodium is described on the basis of its energy-level diagram. This

contains levels arranged in several vertical columns. The selection rule states that transitions connected with emission or absorption of light take place only between levels that belong to adjacent vertical columns. Such transitions lead to the various series: principal, sharp, and diffuse. The spectra of other alkali atoms are strictly analogous.

The *Zeeman effect* of most lines is more complicated than the pattern of three Zeeman components shown by the hydrogen lines.

The *displacement law* states that any singly charged ion exhibits the same type of spectrum as the neutral atom of the element preceding it in the periodic table, but shifted to higher frequencies. This law confirms the rule: atomic number = nuclear charge.

The analysis of the spectrum and its description by the energy-level diagram lead to the prediction of the *energies of excitation and ionization.*

An atom in a *metastable level* is in an energy state such that the selection rule allows it only a small chance of radiating light and falling to a lower energy state. This defect gives it a lifetime much longer than atoms in ordinary excited levels have. In the conventional light sources of the laboratory, atoms in metastable levels ordinarily have no chance at all of emitting light because, during their extended lifetimes in such levels, they are lifted out of the levels by collisions. Nevertheless they may have a chance of radiating light at the very low pressures that prevail in planetary nebulae, the solar corona, and the upper atmosphere of the earth

Bohr's theory does not quantitatively predict the energy levels of more complicated atoms. However, with the additional hypothesis of the electron spin, the theory gives account of the various series constituting an atomic spectrum, in particular of the fine structure of the lines and their splitting in a magnetic field (Zeeman effect). Finally, the hyperfine structure of spectral lines is interpreted by attributing a spin to the nucleus of the emitting atom.

Quantitative spectral analysis is possible only in special cases on the basis of a calibration.

Molecular spectra (band spectra) are interpreted as due to simultaneous changes of electronic energy, vibration, and rotation of molecules.

CHAPTER 17

METHODS OF OBSERVATION

In the present chapter the various processes by which atoms and molecules may *receive* or *give away* energy will be interpreted on the basis of the quantum theory. We shall first consider collision processes, next the emission and absorption of light, then chemical processes involving excited atoms, and finally collisions of the second kind, which will take us back to chemistry. As a general point of view, we shall keep in mind our continued search for additional tests of the theory. For many processes we shall find illustrative cases in nature.

17.1. Excitation and Ionization by Controlled Electron Impact. We derived the excitation energy and ionization energy of atoms from the energy-level diagram, which is constructed solely on the basis of *spectroscopic* observations (Sec. 16.1*a*). In the present section we shall supplement the evidence (1) by a combination of *spectroscopic* and *electrical* observations and (2) by a purely *electrical* experiment. In any case we shall try to find an answer to the question: What happens to electrons which pass through a gas or vapor on their way from a glowing cathode to an anode?

By way of preparation we must find out what happens to electrons if all their collisions with atoms are governed by the laws of *elastic* collisions. These are general considerations that we shall apply later to the various collisions suffered by corpuscular rays in nuclear physics. The electrons emanate from the glowing metal with thermal velocities, which are negligible as compared with those imparted by an electric field acting between cathode and anode. In any elastic collision between a fast electron and a slow atom, because of the vast difference of the masses, the electron keeps practically all of its kinetic energy but changes its direction (see Prob. 14.1). If the electron coming straight from the filament bounces exactly backward, it is *decelerated* by the same potential difference which, before the collision, had *accelerated* it. It behaves the same way as a rubber ball dropped from a certain height and bounced back from the floor. If, instead, the electron bounces off at an angle with the field, the same is true for the forward or backward component of its velocity. Therefore, at any distance from the cathode all electrons have the same kinetic energy, only the *direction of their velocities* may have been changed by collisions. This applies in general to electrons that are deflected in any direction *by elastic collisions* with atoms. Unless the number of intervening collisions is excessive, the elec-

trons when reaching the anode have nearly the kinetic energy given by the potential difference between the cathode and the anode; their velocities are directed preferentially parallel to the electric field.

Franck and Hertz (1914) excited the 2,536A line of mercury atoms by controlled electron impact. This first line of the principal series of mercury is probably the most photographed spectral line, as it is used in many investigations in physics as well as photochemistry (see Sec. 17.10). From the observed wave length the energy difference between the initial and final levels giving rise to the λ 2,536 line is computed to be 4.88 ev (Sec.

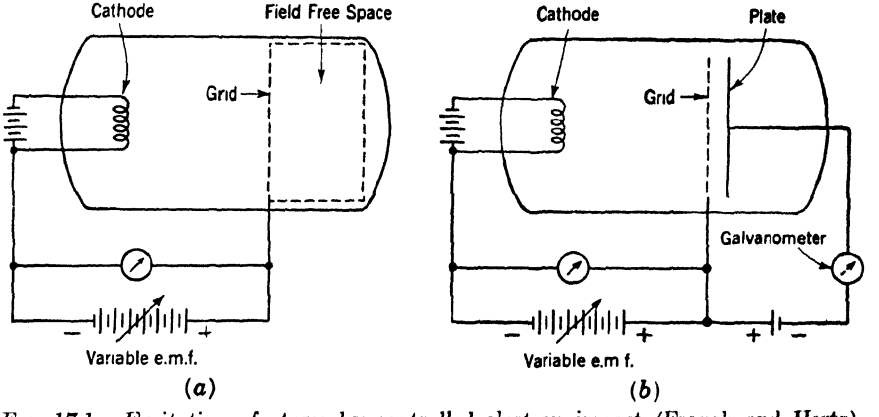


FIG. 17.1. Excitation of atoms by controlled electron impact (Franck and Hertz). (*a*) Electrical and spectroscopic observation combined; (*b*) electrical observation only.

16.1*c*). The experiment is performed in low-pressure mercury vapor through which electrons from a glowing cathode travel. The electrons are accelerated toward a grid, beyond which they shoot into a field-free space and hence keep the velocity they had when passing through the grid (Fig. 17.1*a*). At low values of the accelerating voltage the vapor remains dark but, when the voltage is increased to a certain sharply defined value, the single line λ 2,536 suddenly appears, unaccompanied by any other radiation. The critical voltage is found to be equal to the excitation energy (4.88 ev) of the initial state for emission of λ 2,536, within the experimental error.

In the other experiment to be discussed, first performed by Franck and Hertz (1914), the fate of the impinging electrons is traced by electrical experiments only. One uses a three-electrode tube containing a glowing cathode (preferably an equipotential cathode), a metal grid at a distance of a few centimeters from the cathode, and a plate right behind the grid (Fig. 17.1*b*). Again the electrons emanating from the cathode are accelerated by a *variable* potential difference to the grid. Those passing through the meshes of the grid have to overcome a small, *constant retarding* potential

difference of, say, ½ volt in order to reach the plate. A galvanometer reads the plate current. Other electrons flow through the metal of the grid and so form the other branch of the total current. The tube contains a gas or vapor, like mercury vapor, at such a low pressure that between the cathode and the grid the electrons suffer many collisions, but only a few

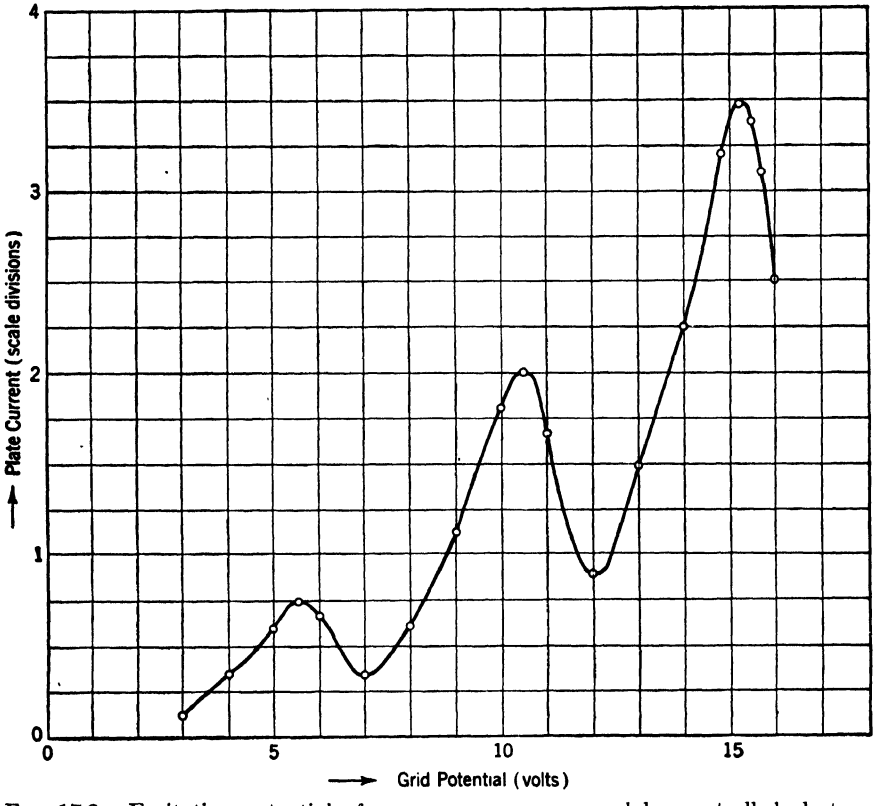


FIG. 17.2. Excitation potential of mercury vapor measured by controlled electron impact (students' laboratory experiment).

or no collisions over the short distance between the grid and the plate.

On the basis of the considerations given above, we can predict what will happen if the collisions between electrons and atoms are *elastic*. Electrons when accelerated by one or several volts and passing through the meshes of the grid should easily overcome the small retarding voltage and reach the plate. If so, they are registered by the galvanometer.

Franck and Hertz measured the plate current as a function of the accelerating potential difference between the cathode and the grid. They found curves like those of Fig. 17.2, characterized by a succession of equally spaced maxima. For mercury vapor, for example, the distance between

peaks is always 4.88 volts, irrespective of any detail of the apparatus. The authors explained the shape of the curves as follows: At low potential differences the current is limited by the space charge (Sec. 10.2), which is not materially affected by the presence of the vapor. This explains the first gradual increase of the current. Above a sharply defined energy limit, 4.88 ev in the case of mercury, the mercury atoms take away the kinetic energy from the electrons in collisions and so obtain their energy of excitation. These collisions are *inelastic* since kinetic energy is changed into another type of energy. If electrons reach the grid with a kinetic energy of 4.88 ev and there are robbed of this energy by mercury atoms, they are unable to overcome the retarding voltage; hence the *plate current drops.* At further increasing accelerating voltage the layer in which this energy loss occurs is being shifted to a position closer to the cathode. Now the electrons, after suffering one energy loss, have a chance to recover and reach the grid with an appreciable energy, which enables them to overcome the small retarding voltage. This explains the second increase of the current. At a definite higher voltage the electrons suffer this first loss already near the middle of the distance, pick up just another 4.88 ev when they reach the grid, and there suffer a second loss of the same size. Hence the plate current drops again and so forms the second maximum. This process continues for higher voltages. (We are not concerned with the fact that the whole curve may be shifted along the V axis depending upon the surface properties of the metals, described as "contact potential difference.") The difference between successive maxima is always 4.88 volts. The outstanding result is that here the excitation energy of atoms, *e.g.*, 4.88 ev for mercury, is measured by a purely electrical method.

What bearing has the experiment of Franck and Hertz on the theory of radiation from atoms? Everybody knows that a very soft touch with the hammer excites a bell to a very low-intensity vibration. The experiment just presented, however, gives evidence that nothing of the kind happens when the electron hits the atom. At low energy the collisions are elastic and fail to give *any* energy of excitation to the atom. Only above a sharply defined limit characteristic for the atom is the atom able to receive energy in an inelastic collision. Then the full, quantized value of the energy of excitation is transferred. Hence the experiment gives a strong confirmation of the fundamental idea of the quantum theory as opposed to the classical theory of radiation. Moreover, a quantitative confirmation is obtained from the fact that both the electrical and the spectroscopic method (Sec. 16.1*a*) lead to the same value of the excitation energy. The intensity of a spectral line emitted from an electric discharge is determined by the number of atoms emitting light and the number of excitation processes suffered by each atom per second; but the individual emission process always occurs with the same energy.

In more detailed experimental investigations it has been found that the chance for a transfer of excitation energy to the atom depends strongly on the excess energy of the impinging electron. Electrons with an energy slightly exceeding the minimum value have the highest probability; with a further increase of kinetic energy, this probability is strongly decreased.

Measurements of this kind have been carried out for all elements available as gases or vapors. For many years, while the technique of the vacuum spectrograph was not yet fully developed, these experiments gave the only available evidence of the excitation energies of the rare gases, the spectra of which were not completely accessible.

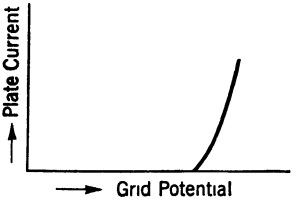


FIG. 17.3. Ionization potential measured by controlled electron impact.

In nearly the same apparatus Franck and Hertz measured the *ionizing* potentials of gases and vapors. For this measurement the retarding potential between grid and plate is made much larger, perhaps as large as 20 volts. This potential keeps electrons away from the plate throughout the experiment. Furthermore, the pressure of the gas or vapor is reduced to so low a value that the mean free path is much longer and the electrons have a good chance of picking up higher kinetic energy without losing it to the *excitation* of atoms. For this arrangement the I-V curve looks entirely different (Fig. 17.3). The current is zero up to a certain limit and then suddenly increases. The galvanometer is deflected in the direction opposite to that of the other experiment. Franck and Hertz explained this curve as follows: The electrons are able to produce ionization only after reaching the ionization energy. The positive ions so produced near the grid are subjected to the field between the grid and the plate and pulled to the plate. (A correction must be applied for the contact potential difference mentioned above.) The results of these *electrical* measurements agree with the ionization energies derived *spectroscopically* from the convergence limits of the series (Sec. 16.1*c*).

17.2. Electric Discharges through Gases. *a. Processes in the Electric Discharge.* Electric discharges through gases may be classified, according to the origin of the carriers of electricity, into self-maintained and non-self-maintained discharges. In the *non-self-maintained* gas discharge the carriers are electrons liberated from metals by photoelectric effect or heat, or they are electrons and ions generated in the gas by X rays or radioactive rays. In any case the carriers are generated by some outside agent, which must continue to act as long as the discharge runs. The intensity of the electric current depends on this agent. Therefore, we employ such non-self-maintained discharges for measuring the intensity of X rays or radioactive rays. An example is the X-ray dosimeter (see Sec. 19.1*d*).

It is less easy to understand the *self-maintained* gas discharge. Well-

known examples are the neon sign, the electric arc, and lightning. Here the discharge itself generates the carriers of electricity by processes that we want to analyze. There are three types of self-maintained gas discharges: the spark, the arc, and the low-pressure discharge. We shall describe the low-pressure discharge in some detail because of the importance of the cathode ray and positive ray, both of which are parts of it.

All gases at atmospheric pressure are good insulators unless the applied voltage is so high that a spark discharge occurs. At reduced pressure, say, of a few centimeters of mercury, a potential difference of a few thousand volts readily starts a discharge. The conductivity of the gas has a maxi-

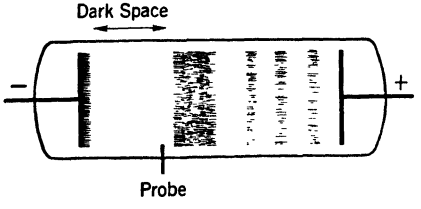


FIG. 17.4. Electric discharge through a gas at low pressure.

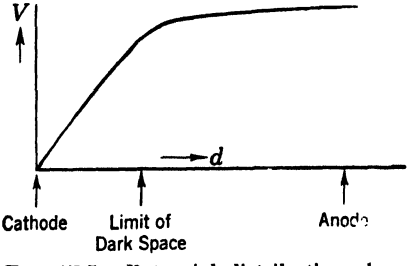


FIG. 17.5. Potential distribution along discharge. V = potential difference against cathode; d = distance from cathode.

mum at about 1 mm pressure. The phenomena we are interested in are most clearly exhibited at a pressure of a few hundredths of a millimeter. Figure 17.4 shows the discharge at this low pressure. The difference between the parts near the two electrodes is striking. Near the negative electrode, the cathode, there is a dark space, called the "Crookes dark space," a few centimeters long. This part of the discharge is rather sharply limited, on one side by the cathode (or rather by a thin luminous layer covering the cathode), on the other side by another luminous layer stretching farther into the discharge. The length of the Crookes dark space increases with decreasing gas pressure and, within a certain range, can be used conveniently for measuring pressures of gases. Its length is of the same order of magnitude as the mean free path of the gaseous molecules (Chap. 5). We are less concerned with the so-called "positive" column, which extends toward the positive electrode and in many cases shows another dark space followed by brilliant striations.

In order to explore the potential distribution along the discharge, we introduce into the tube several probes made of short metal wires sealed through the glass wall, with all but the tips covered with glass. An electrostatic voltmeter between the cathode and any probe measures the potential difference between these two spots. (A thorough investigation shows that the probe method is subject to errors of several volts, but they are negligible

as compared to the effect we shall describe.) The potential distribution over the length of the discharge tube is given in Fig. 17.5. It is evident that the potential is by no means uniformly distributed, as it would be along a conducting wire of uniform cross section. It shows by far the largest gradient, indicating a strong electric field, near the cathode, while along the rest of the discharge the gradient is small. The large potential drop near the cathode is called the "cathode drop."

The processes in the discharge responsible for the observations described are by no means fully understood. We shall discuss only the most important ones responsible for the conductivity and the various effects of the cathode drop.

At atmospheric pressure all gases are good, although not complete, insulators. Their very small conductivity, not easily measured, is presumably due to the ionizing effect of radioactive rays and cosmic rays, which are present everywhere. When a few free electrons resulting from this all-pervading ionization are accelerated sufficiently by an electric field, they are able to ionize atoms or molecules by impact. The free electrons produced in this way go through the same process. This "electron avalanche" is the primary agent maintaining conductivity all along the discharge. It operates better at low pressure, because a long mean free path reduces the danger of many small energy losses suffered by the free electrons in collisions that would prevent them from picking up the large kinetic energy required for ionization. Ionization by electron impact was assumed by Townsend (1899) to be responsible for the conductivity of gases before measurements of the ionization energies of the various gases were carried out.

We shall not explain the cathode drop and the striations, partly because it is not essential for our purpose, partly because no fully satisfactory explanations are known. Let us accept as a fact the high potential drop near the cathode, demonstrated by the probe method, and find out what part it plays in the discharge. We have mentioned the ionization processes creating free electrons and positive ions. Why did we concentrate on the effect of *electrons* in explaining the ionization and disregard the *positive ions?* In the weak field of the positive column the positive ions do not have a good chance to pick up energy because the ions have about the same mass as the atoms or molecules of the gas. Hence the kinetic energy that an *ion* picks up in the electric field is readily given off in a few collisions with atoms or molecules and dissipated into heat. The *electron,* however, when suffering collisions has the advantage of keeping its kinetic energy because of its very small mass (see Sec. 14.1 and Prob. 14.1). Unless the electron loses energy through the relatively rare process of excitation or ionization, it will accumulate kinetic energy as it accelerates in the electric field.

However, the kinetic energy of a positive ion is large when it is accelerated in the very high potential drop that extends from the cathode for about one mean free path. The field is so concentrated that it may give to the ion a kinetic energy of several thousand electron volts, without energy loss in intervening collisions. Endowed with this energy, the positive ion hits the metal of the cathode. It has been found out by special experiments that such impacts of ions on a metal surface liberate electrons. One impinging ion may well free several electrons. The electrons liberated from the cathode by its bombardment with positive ions supply more carriers of electricity, which help conduct the current.

The processes in the *electric spark* are essentially the same, although modified by the much shorter mean free path at atmospheric pressure. In the *electric arc* the bombardment of the cathode with positive ions is so violent that the cathode is heated to several thousand degrees centigrade and so becomes a copious thermal emitter of electrons. This process, most conspicuous in the glowing cathode of the carbon arc, is responsible for the large current carried by the arc.

b. Cathode Rays and Positive Rays. The processes near the cathode of the low-pressure discharge just described explain the production of the cathode ray and the positive ray. Electrons liberated from the cathode are exposed to the strong electric field in the cathode drop, which endows them with high kinetic energy. This process enables the electrons to shoot straight away from the cathode and form a cathode ray. In the low-pressure discharge (Fig. 8.1) one can distinguish two groups of electrons: those belonging to the cathode ray endowed with kinetic energies of thousands of electron volts, and those which may have energies up to 20 or 30 ev due to ionization of gaseous atoms by electron impact.

This origin of the cathode ray explains a strange feature of the electric discharge evident in Fig. 8.1. One might expect that electrons coming from the cathode would be pulled to the anode by the electric field. Actually, however, these electrons forming the cathode ray shoot away from the cathode in a straight direction, irrespective of the position of the anode. This is due to the concentrated potential drop in front of the cathode. If the total potential difference applied between cathode and anode is 10,000 volts, possibly 9,700 volts of this amount will be concentrated right in front of the cathode, accelerating the electrons in the direction of the field, away from the cathode. The remaining weak potential drop of 300 volts is distributed over a considerable distance and fails to deviate the cathode ray noticeably.

A positive ray or canal ray is observed when a canal is drilled through the metal of the cathode (Sec. 8.3). It consists of the positive ions just described as hitting the cathode. Those which happen to pass through the canal form the positive ray observed behind the cathode.

Although we cannot easily explain the potential drop at the cathode, we discussed its importance in the electric discharge. The cathode drop causes three effects: (1) It accelerates positive ions toward the cathode over one mean free path to so high an energy that they knock electrons out of the cathode. (2) It accelerates these electrons away from the cathode so that they form the cathode ray. (3) It enables the positive ions that pass through a canal drilled through the cathode to form a positive ray.

17.3. Excitation and Ionization by High Temperature. So far we have discussed excitation by impact of electrons and positive ions. Now we come to excitation by impacts between neutral bodies. It is well known that a solid body emits light when heated to a high enough temperature.

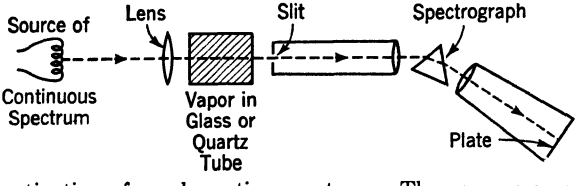


FIG. 17.6. Investigation of an absorption spectrum. The vapor removes light of certain frequencies from the otherwise continuous spectrum.

This fact, demonstrated by every incandescent light bulb, is true for gases, too. The flame of the bunsen burner is not a clear-cut demonstration, because there one cannot readily distinguish the effects of heat and chemical reactions. But gases and vapors in high-temperature ovens emit their characteristic spectra in the absence of electric currents or chemical reactions. This proves that thermal collisions between atoms or molecules may produce excitation. It is true that at the highest temperatures available in the laboratory (a few thousand degrees centigrade) the *average* energy of mutual collisions is only of the order of magnitude $\frac{1}{3}$ ev, which is much too small for the excitation of visible radiation. But at this temperature the occasional collisions of much higher energy are sufficiently numerous to produce light. Ionization, which may be considered as a special kind of excitation, occurs as well.

17.4. Absorption Spectra. Our foremost interest in absorption spectra is based on the evidence they give of atomic structure and processes in gases. (The word "gases" will include vapors since their distinction is of no importance spectroscopically.) Furthermore, absorption of light will give us a good chance to compare the spectra of gases, liquids, and solids.

a. Sharp-line Absorption Spectra of Gases. For the simplest investigation of absorption spectra (Fig. 17.6) we focus on the slit of a spectrograph the light from a source emitting a continuous spectrum. Somewhere between the source and the slit we place the absorbing gas. This may be

contained in a tube closed by glass windows or, for observations in the ultraviolet, quartz windows. For a demonstration experiment, the absorber may be a bunsen burner in which a small piece of metallic sodium is evaporated; a glowing filament (or the crater of the arc) provides the continuous background on which the absorption spectrum of sodium shows up as a black line in the yellow region.

We mentioned before (Sec. 15.1) the fact discovered by Bunsen and Kirchhoff that the *absorption* spectrum contains lines observed also in the *emission* spectrum. The demonstration experiment described gives the new evidence that the absorption spectrum contains only a selection from the emission lines. For example, the *absorption* spectrum of sodium vapor

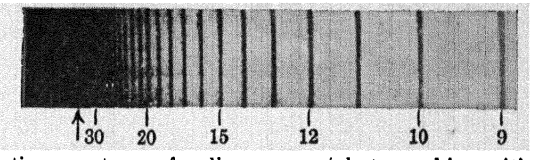


FIG. 17.7. Absorption spectrum of sodium vapor (photographic positive). Notice the continuous absorption beyond the limit of the absorption line series; limit indicated by arrow. (*Courtesy of G. R. Harrison.*)

shows exclusively the principal series and no trace of the sharp or diffuse series (Fig. 17.7). The absorption spectrum of atomic hydrogen (investigated by a more elaborate technique than that of Fig. 17.6) shows only the Lyman series. In general, only those series show up in absorption which are connected with the normal state of the atom.

This restriction is understood on the basis of the quantum theory. An absorption process, lifting an atom from a lower to an upper quantized energy state, is pictured as the reverse of an emission process, in which the energy of the atom goes from the upper to the lower level. The sharp and diffuse series are not absorbed, because the initial state of their absorption (the lowest state of the *second* vertical group, Fig. 16.2) is not present in the vapor, at least under the ordinary laboratory conditions. Their simpler structure makes absorption spectra a powerful tool for the difficult analysis of complex spectra.

Certain observations that are exceptions to the rule just discussed actually confirm the underlying idea. In the atmosphere of the sun atomic hydrogen strongly absorbs the lines of the Balmer series, although this series is not connected with the normal state of the hydrogen atom (Fig. 15.4). This exception is explained by the high temperature of the sun, which exceeds the temperatures available in the laboratory. As a result of this temperature, a small percentage of all hydrogen atoms (four or five out of every thousand million) are always to be found in the first excited level and so are able to absorb the lines of the Balmer series.

Our argument may seem inconsistent because of the following objection: When we observe the absorption of white light by sodium vapor, the first line of the principal series, the well-known yellow line, is strongly absorbed. This process continually creates sodium atoms in this specific excited level which, in turn, is expected to act as the lower level for the absorption of the sharp and diffuse series. Why are not these series noticeable in the absorption spectrum? They fail to show up because of the exceedingly short lifetime of the excited state. It is true that many sodium atoms per second are raised to the excited level, but they radiate after so very short a lifetime that ordinarily no appreciable population of atoms in the excited state is built up. Here we can only vaguely argue that the lifetime of the excited level is exceedingly short. Later (Sec. 17.11) we shall discuss a measurement of the lifetime, which leads to a value of about 10^{-8} sec. The processes by which the lives of the excited levels are terminated, radiation or impacts of the second kind, will be demonstrated later (Secs. 17.6 and 17.10).

The comparison of the absorption spectrum with the energy level diagram (Fig. 16.2) shows that the selection rule applies to absorption as well as to emission of light. Transitions take place only between levels that belong to adjacent vertical columns of the diagram. For example, the normal state of the atom, belonging to the first vertical column, forms absorption lines only with the levels of the second column and not the levels of the first or third column.

The sharp absorption lines show that excitation of an atom *by light* occurs only if the frequency of the light exactly *equals* the value characteristic for the atom. In the case of excitation *by electron impact*, however, the kinetic energy of the electron must *equal* or *exceed* the energy required by the atom.

In most cases the first line of the absorption series gives the energy difference between the normal and the lowest excited state (see Fig. 16.2). From this line we can compute the energy which in the method of controlled electron impact is measured by a voltmeter reading (Sec. 17.1). The combination of these two independent measurements of the same energy provides a new determination of Planck's constant h. The excitation energy is expressed as $h\nu$ on the basis of the spectroscopic measurement and as ϵV on the basis of the electrical experiment. In the equation $h\nu = \epsilon V$ we measure ν spectroscopically, ϵ by the oil-drop experiment, and V by a voltmeter reading. The resulting value of h agrees well with those obtained by other methods.

b. Continuous Absorption Spectra of Gases; Ionosphere. The absorption spectrum of sodium vapor shows *continuous* absorption beyond the convergence limit of the line series, in striking contrast to the good transparency between the sharp absorption lines. (Figure 17.7 shows *darkness* beyond

the series limit in contrast to the *light* between the lines.) This continuous absorption indicates that the sodium atom may receive energy from quanta carrying more energy than that required for the liberation of an electron. It is a plausible assumption that the excess energy goes into kinetic energy of the electron liberated. The *continuous* character of the spectrum is due to the fact that the kinetic energy imparted to the electrons covers a *continuous* range.

This continuous absorption spectrum gradually decays beyond the series limit, indicating that the ionization process by light takes place with highest probability for light just beyond this limit. For higher frequencies this probability gradually decreases. This is of importance in explaining the transparency of all matter observed at much higher frequencies, discussed under X ray absorption spectra (Sec. 19–2*c*).

Our argument describes a process that is closely related to the photoelectric effect (Chap. 11), the only difference being that here the electron is liberated from a *free atom*, while in the conventional photoelectric effect it comes out of a *metal surface*. Our argument, which is based entirely on spectroscopic evidence, when interpreted by the quantum theory, leads to the prediction of an electrical effect. Sodium vapor illuminated by light of wave lengths shorter than the convergence limit of the principal series (2,412A) should become conducting since it is being ionized. This observation has actually been made (although with experimental difficulties with which we are not concerned) and represents another confirmation of the quantum theory; the theory predicts the photoelectric effect on free atoms and even the value of their "work function" (see Sec. 11.3). Molecules as well as free atoms may be ionized by light of sufficiently high frequency. Most gases, however, have ionization energies much higher than sodium, which served as our example. Therefore, in most gases only extreme ultraviolet light, which is not easily accessible in the laboratory, may cause ionization.

Ionization by light of gaseous atoms and molecules is of vital importance for radio communication. In the early history of radio it seemed safe to predict that communication half around the earth would not be possible. Unexpectedly, however, it turned out that radio waves follow the surface of the earth. This is explained by the existence of ionized layers of gases at great heights in the upper atmosphere, which reflect radio waves back to the earth. The alternating reflections between the ionosphere and the surface of the earth keep the radio waves more or less enclosed within a spherical shell and enable them to travel long distances over the surface of the earth. The height of the ionosphere is measured by observing the time interval between the transmission of a radio signal and the arrival of the echo from the ionosphere layer. Thus several separate ionized layers at heights of about one hundred and several hundred kilometers have been

found. The variations of the height and density of the ionosphere between day and night and during eclipses indicate that *light emitted from the sun* is the cause of ionization. This is just the process discovered from the continuous absorption spectrum beyond the series limit of sodium. But in the ionosphere, light of the extreme ultraviolet range is required because the ionization energies of the atmospheric gases are high, between 12 and 16 ev. The ionosphere represents an unusual case in which a very complex process, going on in nature all the time but hitherto unknown, unexpectedly extends the range of our technical devices.

Similar continuous absorption spectra are observed when light in the visible or near ultraviolet range is absorbed by *molecules*. But this absorption is not associated with ionization, for the latter requires higher energy. For example, the absorption spectrum of molecular iodine, I_2, schematically given in Fig. 17.8, shows a range of continuous absorption at wave lengths below 4,995A. The energy range of this spectrum (2.48 ev and higher) is much too low for producing *ionization*. This spectrum is connected with a convergence limit of bands explained by changes in energy of *vibration* of the molecule (see Sec. 16.2). The limiting case of increasing vibration is presumably the *dissociation* of the molecule into neutral atoms. The continuous spectrum beyond this limit results from the absorption of light quanta which impart some kinetic energy, in addition to the dissociation energy, to the products. Only in this respect are molecular *dissociation* continua quite analogous to *ionization* continua. Dissociation processes manifest by these continuous absorption spectra are important in originating photochemical reactions, because the free atoms or radicals produced by light are chemically active and cause secondary reactions (see Chap. 12 and Secs. 17.9 and 17.10).



FIG. 17.8. Absorption spectrum of iodine vapor (diatomic molecules). A row of sharp edges converging toward a limit, each edge consisting of an accumulation of sharp lines. Continuous absorption spectrum beyond the convergence limit.

c. Comparison of Gases, Liquids, and Solids. Absorption of light gives the best chance for a comparison of the spectra of gases, liquids, and solids. The absorption spectra of gases are distinguished by sharp lines. Liquids and solids show more or less diffuse absorption spectra (Fig. 17.9). This fact is explained by the structure of liquids and solids. They consist of atoms and molecules all in close touch with neighbors which affect all quantum transitions. Only in the gaseous state can the transitions take place without any disturbance and so reveal the sharply defined energy levels characteristic of single atoms or molecules. This distinction makes the spectra of gases most important for our knowledge of atomic structure.

The absorption spectra of innumerable liquids and solids have been re-

corded. Figure 17.9 shows the absorption spectra of cyanine (a dye used for making photographic plates green and yellow sensitive, see Sec. 17.10) and chlorophyll. Chlorophyll absorbs reddish-orange and blue light, the remaining green light being responsible for the green color of leaves. By absorption, chlorophyll acts as the receiver of sunlight and so stores up the greatest part of the energy that maintains all organic life and all human activity. We can only briefly describe the process, called "photosynthesis," through which this storage of energy is accomplished. The growth of plants requires the assimilation of the carbon which is contained in the air as carbon dioxide. For this process energy is required to break up the structure of the carbon dioxide molecule. This energy is supplied by the chlorophyll in the excited level to which it is lifted by absorbing sunlight. The details of this complex photochemical reaction by which ultimately carbon is built into the structure of the plant is not yet fully understood.

The vast importance of this process is evident when we consider that all food consists of plants or else of meat from animals which, in turn, live on plants. So ultimately all our food depends upon energy received from the sun by the chlorophyll. The same is true for the greatest part of all energy consumed by industry because our deposits of coal and oil originate from decaying woods and so represent energy of sunlight stored through millions of years. At present we are consuming this vast store of energy at a rate far exceeding the rate of replacement. This lack of balance confronts the human race with the problem of finding other, less exhaustible sources of energy. We shall come back to this problem in the discussion of nuclear energy.

17.5. Application to Astrophysics. The modern science of astrophysics is based entirely on spectroscopy and very largely on the quantum theoretical interpretation of spectra. The starting point was the interpretation by Kirchhoff and Bunsen (1860) of the black lines discovered by Fraunhofer (1817) in the solar spectrum (Fig. 17.10) as absorption lines of elements well known on the surface of the earth. Most of these lines are absorbed by the solar atmosphere, a few others by the atmosphere of the earth. These lines give evidence of the chemical constitution of the solar atmosphere. At present 61 of the known, stable chemical elements have been identified.

The quantum theory enters when the effect of the temperature on a stellar atmosphere is considered. At low temperature molecules like CN or OH can exist. With increasing temperatures (1) molecules dissociate, (2) an increasing fraction of the atoms are excited or even ionized. For a given chemical constitution, quantum theory permits the theoretical prediction of this effect of the temperature. So a scale for the intensities of various spectra of neutral atoms and ions can be theoretically computed as a function of the temperature under the assumption of a uniform chemical composition. The observed spectra of stars have been compared with this

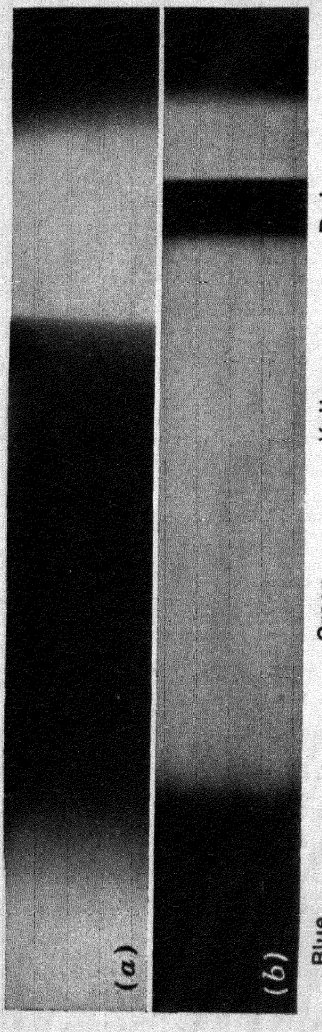


FIG. 17.9. Absorption spectra of liquids (photographic positive). (*a*) Cyanine, a dye used for sensitizing photographic plates; (*b*) chlorophyll.

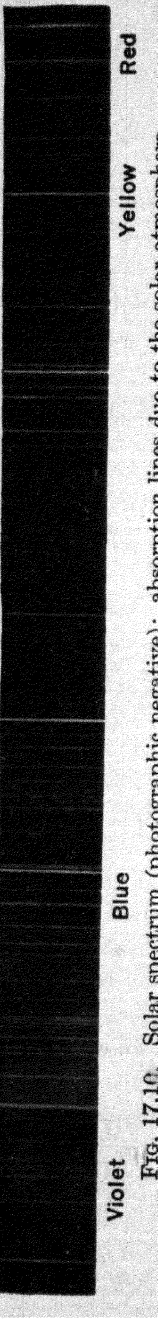


FIG. 17.10. Solar spectrum (photographic negative); absorption lines due to the solar atmosphere.

theoretical scale. Here it proved important that the spectra of ions can be identified as discussed in Sec. 16.1*b*. The unexpected result is that almost all observed spectra of stars fit into the theoretical scale. This agreement leads to the surprisingly simple conclusion that the great majority of all stars contain the same elements in about the same relative abundance as the sun. The same observations lead to the measurement of stellar temperatures.

17.6. Fluorescence. When sodium vapor is illuminated with yellow light, sodium atoms are raised to an excited state. We may ask what hap-

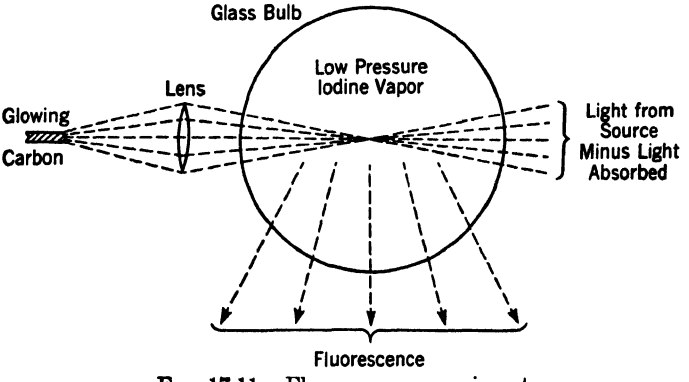


FIG. 17.11. Fluorescence experiment.

pens to the energy thus absorbed and find the answer in the demonstration experiment sketched in Fig. 17.11. Since the experiment, when performed with sodium vapor, requires heating of the glass bulb, it is more conveniently performed with iodine vapor which happens to have the proper vapor pressure at room temperature (see Appendix 2). Intense white light is focused by a lens of large aperture on the glass bulb containing iodine vapor. The light *passing through* shows, by its violet tinge, the loss of green light absorbed by the vapor. In the bulb, *seen from any side*, the greenish bundle of light defined by the lens is clearly visible. The experiment shows that the *light absorbed is reradiated in any direction.* This radiation is called "fluorescence."

More detailed information is obtained by the investigation of the spectrum. If sodium vapor is excited by the yellow sodium line (first line of the principal series), the fluorescence shows only the same line. Because of the analogy with the harmonic vibrator, this is called the "resonance line." If, instead, the source supplies exclusively light of the *second* line of the principal series, the fluorescence contains all emission lines originating, directly or indirectly, *from the level so excited* (second level of second vertical column, Fig. 16.2), *i.e.*, the same line which served for excitation, in addition a few selected infrared lines, and the yellow line. All other

lines that originate from higher excited levels are absent. Thus the observation is in complete agreement with the theoretical prediction.

This observation represents a special case of Stokes' law (1853). It states that fluorescence contains light of the same frequency as the exciting light or lower frequency. This empirical law is immediately understood on the basis of the energy-level diagram and the principle of conservation of energy.

Even some inconspicuous exceptions to Stokes' law are understood. Some molecules have energy levels of vibration so low that even at room temperature a certain fraction of the molecules contain some vibrational energy. If one of these vibrating molecules absorbs a light quantum, it contains a little more energy than that given by the quantum and so has the alternative of emitting light either of the *same* frequency as the exciting light or of a little *higher* frequency. Such a spectral line of higher frequency is called an "anti-Stokes" line. It violates Stokes' law only by the little energy content due to thermal motion, *i.e.*, at room temperature, an amount of the order of $\frac{1}{30}$ ev (see the anti-Stokes lines photographed in the Raman effect, Fig. 17.12).

On the basis of Stokes' law we understand that *ultraviolet* light may produce fluorescence in the *visible* range. This can well be demonstrated when the ultraviolet light from an intense carbon arc is isolated by a filter and incident, for example, on a glass bulb containing kerosene. The invisible light produces a visible fluorescence. In recent years this conversion of ultraviolet into visible radiation turned out to be of importance for the construction of powerful lamps. It so happens that most gases or vapors (atomic and molecular hydrogen, mercury vapor, all rare gases) have their most intense spectral lines, caused by the transitions between normal and lowest excited states, in the ultraviolet. Therefore, a gas discharge like the mercury arc, although bright enough in the visible, wastes the greatest part of its energy as ultraviolet radiation. There are two ways of preventing this waste. One way is using a discharge through sodium vapor, which is exceptional in that it has its most intense line in the yellow. The sodium arc, however, has the disadvantage that its pure yellow light gives a disagreeable impression. The other way consists of converting the intense ultraviolet light, emitted, for example, by mercury vapor, into visible light. This is done by fluorescence of thin crystalline layers covering the inside glass surfaces of fluorescent lamps. This arrangement has the advantage that, by the proper choice of fluorescent material, various colors can be produced; in particular, the intensity distribution of sunlight can be approximated. Fluorescence is predominant in planetary nebulae. These are extended masses of very low density that are intensely illuminated by a central star. The star, because of its very high temperature, emits ultraviolet radiation up to high frequencies with great intensity. This radiation

excites hydrogen atoms to high energy levels from which they may cascade down and, in certain steps, emit visible radiation.

Some fluorescent materials show an afterglow lasting several seconds or even minutes. This is called "phosphorescence." It occurs only in complex molecules in which the absorption of light produces a nearly stable, but not quite stable, rearrangement storing up energy. When, after a while, the molecule goes back to a lower level, light is emitted.

In summarizing we may say that the absorption of light and fluorescence fit well into the picture of the atom given by Bohr.

17.7. Raman Effect. We overstated the case by saying that, for example, sodium vapor is transparent for any wave length between the lines of the absorption series (Sec. 17.5*a*, Fig. 17.7). There is another, much weaker effect, the Raman effect, which may take place for light of *any frequency* (above a certain limit) incident on any substance. In the Raman effect light of a sharply defined frequency is scattered by the substance to be investigated.

Conspicuous is the observation that most of the scattered light has the same frequency as the incident light. Yellow light when scattered is still yellow. Raman (1928) discovered that there is another scattering process, much less intense, which causes a change of frequency characteristic for the scattering substance. The experimental arrangement is similar to the one that serves for the demonstration of fluorescence (Fig. 17.11). But here the source of light, *e.g.*, the mercury arc, emits sharp spectral lines which do not coincide with sharp absorption lines of the scattering material. The bulb is filled, say, with liquid carbon tetrachloride, CCl_4. (A vapor like sodium vapor has so low a density that no Raman effect would be noticeable.) The light scattered sidewise is analyzed by a spectrograph. Figure 17.12 shows that in the scattered light each intense spectral line is surrounded by a pattern of weak lines characteristic for the scattering substance. This is the Raman effect.

The effect is readily explained in terms of the quantum theory. The scattering molecule has its characteristic energy levels among which, in the case of liquids, in particular *vibrational* levels are effective. The molecule may scatter the incident quantum as a whole and so give rise to the undisplaced line in the scattered light, or else it may keep energy amounting to one or a few *quanta of its own vibration* and scatter the balance, which is a spectral line slightly shifted to lower frequency. Thus the frequency difference between incident and scattered spectral lines gives evidence of a characteristic vibration of the molecule. In a five-atomic molecule like CCl_4 various modes of vibration with various frequencies are evident in the Raman spectrum.

So far we have explained only the shift of lines toward *lower* frequencies. Figure 17.12 shows that other lines are shifted to *higher* frequencies and

so apparently violate the principle of conservation of energy. They are explained by the same argument as the anti-Stokes lines observed in fluorescence. At room temperature, a certain fraction of all molecules are endowed with vibrational energy. If such a vibrating molecule is hit by the incident quantum, it may throw its own energy into the scattering process and so scatter a larger quantum, which is a line of higher frequency. Therefore, this shift to higher frequencies is limited to the small range due to thermal energies. The intensity distribution evident in Fig. 17.12 agrees

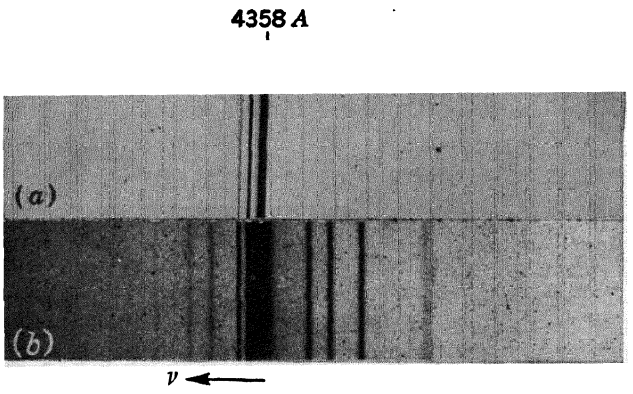


FIG. 17.12. Raman effect (photographic negative). (*a*) Spectrum of mercury arc; (*b*) the same when scattered by CCl_4. Note the symmetry in position but not in intensity. The arrow shows the frequency difference corresponding to the average energy of thermal collisions.

well with this explanation. The isolated mercury line at 4,358A is surrounded by a pattern symmetrical in position (on the frequency scale) but not in intensity. On the high-frequency side, the distant lines are very weak; at increasing temperature, they would gain intensity.

This feature of the Raman effect giving evidence of the characteristic vibrations of molecules makes it an important tool for the investigation of molecular structure.

17.8. Chemical Process Producing Light. We mentioned that we cannot easily decide whether the light emitted from a bunsen burner is due to the high temperature or to a chemical process. In other cases, there is no doubt that a chemical process is producing light. This is true for the green light emitted from the firefly, presumably due to an oxidation process. A similar process is responsible for the glow of yellow phosphorus exposed to air. This property of phosphorus explains its name which means "carrier of light." Light produced by a chemical process, called "chemiluminescence," is not of great importance. (The word "phosphorescence" may mean this property of phosphorus although, conventionally, it means the afterglow observed in some cases of fluorescence, see Sec. 17.6.)

17.9. Light Producing a Chemical Process. Differing from chemiluminescence, the chemical processes produced by light, investigated in *photochemistry*, are most important. Such processes were discussed in Chap. 12 in presenting an argument for the quantum theory of light. They are listed here in order to make our survey of methods of observation complete. In all cases the primary photochemical reaction, *i.e.*, the immediate effect of the light absorbed, is described by Einstein's fundamental law of photochemistry, one of the foundations of the quantum theory of light. Frequently, however, the complexity of the secondary reactions masks the simple primary reaction.

17.10. Impacts of the Second Kind. A new type of process, which is not predicted by the theory but fits well into it, is evident in the demonstration experiment on fluorescence, *e.g.*, of iodine vapor (Sec. 17.6, Fig. 17.11), when we admit a foreign gas of atmospheric pressure to the iodine vapor of low pressure (0.2 mm) contained in the bulb. The bright fluorescence observed without the foreign gas disappears completely. Which of the two processes responsible for fluorescence (absorption of light and reemission) is prevented by the foreign gas? The *absorption* is not disturbed as is evident from the violet color of the light passing straight through; this may be confirmed by observing the absorption spectrum. Hence we must assume that in the presence of the gas the molecules excited by light dispose of their excitation energy without radiating it. This leads to the assumption of a new process in which excited atoms or molecules, when colliding during their lifetimes, may *give away* their energy of excitation without radiating it. Such processes are called "impacts of the second kind," contrasting with "impacts of the first kind" in which excitation is *produced*.

What happens to the energy given away? The various answers to this question have been explored in detail by Franck and his collaborators. The answer is obvious in the simplest case. Mercury vapor when excited by light of its "resonance line" 2,537A shows fluorescence radiation. (Only because of its location in the ultraviolet range it cannot be demonstrated so easily as fluorescence radiation of iodine vapor.) This radiation is quenched by 1 atm of a rare gas, helium or argon. Because of the chemical inertia of the gas, no chemical reaction can occur, and the only assumption left is that, by the collision, the energy of excitation is changed into *kinetic energy* of the partners.

Next Franck investigated whether excitation energy may be transferred during the collision into *excitation energy* of the colliding atom. Again fluorescence radiation of mercury vapor is excited by light of the wave length 2,537A. Since the gas added must have a lower excitation energy than mercury in order to make a transfer of energy possible, sodium vapor is chosen as the added gas. It reduces the intensity of the mercury fluorescence and adds a new effect: sodium lines appear in the fluorescence

radiation. In a control experiment it is checked that sodium vapor in the absence of mercury, illuminated by the same light, shows no fluorescence whatever. Hence we must assume that mercury atoms, excited by light, when colliding during their lifetime with sodium atoms, may transfer their energy of excitation to the sodium atoms.

This interpretation is corroborated by the spectroscopic analysis. The mercury atom excited by light of 2,537A contains an energy of 4.88 ev. The sodium spectrum excited in the experiment described is not as complete as when excited in the electric discharge. Here only those spectral lines are observed which originate from energy levels of sodium requiring 4.88 ev or less for their excitation. This completely agrees with the theoretical prediction. Thus the experiment proves that excitation energy may be transferred in collisions from one to another atom.

The next problem Franck solved was whether excitation energy may be transferred into *chemical energy*. For this investigation a chemical process had to be chosen which requires less than the 4.88 ev available in the excited mercury atom. The dissociation of hydrogen molecules requiring 4.45 ev meets this requirement. Hence hydrogen is added to the mercury vapor and the mixture exposed to light of the wave length, 2,537A. As expected, atomic hydrogen is so generated. (Its production is tested by the reduction of copper oxide.) A control experiment shows that in the absence of the mercury vapor the same light fails to produce any reaction. This combination of experiments proves that light quanta of sufficient energy content, although not directly accepted by the hydrogen molecules, may be accepted by mercury atoms and their energy transferred in collisions to hydrogen molecules. This is called a "sensitized photochemical reaction" meaning that the hydrogen, although originally insensitive to the light, can be made sensitive by the addition of mercury vapor.

This reaction has technical interest in that it helps explain a process that had been known for many years, the sensitization of photographic plates. Ordinary photographic plates (see Sec. 17.9) are sensitive only to blue light or light of higher frequency. That is why they are conveniently developed in red light. We conclude that red light does not dissociate silver bromide, AgBr. However, the plates can be sensitized for red light by bathing them in a dye like cyanine which absorbs red (see its absorption spectrum in Fig. 17.9). It is plausible to explain this sensitization by the same process discovered by Franck in the mixture of mercury vapor and hydrogen. Here it is assumed that the dye molecules when absorbing red light are brought to an excited level, which may transfer its energy and so dissociate a neighboring silver bromide molecule.

To begin with one may guess that red light has no effect on the nonsensitized photographic plate because the quanta are too small to dissociate the AgBr molecules. The experiment described shows that this guess is wrong

because the same quanta when accepted by the dye are able to blacken the plate. Here we are forced to assume that the absorption of light by molecules, *e.g.*, AgBr, is limited by properties of the molecule other than the energy required for a certain process. This is explained in the theory of molecular spectra. On the other hand, there is no prospect of extending the sensitization far into the infrared because we are sure that the quanta of far infrared radiation are too small to produce dissociation of AgBr. No absorbing dye can circumvent the principle of conservation of energy.

This example illustrates the general rule: The wave-length range effective in producing a photochemical reaction must meet two requirements: (1) it must have quanta large enough to initiate the reaction and (2) it must be absorbed by the molecules to be affected.

Summarizing impacts of the second kind, we may say that an atom or molecule when colliding during the lifetime of an excited state may change its energy into kinetic energy, energy of excitation, or chemical energy.

17.11. Lifetime of Excited State. On several occasions while discussing absorption spectra and impacts of the second kind, we introduced the lifetime of an excited state of an atom. This places us under an obligation to describe the elaborate measurement of the lifetime performed by Wien in a canal-ray experiment. In the discussion of electric discharges we described the canal ray (or positive ray) as consisting of positive ions accelerated toward the cathode by the concentrated potential difference in front of the cathode and shooting through a canal drilled through the metal.

According to this explanation it is surprising that the canal ray contains neutral as well as positively charged atoms, as is evident when we try to deflect the ray by an electric field; only a part is deflected while another part shoots in a straight line indicating neutral particles. In order to explain this and similar experiments, we are forced to assume that the particles, originally positively charged, readily exchange their charges in collisions, becoming neutral and going back again to their charged status, possibly even becoming negatively charged. This change of charge, while of no importance for our present experiment, justifies the fact that we observe the lines of the Balmer series, although belonging to neutral hydrogen atoms, as a part of the spectrum of the canal ray.

Wien built his canal-ray tube (Fig. 17.13) such that the discharge proper operating at a pressure of a few thousandths of a millimeter communicated with the canal-ray chamber behind the cathode only through the narrow canal drilled through the cathode. This enabled him to pump out the canal-ray chamber to high vacuum, independent of the low-pressure gas which is indispensable in the discharge chamber. In this condition the canal ray fades away behind the cathode and becomes completely invisible within a few centimeters distance. The important observation is that the whole ray does not completely disappear although, because of the high vacuum in the canal-ray chamber, the atoms constituting the ray do not suffer collisions. The experiment is unique in that light is emitted

from places in which no exciting agent is active. Therefore, we must assume that the atoms carry their excitation energy from the discharge chamber into the canal-ray chamber and there only gradually give it away. Thus the decay of light intensity along the ray demonstrates the lifetime of the excited state. The highest intensity indicates the largest number of excited atoms as present near the cathode; the decaying intensity, a diminishing number farther away.

A quantitative determination of the average lifetime is based on the combination of two measurements: (1) the linear velocity of the ray and

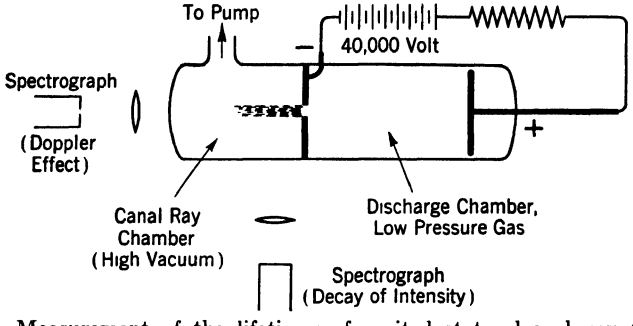


FIG. 17.13. Measurement of the lifetimes of excited states by observation of the decay of the light emitted from a canal ray. Note the different functions of the two spectrographs. The light emitted from the discharge proper is about the same as in Fig. 17.4.

(2) the decay of the intensity along the ray. For the determination of the linear velocity, the Doppler effect is recorded by a spectrograph photographing the light emitted from the ray "end on." Since the atoms are shooting toward the spectrograph, all spectral lines are shifted toward higher frequencies. This shift, *e.g.*, for the red hydrogen line, ($\nu = 0.457 \times 10^{15}$ sec^{-1}) is measured as $\Delta\nu = 0.15 \times 10^{13}$ sec^{-1}. The well-known formula for the Doppler effect leads to a velocity of the atoms = 10^8 cm/sec. In other words, the excited atoms at a distance of 1 cm from the cathode are 10^{-8} sec older than the atoms at the cathode itself, the atoms at a distance of 2 cm are 2×10^{-8} sec older, etc. Thus the linear extension of the ray is used as a time scale.

In the second experiment, a spectrograph, viewing the canal ray *sidewise*, records the intensity of the ray as a function of the distance from the cathode. The result is a decay of intensity following an exponential function $I = I_0 e^{-\lambda x}$ (x = distance from cathode, I_0 = intensity near cathode, I = intensity at distance x; λ = empirical factor). The "decay constant" λ is measured, for example, as 1 cm^{-1}. This means that the intensity decays *along each centimeter* to the fraction $1/e$ of its initial value. Since in the first measurement we found the time required to cover 1 cm as 10^{-8} sec, we may say, instead, that the intensity decays *during* 10^{-8} *sec* to

the fraction $1/e$ of its initial value. This is a result of the same type as obtained in the observation of radioactive decay. It may seem confusing to call it a lifetime because we do not observe birth and death of an individual excited atom but make only a statistical observation of the decay of many atoms. In any case, 10^{-8} sec is the order of magnitude of the lifetimes of many atoms in their excited states. For various reasons, this ingenious method furnishes only results of low accuracy.

The very short lifetimes of excited levels here measured explain the fact that no appreciable population of excited atoms or molecules accumulates in electric discharges or fluorescent gases (see Sec. 17.6). At any moment the great majority of all atoms and molecules reside in their normal states except for the very low energy levels that may be reached by thermal collisions.

SUMMARY OF CHAPTER 17

1. In the excitation or ionization by controlled electron impact the limiting kinetic energy of the impinging electron, which is just able to produce excitation or ionization of a certain atom, is measured (method of Franck and Hertz).

2. Electric discharges through gases are classified into non-self-maintained and self-maintained discharges. In the non-self-maintained discharge, the conductivity of the gas is caused by an external agent like X rays or radioactive rays or a hot metal emitting electrons. The self-maintained discharge (arc, spark, low-pressure discharge) starts by a few stray electrons, which are present everywhere. Further carriers of electricity are generated in the gas by electron impact and at the cathode by liberation of electrons due to positive-ion impact.

The cathode ray consists of the electrons liberated from the cathode of the low-pressure discharge by the process just mentioned accelerated by the high potential difference located in front of the cathode. The positive ray (canal ray) consists of positive ions accelerated by the same potential difference shooting through a canal drilled through the cathode.

3. At sufficiently high temperature, excitation and ionization are produced by thermal collisions.

4. An absorption spectrum of a monatomic gas contains only those spectral lines which are connected with the normal state of the atom. A continuous range of absorption starting from the convergence limit of the absorption series, extending toward higher frequencies, indicates ionization of gaseous atoms, *i.e.*, photoelectric effect in the gas. By this process extreme ultraviolet light from the sun ionizes the upper atmosphere of the earth.

Gases show sharp-line absorption spectra (apart from the continuous ranges just mentioned), liquids and solids more or less diffuse absorption

Table 17.1. *Elementary Processes by Which Atoms or Molecules Receive or Give Away Energy of Excitation*

A. Processes by which energy is received

Excitation energy is received from	Experiment	Result of experiment
1. Electron impact ("impact of first kind")	*a.* Electric discharge *b.* Controlled electron impact	Complete spectrum is excited Energy levels excited only up to limit, given by W_k of impinging electrons
2. Thermal impact (another example of "impact of first kind")	Gas burner, oven	At temperatures available at laboratory, preference for low excited energy levels, but no sharp limit
3. Light	*a.* Absorption spectrum observed Exceptional observation: Absorption spectrum observed at highest temperature (solar atmosphere) *b.* Fluorescence spectrum observed, mainly at low pressure *c.* Chemical change due to light is observed *d.* Scattered light may change frequency (Raman effect)	All possible transitions connected with normal level; *i.e.*, principal series Some excited levels contribute absorption spectrum; absorption of Balmer series in solar atmosphere At low pressure the light energy absorbed is re-emitted (demonstration with iodine vapor) *Example:* Decomposition of AgBr in photographic plate Scattering molecule may keep part of incident quantum
4. Chemical energy	Glow of yellow phosphorus; firefly	
5. Transfer from an excited atom ("impact of second kind")	Mixture Hg + Na illuminated by mercury arc, which fails to excite Na directly but does excite Hg	Fluorescence radiation contains Na spectrum; the excitation is limited by the energy 4.88 ev indicating energy transfer from excited Hg to Na in collisions

B. Processes by which energy is given away

Excitation energy given away into	Experiment	Result of experiment
1. Light	Any electric-discharge or fluorescence or high-temperature experiment	Each excited atom has an intrinsic probability of radiation after very short lifetime of excited state

Table 17.1 (*Continued*)

Excitation energy given away into	Experiment	Result of experiment
2. Transfer to other atoms colliding during lifetime of excited state	*a.* Fluorescence quenched by addition of foreign gas (demonstration of iodine with 1 atm air)	Excitation energy transferred into *kinetic energy* (heat produced)
	b. Mixture Hg + Na; (A 5 of this table)	Hg transfers its excitation energy into *excitation energy* of Na
	c. Mixture Hg + H_2, illuminated with mercury arc, exciting the Hg	H atoms produced; Hg transfers its excitation energy into *chemical energy* (dissociation of H_2)

spectra. Of outstanding importance is the absorption spectrum of chlorophyll. The absorption of red sunlight enables the chlorophyll to break up the CO_2 molecules contained in the air and assimilate the carbon atoms. Animal life and industrial activity are maintained almost exclusively by energy ultimately received from the sun by this process.

5. Astrophysics is based largely on the investigation of emission and absorption spectra and their interpretation by the quantum theory.

6. In fluorescence, atoms or molecules that have just been excited by absorption of light reradiate light (mostly of the same or lower frequency) in any direction.

7. Light of a sharply defined frequency, when scattered from molecules of a solid, liquid, or gas, shows shifted spectral lines in addition to the incident spectral line (Raman effect). This is explained by the ability of the molecule to keep a small part of the energy of each incident quantum (shift to low frequencies) or add some of its own vibrational or rotational energy to the quantum (shift to high frequencies). The Raman effect is an important tool in the investigation of molecular vibrations.

8. Some chemical processes produce light (oxidation of phosphorus).

9. The production of chemical processes by light is the basis of photochemistry.

10. An excited atom or molecule when colliding during its lifetime may give away its energy of excitation as kinetic energy, energy of excitation of the other particle, or chemical energy (impacts of the second kind). An example for the last process is given by the sensitization of a photographic plate for yellow or red light.

11. The lifetime of the excited state of atoms has been measured in a canal-ray experiment as about 10^{-8} sec.

PROBLEMS

17.1. *Ionization energy.* The principal series of potassium converges at 2,870A. Compute the energy of ionization of potassium atoms in ev.

17.2. *Lowest excitation energy.* Before the extreme ultraviolet was explored by the vacuum spectrograph, Franck and Hertz measured the excitation potentials of neon and argon as 16.6 and 11.5 volts, respectively. Compute the wave lengths of the corresponding spectral lines. Years later these lines were actually observed.

17.3. *Relation between wave length and energy.* The wave length of a spectral line (in A) times the energy difference between the levels (in ev) is a constant. Compute its numerical value.

17.4. *Inelastic collisions; excitation by positive-ion impact (difficult problem).* A collision in which a part of the kinetic energy is changed to another type of energy is called "inelastic." This applies to excitation of atoms by impact. The lowest excitation energy of neutral helium atoms (mass M), determined by controlled electron impact (Sec. 17.1), is $W = 19.75$ ev. Helium ions He^+, however, of this kinetic energy (velocity u_1), when impinging on neutral helium atoms that are at rest before the impact, fail to cause excitation because a considerable fraction of their kinetic energy is necessarily distributed as kinetic energy between the two particles (the common center of gravity continues its path). How large a kinetic energy is required to enable a He^+ ion to excite the neutral He atom? Consider only the most favorable case of a head-on collision (Fig. 17.14, all motion along a straight line).

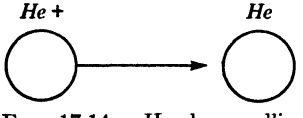


FIG. 17.14. Head-on collision of He^+ ion and neutral He atom.

HINT: (*a*) State the laws of conservation of energy and momentum. They lead to the same equations as in Prob. 14.1, except that in the final state there is the additional energy W. The equations are simplified by equal masses of bullet and target. (*b*) Solve for the final velocities v_1 and v_2 as unknowns. (*c*) The quadratic equations so obtained have real solutions only for values of the initial kinetic energy above a certain limit. This is the limit of kinetic energy the impinging ion must exceed.

17.5. *Light passing through an absorbing body (calculus problem).* This problem is important for its method. The same method will be applied to radioactive decay (Prob. 21.3). It has been observed that light of incident intensity I_0 when passing through a *thin* absorbing layer (thickness Δl) suffers a loss of intensity ΔI, which is approximately proportional to the thickness Δl and the incident intensity I_0. The factor of proportionality α, called "absorption coefficient," is characteristic of the material. (It may depend strongly on the wave length of light.) This approximation is more accurate the smaller the thickness Δl of the absorbing layer. Compute the intensity I_1 transmitted by a *thick* absorbing plate (thickness l_1) on which light of intensity I_0 is incident.

HINT: (*a*) Write the statement for the thin layer as an equation keeping in mind that an *increase* of the thickness l causes a *decrease* of the intensity I. (*b*) Rearrange the equation so that the variable I appears only on the left and the variable l only on the right side. (*c*) The thick plate is supposed to be subdivided into many thin layers of equal thickness Δl, and the equation just written is applied to each layer. In order to express the effect of the thick plate, write the sum of these individual equations. The limits of the two sums so obtained are determined by the consideration that, while the thickness traversed increases from 0 to l_1, the intensity I decreases from I_0 to I_1. (*d*) Go to the limit of vanishing Δl, *i.e.*, replace the two sums by integrals, and perform the integrations. (*e*) Rewrite your result, which contains a logarithm, in terms of an exponential function; express I_1 in terms of I_0, α, and l_1.

CHAPTER 18

PERIODIC TABLE OF ELEMENTS

The periodic system of elements, discovered in 1869, gives a systematic survey of the chemical properties of all elements. In our discussion we do not want to present material properly belonging in a textbook of chemistry since we suppose that the student is familiar with the foundations of that science. Our purpose is to consider the extent to which the theory of the nuclear atom helps us to correlate the chemical properties of the elements with the results of spectroscopy and experiments on controlled electron impact. After a brief survey of certain groups of related elements, we shall try to interpret their chemical behavior jointly with their spectroscopic properties.

18.1. Survey of Some Facts of Chemistry. Certain groups of elements of widely differing atomic weights are chemically closely related. For example, the *alkalies* (Li, Na, K, Rb, Cs) are all metals of low density with the power to decompose water. All are univalent electropositive; *i.e.*, in electrolysis they form singly charged positive ions like Li^+. This property is confirmed in the positive-ray (canal-ray) experiment where, by electric and magnetic deflection, we find ions like Li^+ in great abundance but no doubly charged ions Li^{++}. We conclude that the alkali atom readily loses 1 but not 2 electrons. The *rare gases* (He, Ne, A, Kr, Xe, Rn) form another group of related elements. All are gases except at very low temperatures. They are chemically inert, hence have molecules identical with single atoms. The *alkaline earths* (Be, Mg, Ca, Sr, Ba, Ra) are bivalent electropositive in electrolysis. Correspondingly, in the positive ray they easily show up singly or doubly charged, but not triply charged. The *halogens* (F, Cl, Br, I) are all univalent electronegative; *i.e.*, in electrolysis they form singly charged negative ions. In the canal ray (which in this case we cannot call "positive ray") they readily form the same ions.

In order to define the atomic number, we write all elements in the order of their atomic weights beginning with hydrogen (atomic weight, 1.008), continuing with helium (atomic weight, 4.00), lithium (atomic weight, 6.94), etc. The atomic number is defined as the number of the element counted in this order, 1 for hydrogen, 2 for helium, 3 for lithium, and so on through the whole list of elements.

Mendeleeff and Lothar Meyer (1869) discovered the fact that in the row of elements so written their chemical properties are a periodic function of

their atomic numbers. In other words, the same sequence of neighboring elements occurs over and over again. The simplest example is given by the sequence: a halogen, a rare gas, an alkali, and an alkaline earth, like F, Ne, Na, and Mg.

It is true that, to a minor extent, this regularity is enforced by rearranging the order of the elements at a few places. For example, argon (atomic weight, 39.94) is placed before potassium (atomic weight, 39.10). Later, discussing X-ray spectra, we shall find another powerful argument for this rearrangment. Furthermore, we shall find a certain excuse for it in the discussion of isotopes where it will be evident that the chemical atomic weight is not a property characteristic for the individual atom but for a mixture of atoms.

This periodic occurrence of the same sequence of elements is well represented in a table when we break off the row of elements after each rare gas and begin a new horizontal line, called a new "period," with the following alkali (see Table 18.1 and Appendix 4). In this way of writing, all alkalies are the first elements of their periods, the alkaline earths the second elements, the rare gases the last elements, the halogens the last but one. What we have described is a systematic arrangement of the elements according to their atomic weights and chemical properties and is much older than the theory of the nuclear atom.

Table 18.1. *Periodic Table of Elements*

H																	He
1																	2
Li	Be											B	C	N	O	F	Ne
3	4											5	6	7	8	9	10
Na	Mg											Al	Si	P	S	Cl	A
11	12											13	14	15	16	17	18
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Rb	Sr	Y	Zr	Cb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
55	56	57*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm								
87	88	89	90	91	92	93	94	95	96								

* The asterisk indicates the position of the rare earths here omitted (see Appendix 4).

18.2. Nuclear Atom. We wish to correlate this abbreviated description of chemical properties with our theory of the atoms consisting of positively charged nuclei surrounded by electrons. Of basic importance is the rule stating that the atomic number equals the nuclear charge. This rule is well established: for heavy elements, by the investigation of the scattering of alpha particles; for light elements, by Bohr's theory as applied to He, He^+, Li^{++}, etc. The number of external electrons is the same as the nuclear charge for neutral atoms, less than that for positive ions, and more than that for negative ions. We are interested in the arrangement of these electrons in the normal states of atoms because these are the states that play the greatest part in chemical reactions.

18.3. Stability of Rare-gas Electronic Structures. The rare gases are chemically inert, in strong contrast to their neighbors, the alkalies, which are chemically so active that they can even break up water molecules. The same contrast is quantitatively expressed by comparing the energy-level diagrams, for example, of the first rare gas, helium, and its neighbor, the first alkali, lithium. We are interested only in the energies of excitation and ionization, derived from analysis of the spectra and confirmed by controlled electron impact. They are shown in Fig. 18.1. (We indicate all other energy levels summarily by light lines.) Helium has an excitation energy 11 times as high as lithium and an ionization energy 4.6 times as high. These diagrams may be considered as measuring the high "stability" of the helium atoms since it is plausible to measure the stability of a structure by the energy required to change it. The chemical inactivity of helium is another aspect of this high stability. This is the extreme case of a general rule stating that the rare-gas atoms are much more stable than the alkalies, their successors in the periodic table.

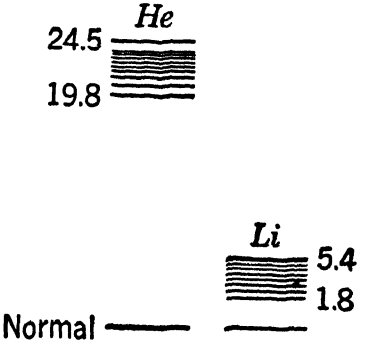


FIG. 18.1. Energies of excitation and ionization of helium and lithium atoms (in electron volts).

What applies to the neutral helium atom applies as well to the lithium positive ion which carries the same number of external electrons since it consists of the nucleus with the positive charge 3 surrounded by 2 electrons. The spectrum of this ion again indicates a special stability. So we may say in general that the electronic structures of the rare gases, which consist of 2 or 10 or 18 or 36 or 54 or 86 external electrons, are particularly stable. The same applies to any ion which, by loss or gain of electrons, has been changed so that it has the same number of external electrons as a rare gas. In any case the addition to the rare-gas structure of one more external electron (as in Li or Be^+ or B^{++}, etc.) produces an electronic structure of

much less stability. For the time being we accept the stability of the electronic structures containing the numbers just listed as an observed fact without explaining the mysterious significance of these numbers (see Sec. 18.9).

We may understand the word "stability" somewhat differently. In nature there is a general tendency toward the most stable configuration. For example, a rock located high up on a slope has the tendency to roll down into the valley, *i.e.*, to its most stable position. Another example is given by an electron that is raised to a high and, therefore, unstable orbit; it has the tendency to fall down toward the nucleus into the stable state. Correspondingly, the great stability of the rare-gas electronic structure, just expressed in terms of energies, suggests that there is in nature a general *tendency toward the rare-gas electronic structure.* Let us tentatively assume this general tendency as our basis for the following discussion of the periodic table.

18.4. Neighbors of Rare Gases and Their Ions. On this basis we easily interpret some facts surveyed in Secs. 18.1 and 18.3. The alkalies have low energies of ionization; in other words, they readily form singly charged positive ions because these ions have the electronic structures of rare gases. For example, Na^+ has the structure of Ne. Correspondingly, the doubly charged ion of an alkaline earth has a rare-gas structure, *e.g.*, Ca^{++} the structure of A. On the other hand, the halogens readily attach 1 electron to their structure in order to reach the rare-gas status, like Cl^- which has the same structure as A. This explains the electronegative behavior of the halogens.

18.5. Polar Molecules and Crystals. The concept of the tendency toward a rare-gas electronic structure explains the structure of a large class of molecules, the "polar molecules." For example, in NaCl vapor the diatomic molecule is presumably formed by a sodium and a chlorine atom bound together because the sodium has lost its excess electron and the chlorine has swallowed this electron to make up its deficiency. Thus a positive ion is formed with the structure like neon and a negative ion with a structure like argon. The Coulomb attraction keeps the two ions together as a molecule.

The same picture applies to numerous molecules. For example, neutral $CaCl_2$ is supposed to consist of a doubly charged positive ion Ca^{++} bound by the Coulomb force to two singly charged negative ions Cl^-. When we consistently attribute to the oxygen atom, the precursor of fluorine, the tendency to swallow 2 electrons and so acquire the rare-gas electronic structure of 10, we understand the structures of CaO, Na_2O, and similar molecules. The hydrogen atom, having 1 external electron, is supposed to have chemical properties similar to the alkalies although the hydrogen positive ion has no electron at all. Assuming this similarity, we consistently

understand the structures of HCl, H_2O, NaOH, and many other molecules.

The general idea is that atoms belonging to the left wing of the periodic table form polar molecules with atoms belonging to the right wing; in any case, positive and negative ions are formed, all with rare-gas electronic structures, and kept together as molecules by the Coulomb attraction. This picture does not explain the structures of all molecules. Those formed of atoms of the same element, like H_2, O_2, N_2, Cl_2, and many others, because of their symmetry, cannot be described by the same idea. They are called "nonpolar" molecules. Their formation is due to other effects not so simply understood and not to be discussed here (see Chap. 26). It should be added that these other effects contribute to the formation of the polar molecules, too, so that our picture gives only one important aspect of the molecular forces without claiming to be complete.

What applies to molecules applies as well to crystals. For example, the rock-salt crystal, NaCl, which forms a simple cubic structure, is thought of as consisting of Na^+ and Cl^- ions, alternating in their positions at the corners of cubes, the whole structure being held together by the Coulomb attraction (see Fig. 19.6). Again, this explains only one type of crystal, the polar crystal, in which atoms of the right and left wings of the periodic table unite. There are other crystals, *e.g.*, iodine, I_2, which, because of their symmetry, cannot be polar and are held together by the same forces as nonpolar molecules, not to be discussed here (see the brief discussion in the chapter on wave mechanics, Chap. 26).

18.6. Ions in Solution. In our discussion of electrolysis (Sec. 8.1) we gave an outline of the Arrhenius theory of electrolytic solutions (1887). Arrhenius assumed that crystals like NaCl when dissolved in water are dissociated into ions Na^+ and Cl^-. This assumption, giving the sodium particles an independent existence and motion in the water, must appear bold to everybody who is familiar with the violent reaction of sodium and water. Arrhenius was forced to make the additional assumption that the sodium ions Na^+ have chemical properties different from those of sodium metal. This assumption is justified by our theory of the periodic table. By attributing to the ion Na^+ a rare-gas electronic structure, we understand that Na^+ is chemically as inert as a rare gas. This applies to all ions in solution. When the sodium ion arrives at the negative electrode, it is neutralized and goes into a reaction with H_2O.

18.7. Metallic Conduction. Finally, our theory contributes to the understanding of metallic conduction. The left wing of the periodic table contains those elements which have one or more excess electrons and which, at the same time, are metallic conductors. The consistent picture is that these electrons are the ones that are given off and, therefore, are free to move and able to carry the electric current. On the other hand, the pre-

cursors of the rare gases, *e.g.*, iodine crystals, are insulators because the halogen atoms have no excess electrons.

18.8. Electronic Structure of Heavy Atoms. The only hypothesis we need for our elementary interpretation of the periodic table is the general tendency toward a rare-gas electronic structure. A more detailed picture is suggested by the high ionization energy belonging to the rare gases and the much lower values belonging to the alkali atoms, each containing 1 additional electron. Suppose a lithium nucleus endowed with the positive charge 3 is supplied, to begin with, with only 2 electrons. The great stability of this structure suggests that the electrons are close to the nucleus. When the third electron is added and so a neutral lithium atom formed, this last electron goes into a position from which it is comparatively easily torn off. This fact suggests that it is not located in a position so close to the nucleus as the two other electrons. The same general statement applies to the fourth electron in the neutral Be atom. This comparison of stabilities indicates that there are only two places provided for electrons very close to the nucleus. If the nucleus has a larger nuclear charge than 2, it can assemble additional electrons only in more distant orbits. In other words, the two innermost electrons form a "closed shell" unable to accept more electrons. We do not discuss the cause for this limitation, we only infer this property of the shell from the comparison of the rare gas and the alkali. The same argument applies to any rare gas and the alkali that follows it in the periodic table.

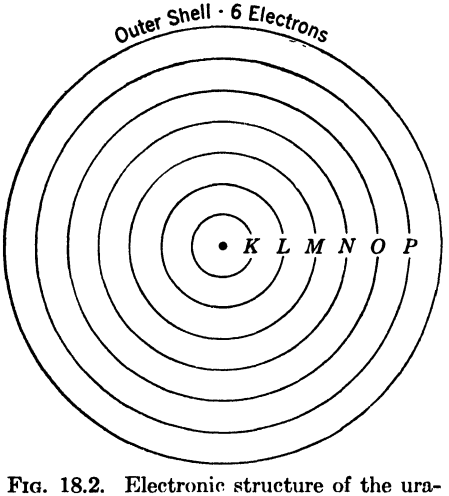


FIG. 18.2. Electronic structure of the uranium atom. The designation of the "shells" as K, L, M, N, O, and P will be introduced in the section on X-ray spectra (Sec. 19.2*b*).

Suppose we gradually build up the electronic structure of uranium (atomic number, 92) starting from the nucleus, allowing 1 electron after the other to join (Fig. 18.2). Then the first two electrons form a "shell" which, for unknown reasons, is closed, *i.e.*, excludes any additional electron. The third electron takes a place farther away and so starts the structure of the second "shell" of electrons, which in turn is closed when it contains 8 electrons (total number of electrons = 2 + 8) as is indicated by the rare-gas nature of neon, element number 10. The eleventh electron, because of its low energy of separation, is assumed to reside farther away, starting the structure of the third shell of electrons, etc. Finally, as far as this argu-

ment goes, a heavy element like uranium, in its neutral state, is supposed to have most of its 92 electrons in closed groups, easily computed from the rare-gas structures as containing 2, 8, 8, 18, 18, and 32 electrons, respectively. (In Sec. 18.9 it will be reported that, in the more detailed treatment, these numbers are somewhat modified.) In the discussion of X-ray spectra (Sec. 19.2*b*) the conventional designation of these shells by the letters K, L, M, N, O, and P will be introduced. The remaining 6 electrons of the uranium atom form the surface shell which is far from completed.

At the present stage of the argument it remains unexplained why just the numbers mentioned are endowed with this mysterious power and, furthermore, why there is no stable element heavier than element 92, uranium. For many years it was guessed that the nuclei heavier than uranium spontaneously disintegrate like radium. This was suggested by the fact that all radioactive elements are located near the end of the periodic table. This guess was finally proved to be correct by the fact that elements beyond uranium have recently been manufactured and actually proved unstable, all being radioactive. This will be discussed in the chapter on Artificial Transmutation (Chap. 22).

One may well object that so detailed a picture of the electronic structure of atoms is not warranted by such scanty evidence as the contrast between the rare gases and the alkalies. However, this picture will help greatly in the understanding of X-ray spectra presented in the next chapter. Thus these spectra will provide a powerful confirmation of the idea of electron shells as constituting the atoms.

18.9. Report on Further Developments. Since in our discussion of atomic spectra (Sec. 16.1*e*) we did not systematically introduce the elaborate system of quantum numbers required for the description of more complex spectra, we shall only briefly report on the relation between the periodic properties of atoms and their spectra. The more detailed discussion is all based on the picture of the shells of electrons. For example, the spectra of the alkalies, the simplest atomic spectra except that of atomic hydrogen, are satisfactorily explained as due to transitions of *one* easily excited electron. In the lithium atom (atomic number, 3) this electron revolves not simply about the nucleus but about a core consisting of the nucleus of positive charge 3 closely surrounded by the 2 innermost electrons representing the "K shell"; hence this core as a whole has the resulting positive charge 1. Correspondingly, the alkaline earths, which are expected to have 2 electrons outside of a rare-gas structure, show spectra explained in detail as due to *two electron systems*. Thus the investigation of atomic spectra confirms our theory of the shell structure of atoms.

The theory of the periodic table has been developed with the help of spectroscopy far beyond the range just discussed. Progress has been made on the basis of the theoretical interpretation of complex atomic spectra.

In this theory, briefly reported in Sec. 16.1*e*, the assumption is made that each electron, like a planet revolving about the sun, has an angular momentum due to its *orbital motion* and an additional angular momentum due to its *spin about its own axis.* These momenta as well as the mutual orientations of all momenta are described by quantum rules. Similar quantum rules describe the orientation of the resulting angular momentum in a magnetic field. The orientations are described in terms of the quantum numbers originally introduced for the interpretation of atomic spectra. In particular, the quantum number n, introduced by Bohr, largely determines the energy of the electrons in the various shells, $n = 1$ characterizing the lowest shell, which, in the analysis of X-ray spectra (Sec. 19.2*b*), will be given the name K shell, $n = 2$ characterizing the second shell, the L shell, etc. This system may impress the student as all too arbitrary although it is justified by the fact that it explains a vast material of spectroscopic observations.

The confidence in this sytem of quantum numbers is greatly strengthened by the fact that the same system, although introduced for the interpretation of spectra, is surprisingly successful in predicting the mysterious numbers constituting the rare gas electronic structures (Sec. 18.8). This requires the additional simple assumption, known as the "Pauli exclusion principle," that within 1 atom no electron can have all its quantum numbers identical with those of any other electron (1925). On this basis Pauli was able to demonstrate that only 2 electrons can be accommodated in the lowest shell and only 8 in the second shell, in agreement with the numbers of elements contained in the first and second periods. Some apparent discrepancies in the higher shells are well explained by spectroscopic and chemical properties of atoms and by no means detract from the validity of the principle.

The student may be disappointed that here one mystery, the preferred atomic numbers of the rare gases, is replaced by another, the quantum numbers and the Pauli principle. The student may feel that the "understanding" ultimately should imply an explanation based on the familiar laws of classical physics. However, there seems to be no chance of invoking classical physics in the explanation of atomic structure. All we can hope for is to reduce the atomic theory to as few and as simple laws as possible, capable of predicting as large a group of observed phenomena as possible. Keeping this point of view in mind, we recognize the great progress due to the discovery that the same principles introduced for the description of spectra also account for the chemical properties of the elements.

SUMMARY OF CHAPTER 18

When all elements are written in the order of their atomic weights, certain sequences of elements appear periodically, in particular the sequence

Table 18.2. Periodic Table of Elements

Observed Fact	Theory
A. Nuclei.	
Scattering of α particles by gold foil	Rutherford's nuclear atom
Scattering of α particles compared for different substances.	Atomic number = nuclear charge (positive)
Spectra of H, He^+, Li^{++}, Be^{+++}, etc.	= number of external electrons of neutral atom
B. Rare gases	
Chemical inactivity; highest excitation and ionization energies	Stability of rare-gas electronic structure. *The hypothesis is assumed that in any case the structure of* 2, 10, 18, 36, 54, *or* 86 *outer electrons is particularly stable*
C. Heavy atoms as built up of electrons.	
Alkali: univalent; electropositive; in electric discharges only Na^+, never Na^{++} or Na^-; simplest spectra of neutral atoms, except H; follow rare gases in periodic system	Alkali atom has rare-gas electronic structure + 1 outer electron
Alkaline earth: bivalent; electropositive; in electric discharges Mg^+ and Mg^{++}; follow alkali in periodic system	Alkaline earth has rare-gas structure + 2 outer electrons
Halogen: univalent, electronegative; in electric discharges Cl^-; precede rare gas in periodic system	Halogen atom has rare-gas electronic structure − 1 outer electron
Oxygen group: bivalent, electronegative; precede halogens in periodic system	Atom of oxygen group has rare-gas electronic structure − 2 outer electrons
D. Certain molecules and crystals.	
Vapor molecules: NaCl; H_2O; NaOH Crystals: NaCl; H_2O; MgO	Polar molecules and polar crystals consist of positive and negative ions (each with rare-gas electronic structure) kept together by Coulomb attraction
E. Electrolysis.	
Faraday's laws	Theory of electrolytic dissociation; NaCl, for example, dissociates into Na^+ and Cl^-. Both ions are chemically inactive, different from the neutral atoms
F. Metallic state.	
The elements following rare gases in the periodic system are metals (high electric conductivity)	In the liquid and solid state the elements following the rare gases give off electrons. These represent the free electrons responsible for the electric conductivity of the metals

given by an element of the oxygen group, a halogen, a rare gas, an alkali, an alkaline earth.

Their properties are interpreted by the theory of the nuclear atom and the additional hypothesis that there is a general tendency toward the rare-gas electronic structure. This assumption explains the valence of the neighbors of the rare gases, their behavior in electrolysis and gas discharges, and the formation of polar molecules and crystals. This interpretation leads to a detailed picture of heavy atoms as consisting of several "shells" of electrons with each rare gas indicating the completion of such a shell. This picture will be confirmed by X-ray spectra.

CHAPTER 19

X RAYS

Our discussion now turns to phenomena which, at the surface of the earth, are not evident in nature but are observed only as products of a highly developed laboratory technique. In the first section we shall study the properties of X rays, largely by comparing them with light. Here we shall find sharp-line spectra, related to the "optical spectra" discussed in the preceding chapters. In the second section we shall try to derive evidence from these line spectra regarding the electronic structure of atoms and so supplement our theoretical picture, which so far has been based largely on optical spectra and chemistry.

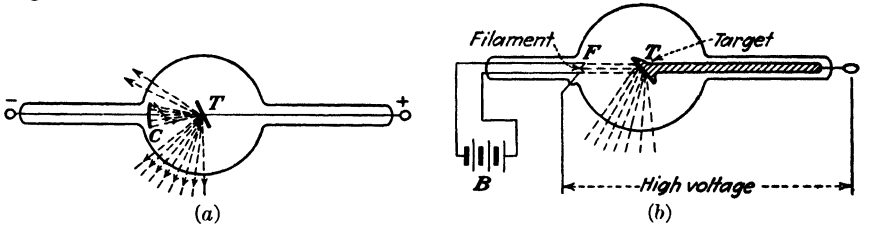


FIG. 19.1. X-ray tubes. (*a*) Electric discharge through a gas of about 1/1,000 mm pressure; (*b*) highly evacuated tube, electron current supplied by glowing filament; "Coolidge tube."

19.1. Properties of X Rays. *a. Discovery.* Roentgen (1895) began the first publication of his new discovery by describing the observation as follows:

When the discharge of a large induction coil passes through an evacuated discharge tube covered by black cardboard, one sees in the darkened room the fluorescence of a paper screen which is painted with platinum barium cyanide, irrespective of which side of the screen is turned toward the discharge tube. The fluorescence is visible over distances up to two meters.

Roentgen made sure that a new kind of radiation of a penetrating power heretofore unknown emanates from glass or metal when hit by cathode rays. This radiation, which he called X rays, was being studied all over the world less than a month after his first publication and is now familiar to all in the form of the X-ray photograph of a hand in which the bones are sharply visible because they are less transparent than the soft tissue.

b. X-ray Tubes. There are two types of X-ray tube: gas-filled and high-vacuum tubes. Gas-filled tubes (Fig. 19.1*a*) are similar in construction to Roentgen's original apparatus except that a block of heavy metal like

tungsten is provided, which, serving as a target for the cathode ray, emits the X rays. These tubes are rarely used any more. At present, high-vacuum tubes, first designed by W. D. Coolidge, are almost exclusively used. In these the electrons are supplied by a glowing cathode and accelerated toward the target by high voltage. This construction has the great advantage that the potential difference accelerating the electrons can be varied entirely independently of the current hitting the target which is a function of the temperature of the cathode. Figure 19.1*b* shows an X-ray tube of this type. At present X-ray tubes are operated with potential differences up to a million volts or even more.

c. Effects Produced by X Rays. Roentgen very thoroughly explored the properties of the newly discovered radiation. We may briefly list the properties as follows:

X rays produce light on a fluorescent screen.

They affect a photographic plate in the same way as visible light does.

On metal surfaces they produce the photoelectric effect.

They render air and any other gas through which they pass conducting by ionizing the molecules. (This effect can easily be demonstrated by aiming a bundle of X rays, limited by lead diaphragms, across the space between the plates of a charged condenser in air and observing the discharge.)

The absorption of X rays depends on the atomic weight of the absorber, elements of high atomic weight showing much stronger absorption than those of low atomic weight.

X rays are diffusely scattered by all substances.

X rays are not deflected by electric or magnetic fields.

The most easily evident biological effect is the production of erythema, *i.e.*, reddening of the skin, which leads to permanent destruction of the tissue when a larger dose is applied. Another biological effect of X rays is the increase in the rate of mutation, which represents a variation of the offspring making them different from the parents.

Roentgen also investigated whether X rays showed any of the properties of light other than rectilinear propagation. His results were all negative. He found no reflection from mirrors, no refraction by glass or any other substance, no diffraction by gratings, and no polarization. Later we shall see that a refined technique has revealed all these effects, most of them only in minute traces.

d. Intensity, Dose, and Hardness. The outstanding characteristics of X rays are their intensity and hardness (or penetrating power). In order to measure the penetrating power, first we must measure their intensity. Although the conventional method fails to give results as complete as the physicist wants them, we shall describe it in detail since it is important for medical purposes as the measurement of the X-ray dose.

Arbitrarily we measure the intensity of X rays by their effect of ionizing

air. This effect is measured by the discharge of a plate condenser when an X-ray beam is passing through the air between the plates. The plates themselves are protected from the X rays in order to exclude photoelectric effect on the metal surfaces. The simplest wiring diagram of an ionization chamber is given in Fig. 19.2. Before the exposure to X rays the insulated plate of the condenser is charged; then the rate of the discharge of the electroscope gives a measure of the intensity of the rays. As the practical unit of X-ray quantity or "X-ray dose," 1 roentgen is defined as follows: The roentgen is a quantity of X radiation such that the associated corpuscular emission of 1 cc air under standard conditions produces ions carrying 1 electrostatic unit of electric charge of either sign. The corresponding unit of X-ray *intensity* is 1 roentgen/sec. From the point of view of physical measurements, this definition is inadequate. It has been found that X rays, depending upon the construction and operation of the tube, have penetrating powers varying over a wide range. (Later we shall see that the penetrating power, called the "hardness," depends upon the wave length and, therefore, is analogous to the color of visible light.) Very penetrating rays, called "hard" X rays, deliver much less energy to the air of the ionization chamber than soft X rays, *i.e.*, rays of low penetrating power. Hence, when observing the rate of the discharge, we fail to differentiate between hard rays of high intensity, delivering only a small fraction of their energy, and, on the other hand, soft rays of low intensity delivering most of their energy. The physicist would prefer to base the measurement of the intensity, like that of the intensity of visible light, on the total energy carried per square centimeter per second. But this cannot easily be done since we cannot easily construct a "black body" for X rays, *i.e.*, a body that is sure to absorb them completely. For medical purposes, however, the situation is different. It is assumed that the biological effect of X rays is due to the ionization caused in the tissue. Later, in the discussion of absorption spectra (Sec. 19.2*c*), we shall find that for any hardness of X rays, air shows approximately the same ionization as the substances of the animal body. Hence for this special purpose the ionization of the air is an adequate indicator of the quantity or "dose" of X rays. The doctor applying X rays, of course, must know the penetrating power of his rays in order to judge whether they will be effective only near the surface of the body or at greater depth as well.

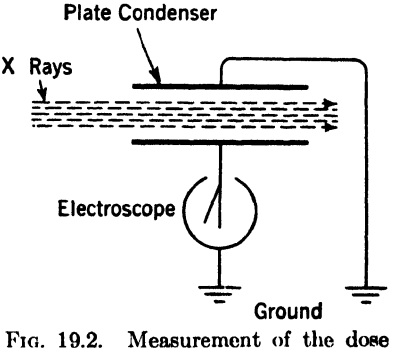


FIG. 19.2. Measurement of the dose and intensity of X rays by the ionization chamber.

The instrument described (Fig. 19.2), although based on the arbitrary choice of air as the absorbing gas, serves for the measurement of the penetrating power of X rays. For this purpose layers of various thicknesses are placed between the source and the instrument. In some cases the absorption so produced can be represented by the well-known formula describing the absorption of light in colored glass:

$$I = I_0 e^{-\mu d}.$$

where I_0 = incident intensity
I = transmitted intensity
d = thickness of absorbing layer
μ = absorption coefficient characteristic of the material and the type of X ray

In many other cases it is found that the transmitted intensity I plotted against the thickness d of the absorbing layer shows a more complicated curve, which can be analyzed as the superposition of two (or possibly more) exponential curves, hence mathematically represented by a formula like $I = I_1 e^{-\mu_1 d} + I_2 e^{-\mu_2 d}$. This observation indicates the superposition of two types of X radiation. Later we shall find, with better techniques for analyzing X rays, that these two or more types consist of X rays of different wave lengths.

When the absorbing power of various elements for X rays is described, the situation is much simpler than for visible light. The absorption of X rays by a certain element depends only on the presence of this element irrespective of its chemical combination or its physical state, be it gaseous, liquid, or solid. Therefore, we easily describe the absorption of X rays caused by any element by stating its mass-absorption coefficient $\mu_m = \mu/\rho$ where μ is the absorption coefficient as defined above and ρ the density. This definition saves the trouble of giving separate figures for the gas, liquid, solid, and various compounds. The mass-absorption coefficient, however, depends strongly upon the quality of the X rays, as we shall see in Sec. 19.2c. The usefulness of this new definition will be evident in Prob. 19.3.

e. Polarization. Through many years the nature of X rays remained unknown. Considering their high penetrating power it seemed impossible to explain them as rays of *corpuscules*. On the other hand, at the outset, no indications of a *wave* nature could be found. In the next three sections, following the historical development, we shall describe the gradual discovery of the various wave properties, most important of which is the discovery of X-ray diffraction.

Within the ten years following Roentgen's discovery no new effect of fundamental importance was found until, in 1906, Barkla discovered the polarization of X rays. His argument is based on the classical theory of the polarization given to transverse waves by scattering. The basic idea, which here is applied to an atom scattering light, is that an antenna emits

energy with the maximum intensity in its equatorial plane and zero intensity along its axis (Fig. 19.3). Light from an X-ray tube, traveling in the horizontal plane, is incident on scattering material. Let us tentatively draw conclusions from the assumption that X rays consist of transverse waves, capable of being polarized like visible light. Presumably the primary ray, *i.e.*, the ray coming from the X-ray tube, is nonpolarized. The transverse electric force present in this ray starts the vibrations of charged particles in *any direction perpendicular to the ray.* Thus these particles scatter radiation. A ray scattered in a direction perpendicular to the primary ray (see the scattered ray indicated in the horizontal plane of the figure) is expected to be polarized because only the vertical, not the horizontal, electric vibration radiates in the direction considered. This polarization is discovered by a second scattering process. In the atom on the right side the incident ray, since it is polarized, starts *only a vertical vibration.* This radiates with full intensity everywhere within the horizontal plane and with zero intensity in the vertical direction. Here, finally, we predict an observable effect: The theory, based on transverse waves, predicts for the second scattering process a *preferred intensity* in a certain direction and zero intensity in a direction normal to it. The observation first made by Barkla confirms this prediction and so proves the polarization of X rays, leading us to infer that X rays have the same character as light because light shows the same characteristic polarization.

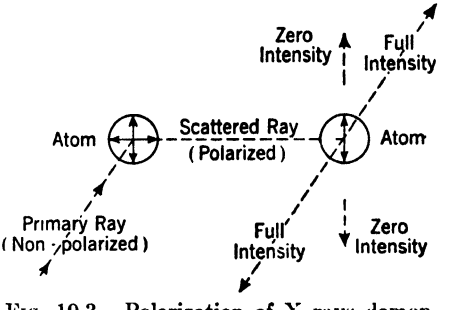


FIG. 19.3. Polarization of X rays demonstrated by double scattering. All rays travel in the horizontal plane except those marked "zero intensity."

f. Diffraction; X-ray Spectrometer. In the endeavor to ascertain the nature of X rays the diffraction through very narrow slits was explored (Walter and Pohl, 1909). Only small traces of an effect presumably due to diffraction were found which, if interpreted by the wave nature of X rays, led to a wave length as short as 4×10^{-9} cm, *i.e.*, about 1/10,000 of the wave length of visible light. Although no reliable conclusion could be drawn from these experiments, they were of importance in that they started von Laue on the way to his discovery of diffraction of X rays by a crystal. Von Laue's argument was as follows. The simple theory of diffraction by an ordinary, optical grating, manufactured on the ruling machine, indicates that the distance between adjacent grooves should be somewhat larger than the wave length of the light to be analyzed. If the distance is smaller, no interference maxima are obtained. On the other

hand, if it is much larger, these maxima are placed so close together that the dispersion is small. Hence for the analysis of X rays we wish to rule a grating with the grooves as close together as, say, 10^{-8} cm. Unfortunately this is technically impossible (see Sec. 19.1*h*). However, the mutual distances of the *atoms in a crystal* are just of this order. Hence one may expect that the scattering of X rays by all the atoms, regularly spaced in a crystal, should lead to interference maxima in certain preferred directions, comparable to the interference maxima, *i.e.*, the spectral lines produced by a ruled grating.

The experiment of Friedrich, Knipping, and von Laue is sketched in

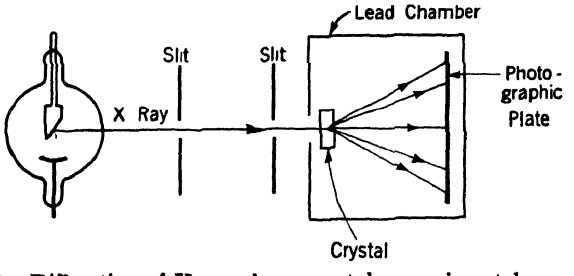


FIG. 19.4. Diffraction of X rays by a crystal; experimental arrangement.

Fig. 19.4. A pencil of X rays, narrowed down by two small circular diaphragms, is incident on a zinc blende crystal. As anticipated, the photographic plate, placed at some distance behind the crystal, shows a striking and complicated diffraction pattern (Fig. 19.5). This important discovery proves the wave nature of X rays and opens up two avenues of research. With a given crystal of known structure, X rays from various sources can be analyzed, thereby leading to X-ray spectroscopy, a field nowadays as well developed as optical spectroscopy and equally important for our knowledge of atomic structure. On the other hand, with X rays of a known wave length various crystals may be investigated resulting in a detailed knowledge of crystal structure. We are not concerned with crystal structure and shall discuss only X-ray spectroscopy.

In order to derive the wave lengths from the diffraction pattern observed we shall give the argument of W. L. Bragg. Suppose that X rays are incident on a cleavage face of a crystal, *e.g.*, the face of a simple cubic crystal like sylvite (KCl) shown in Fig. 19.6. We shall prove that, for a given wave length, the ray incident at some preferred angle is diffracted *at the same angle*, *i.e.*, apparently reflected. We consider the scattering of a narrow pencil of X rays (wave length λ) incident on a cleavage face of KCl at an angle θ with the face (not the normal to the face as usually defined in optics) as shown in Fig. 19.7. This narrow pencil enters the crystal and is scattered by all its atoms. Furthermore, rather arbitrarily, we

consider the scattered ray leaving the face *at the same angle* θ. (This will be justified later.) Constructive interference takes place, hence an appre-

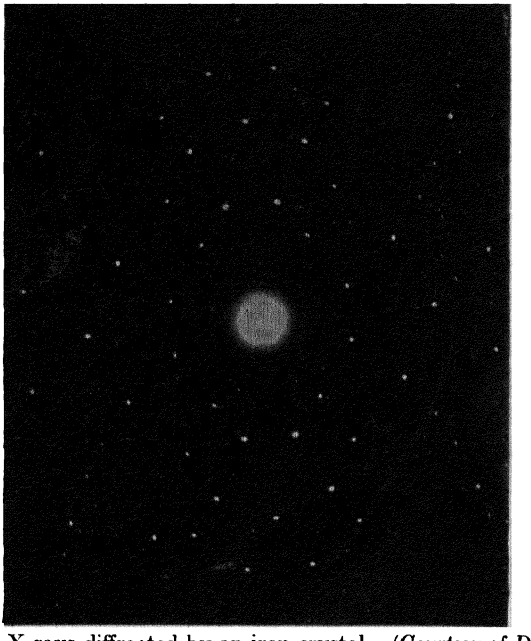


FIG. 19.5. X rays diffracted by an iron crystal. (*Courtesy of Dr. G. L. Clark.*)

ciable intensity shows up when rays scattered *from all atoms* show differences in the distances traveled of λ, 2λ, 3λ, ... We compute the path difference of two rays belonging to the same parallel bundle, incident and

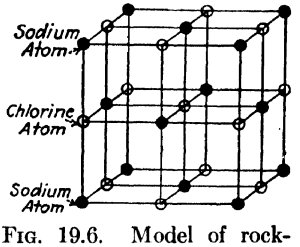


FIG. 19.6. Model of rock-salt crystal; simple cubic crystal.

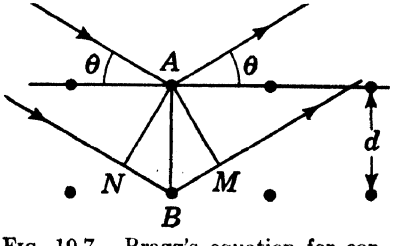


FIG. 19.7. Bragg's equation for constructive interference of X rays; d = grating constant, θ = angle between X ray and crystal plane.

diffracted under the same angle θ, aimed at two adjacent atoms: atom A in the surface layer and atom B in the next lower layer. From atom A we construct the two normals, AN and AM, on the other ray. Then the

path difference equals $NB + BM$. By a simple geometrical consideration we find $NB + BM = 2d \sin \theta$. Hence, for this pair of rays the condition for constructive interference is

$$2d \sin \theta = n\lambda \tag{19.1}$$

where n is any integer. This equation, called "Bragg's" equation, is as important for diffraction of X rays by a crystal as the familiar similar equation for diffraction of light by a grating.

The conventional derivation of Bragg's equation just given should be supplemented by the following argument. Anybody familiar with the ruled grating used for optical spectra may ask: Why do we *presuppose* that the angle of diffraction equals the angle of incidence? Why don't we consider other combinations of angles for which again the path difference would be λ, or 2λ, or 3λ, etc.? We must add another condition for constructive interference. The argument based on Fig. 19.7 is too special in that it considers only the rays scattered by any two atoms, A and B, located on a line *normal to the surface.* In addition, for constructive interference, we must postulate that, at the same angles of incidence and diffraction, *all other atoms* of the crystal add their contributions. This occurs only if the angle of diffraction equals the angle of incidence, *i.e.*, for the reflected ray.

Although geometrically the diffracted ray follows the law of reflection, the process taking place here is widely different. *Reflection, e.g.*, on a metal surface, takes place at the surface proper and requires a well-polished surface. On the other hand, X-ray *diffraction* is a process taking place within the body of the crystal although usually in a layer close to a surface.

In order to compute the distance d between adjacent atoms in a cubic crystal (Fig. 19.6), we equate the density ρ of the crystal which is easily measured to the total mass of all atoms contained in 1 cm³ which is easily computed. The chemical atomic weights of the 2 atoms, for example K and Cl are called m_1 and m_2, hence the average atomic weight of K and Cl = $(m_1 + m_2)/2 = m/2$, where m = molecular weight of KCl. Then we argue, considering Eq. (2.3):

Number of atoms per cm along edge	$= 1/d$
Number of atoms per cm³	$= (1/d)^3$
Mass per cm³	$= m/2Nd^3 = \rho$

Hence,

$$d^3 = \frac{m}{2N\rho} \tag{19.2}$$

Here we presuppose that KCl has a *simple cubic* structure. As a matter of fact, there exist two other types of cubic structure, which, however, are ruled out because, for crystal planes of different orientations in space, they have different values of the grating constant d. We shall not discuss this distinction in detail.

Bragg's equation for the crystal grating, although superficially resembling the equation for the ruled grating, is fundamentally different and leads to

a different operation of the spectrometer. This will be evident from a comparison of the two types of grating. Suppose that light of one wave length λ is incident on a *ruled grating* (d = distance between grooves). Constructive interference takes place if

$$n\lambda = d(\sin \alpha - \sin \beta)$$

where n is an integer, α and β are the angles of incidence and diffraction, respectively. (Here we do not suppose the special case of normal incidence, $\alpha = 0$, which leads to the simpler equation given in elementary textbooks.) When we arbitrarily select the angle of incidence α, for any values of λ and n we can compute the angle β, *i.e.*, the position of the spectral line. Hence for a stationary grating and slit we can observe all spectral lines. This is important for the ruled grating as used for the investigation of optical spectra.

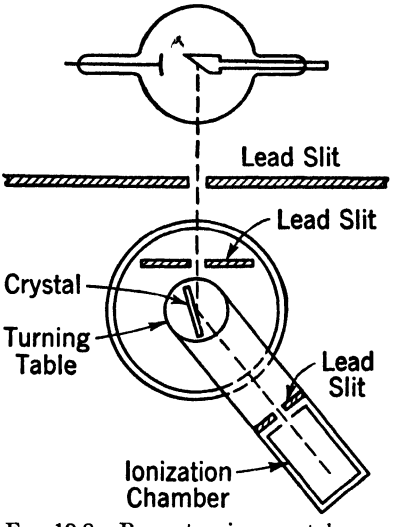


FIG. 19.8. Bragg turning-crystal spectrometer. The ionization chamber is turned through twice the angle through which the crystal is turned.

The situation is different for the *crystal grating* (crystal constant = d). Again we suppose that light of one wave length λ is incident. The condition for constructive interference, *i.e.*, Bragg's equation, contains only the one angle θ, the same for incidence and diffraction. Hence for given values of n, λ, and d the angle θ is determined. This means that the spectral line appears on the photographic plate only for the special position of the crystal described by this angle. If the spectrum consists of several spectral lines, we must turn the crystal in order to obtain the spectral lines successively on the photographic plate. The order n is easily determined since the first order belongs to the spectrum recorded at the smallest angle θ.

This discussion leads to the construction of Bragg's turning crystal spectrometer (Fig. 19.8). The X rays emanating from the target T are narrowed down to a thin beam by two slits. This beam is incident on the turning crystal, and the diffracted beam leaving the crystal under the same angle is registered on the photographic plate. Instead of the plate, an ionization chamber (Fig. 19.2) or Geiger counter (see Sec. 21.1) may serve for recording the ray. The X rays are admitted to one or the other recording device by a slit so narrow that only a thin beam of them can pass through. When the crystal is turned, the recording device must be

turned by twice the angle since the diffracted ray leaves the crystal in a direction as if it were reflected.

A different technique, which dispenses with the turning of the crystal, was introduced independently by Hull and by Debye and Scherrer (1916). In the Bragg spectrometer (Fig. 19.8) the incident beam of X rays is limited by two slits, hence occupies a part of the plane defined by the two parallel slits. This plane intersects with the reflecting plane of the crystal in a line about which the crystal is turned by the operation of the spectrometer. If the reflected beam is monochromatic, it forms on the photo-

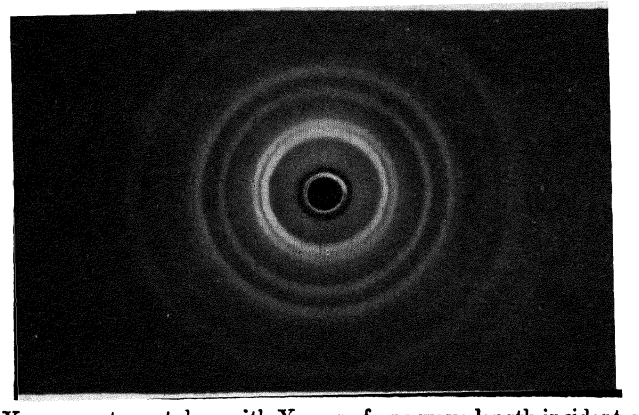


FIG. 19.9. X-ray spectrum taken with X rays of one wave length incident on aluminum powder (photographic positive). The black circle masks the spot of the direct X-ray beam. (*Courtesy of B. E. Warren.*)

graphic plate two spectral lines symmetrically placed on both sides of the direct beam, which may be called the "zero-order" spectrum. (Here we suppose that the turning crystal of Fig. 19.8 is used for reflecting the X rays both to the right and to the left.) Now let us suppose that the incident beam is limited not by slits but by two very narrow holes, hence represents a narrow pencil. Thus each spectral line shrinks to a very small spot which still has the same distance from the zero order, itself representing only a small spot. But now the definition of the axis about which the crystal is turned loses significance so that we may as well turn it about *any axis* passing through the point where the pencil of rays hits the crystal. When we turn the crystal about very many different such axes in succession, all spectral spots so produced, each pair belonging to a certain direction of the axis, merge and so form a continuous circle about the direct beam. The various circles observed are due (1) to different wave lengths present in the spectrum, (2) to different orders of interference, and (3) to reflections on different crystal planes. Instead of wiggling one crystal, a crystal powder is used in which crystals of practically all possible orientations are present (Fig. 19.9).

The crystal-powder analysis can be carried out with those numerous crystals which are available only in small pieces or in powder form. Hence this method is largely used for crystal analysis. However, the problem we are most interested in, *i.e.*, the analysis of various X-ray spectra, is best solved by the turning-crystal method in which one of the standard crystals, rock salt or, more commonly, calcite, is used.

g. Other Optical Properties. Before discussing the important results obtained with the turning-crystal X-ray spectrometer, we shall finish the discussion of the optical properties of X rays. In addition to polarization and diffraction, traces of refraction and reflection have been found. In high-precision determinations of X-ray wave lengths it was discovered that the different orders ($n = 1, 2, 3$) did not yield exactly the same results. This was explained by the assumption that within the crystal the wave length differs slightly from the value it has outside the crystal because the *index of refraction* differs slightly from unity. This explanation led to a measurement of the index of refraction by a technique much more highly developed than that of Roentgen who, in 1896, failed to find any refraction of X rays. Glass, crystals, and metals have indices of refraction slightly smaller than 1. For example, the index of refraction of crown glass for X rays ($\lambda = 0.708$A) has been determined to be $n = 0.99999836$. The very small deviation from unity explains why the effect escaped the detection by the less highly developed technique of Roentgen.

The fact that the index of refraction is smaller than unity leads to the prediction that *total reflection* should take place when X rays are incident in air on a glass surface. It is remembered that *total reflection* directly follows from the law of refraction

$$\frac{\sin \alpha}{\sin \beta} = n$$

where α = the angle of incidence, say, in air
β = the angle of refraction, say, in water
n = the index of refraction characteristic for the transition from air to water.

When α varies between 0 and 90 deg, the angle β observed in the water varies only between 0 and a limiting angle β' given by $\sin \beta' = 1/n$. For any angle of incidence α only a part of the light intensity enters the water, the balance is reflected. When light strikes the same surface coming from under water, some of the intensity can get out into the air only if β is between the same limits. For larger values of β, *i.e.*, for angles of incidence under water approaching grazing incidence, no light at all can get out and the total intensity goes into the reflected light. This is total reflection. For X rays, the unusual situation prevails that the transition *from air to glass* has an index of refraction smaller than unity, although

only very slightly smaller. Thus Compton predicted that total reflection of X rays should occur within a small angle of a few minutes near grazing incidence. Actually he found that within this narrow range the surfaces of glass and metals reflect X rays.

h. Determination of the Electronic Charge. This discovery led a step farther. On a metal surface a grating is ruled of the same type as the well-known Rowland grating. At grazing incidence X-ray spectra are measured by exactly the same technique as had been applied through decades to optical spectra. It is true that the resolving power of these gratings is not so high as that of crystals because the grating constant is much larger than the wave length of the X rays. Nevertheless X-ray wave lengths have been measured with ruled gratings with a precision of a few parts in 100,000.

Bäcklin (1928) used this new application of the ruled grating for an independent determination of the electronic charge. The aim of his experiment will be clear when we recapitulate the argument based on the measurement of the electronic charge by the oil-drop experiment.

1. Measure the electronic charge ϵ.

2. Measure the Faraday constant F. Compute Avogadro's number N from $F = N\epsilon$ [Eq. (8.3)].

3. Measure the density ρ of a crystal. Compute the distance d between atoms from $d^3 = m/(2N\rho)$ [Eq. (19.2)].

4. Measure the angle θ of X-ray diffraction with the Bragg spectrometer. Compute the wave length λ from $n\lambda = 2d \sin \theta$ [Eq. (19.1)].

On the other hand, the new method starts from the measurement of the wave length λ with the *ruled grating*, the constant of which is given by the adjustment of the ruling engine. Then the measurements and equations listed above are applied in the reverse order and so d, N, and, finally, the electronic charge ϵ are computed. The result deviated from the result of the oil-drop experiment by 0.6 per cent. It turned out that the latter value needed a minor correction since the value applied for the viscosity of air was slightly in error. This led to a full agreement of the results obtained by the two entirely different methods.

i. Continuous and Line Spectra. Von Laue's discovery of X-ray diffraction and Bragg's construction of the turning-crystal spectrometer opened up the wide field of X-ray spectroscopy. A typical X-ray spectrum is given in Fig. 19.10. It consists of a continuous spectrum on which sharp lines are superimposed. The continuous spectrum shows a strikingly sharp limit on the short wave-length side depending only on the voltage supplied to the X-ray tube, not on the material of the target. We shall study the sharp-line spectrum which is characteristic of the material of the target in the section on properties of atoms as revealed by X rays (Sec. 19.2). In the present section we shall investigate the continuous spectrum, which is independent of the material of the target.

The continuous spectra emitted from a tungsten target at various potential differences are plotted in Fig. 19.11*a*. The curves show that with increasing energy of the electrons the sharp limit is shifted to shorter wave lengths, *i.e.*, higher frequencies. (The superimposed sharp-line spectrum of tungsten does not show up since, under the conditions of this experiment, it is located at longer wave lengths, not shown by the figure.) From the data given in the figure, one finds the relation stating that the limiting frequency ν_l of the spectrum is proportional to the potential difference V accelerating the electrons (Fig. 19.11*b*). The factor of proportionality turns out to have the value ϵ/h (ϵ = charge on the electron; h = Planck's constant). Hence the experiments lead to the simple law

$$h\nu_l = \epsilon V \qquad (19.3)$$

called the law of Duane and Hunt (1915). Taking this law for granted Duane used it for one of the most precise determinations of

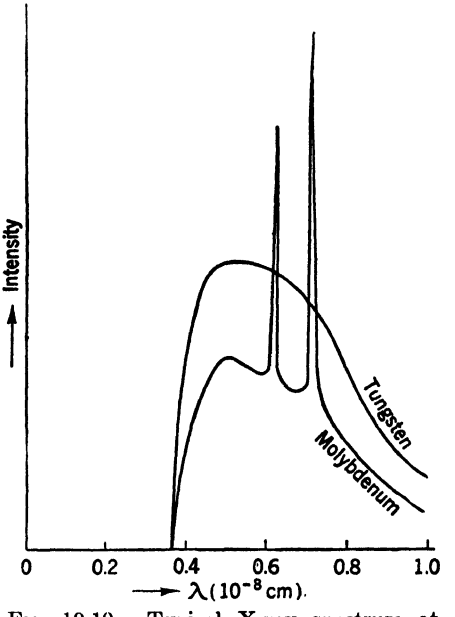
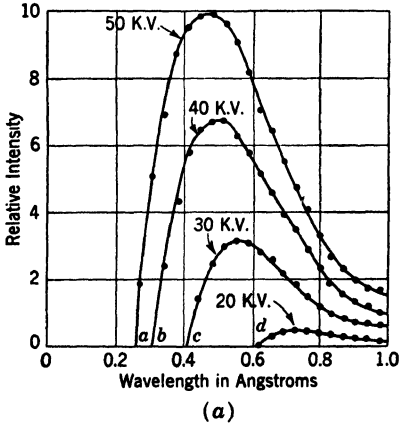
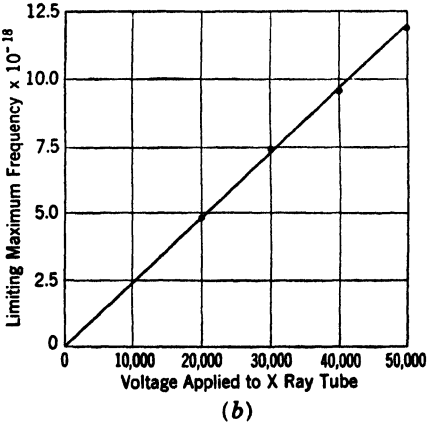


FIG. 19.10. Typical X-ray spectrum at 35,000 volts. Bragg spectrometer. Molybdenum shows the lines of the K series superimposed on the continuous spectrum.



(*a*)

FIG. 19.11*a*. Continuous X-ray spectra of tungsten at various voltages. (*Courtesy of C. T. Ulrey.*)



(*b*)

FIG. 19.11*b*. Relation between frequency limit and voltage, derived from Fig. 19.11*a*. (*Courtsey of C. T. Ulrey.*)

Planck's constant, measuring the limiting frequency ν_l for a given accelerating voltage V and using Millikan's value of the electronic charge ϵ.

How are the experimental results just reported interpreted by the quantum theory? The law of Duane and Hunt bears a striking resemblance to Einstein's equation of the photoelectric effect $h\nu = P + \epsilon V_s$ [Eq. (11.1)]. Einstein interpreted this equation by the idea that a quantum of light $h\nu$ spends the energy P for the liberation of an electron from a metal surface and the balance ϵV_s (V_s = stopping potential) for imparting kinetic energy to the same electron. For the photoelectric effect by X rays the same equation is true but may well be simplified by neglecting the work function P because the energy $h\nu$ is so high, many thousand electron volts, that the work function P of a few electron volts is negligible. Thus the equation for the photoelectric effect due to X rays, $h\nu = \epsilon V_s$, still more strikingly resembles the law of Duane and Hunt describing an entirely different process.

This similarity of the equations suggests the explanation of the continuous X-ray spectrum. While in the photoelectric effect the energy of the quantum $h\nu$ is changed into kinetic energy of the electron, in the emission of the continuous spectrum the reverse process takes place, *i.e.*, the kinetic energy ϵV of the impinging electron is changed into the energy of a quantum $h\nu$. Since the spectrum has a continuous spread, although all electrons hit the target with the same energy, one must more specifically assume that the process described is the limiting case. In the great majority of emission processes, the electron is not stopped at once but loses its energy in several steps, in each step emitting a smaller quantum.

Summarizing, we note that the continuous X-ray spectrum fits well into the quantum theory; it is emitted in a process that may be described as the reverse of the photoelectric effect.

j. Compton Effect. When introducing the quantum theory of light (Part IV), we based our argument largely on Einstein's equation of the photoelectric effect and its interpretation. We supported his argument by a qualitative discussion of the Compton effect (Chap. 13). Having discussed the X-ray spectrometer, we are prepared to discuss Compton's discovery in detail. A. H. Compton investigated the spectrum of scattered X rays. Figure 19.12 shows his arrangement. X rays of a sharply defined frequency, *e.g.*, of a characteristic line of molybdenum, are incident on a block of carbon. The scattered X ray is analyzed in a spectrograph. Compton found that the spectrum of the scattered ray shows the same sharp line as the "primary ray" and in addition another line shifted to longer wave lengths. The wave-length difference between this new line and the original line increases with the angle at which the scattering is observed. The experimental results are given by Fig. 19.13.

Compton interpreted this effect by a theory that represents the boldest

application of the quantum theory of light. He assumed that the incident light consists of quanta of energy $h\nu$, traveling with the velocity c, hitting the electrons of which the carbon atoms are largely constituted.

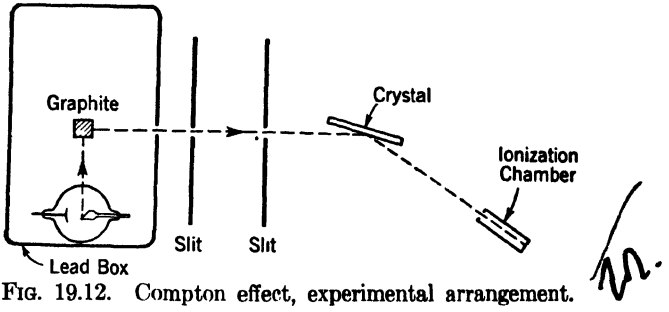


FIG. 19.12. Compton effect, experimental arrangement.

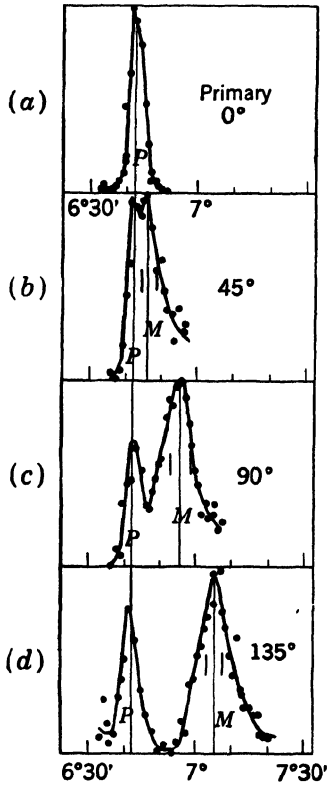


FIG. 19.13. Compton effect, result. The modified line M is shifted with respect to the primary line P, depending upon the angle of scattering.

In this process each quantum imparts some of its energy and momentum to an electron according to the same laws that govern the collisions between billiard balls, *i.e.*, the laws of conservation of energy and momentum. With this idea in mind, we describe first the scattering material and then the incident X ray. In a light atom the detachment of electrons requires energies so small as compared with the X-ray quantum $h\nu$ that the electrons may be considered to be free. Since their velocities are small as compared with the velocities that, as we shall see, will be imparted to them, we may neglect their original velocities. Thus, rather strangely, the scattering material is described as consisting of free electrons with negligible velocities.

For the description of the quantum, we must specify its energy, well known as $h\nu$, and also ascribe to it a momentum expressed in the following manner. In our discussion of cathode rays (Sec. 8.4) we introduced what we called the "principle of the equivalence of mass and energy." (We stated historically that Einstein derived this equivalence from his more fundamental principle of relativity, Appendix 7.) The principle states that any energy represents a mass = energy/c^2, where c = velocity of light. Thus

we ascribe to the quantum of energy $h\nu$ the equivalent mass $h\nu/c^2$. Furthermore, to this mass we attribute the linear momentum = mass × velocity, hence

$$\text{Momentum of quantum} = \frac{h\nu}{c}$$

Now we are prepared to state the laws of conservation of energy and momentum. (Here the student should review Prob. 14.1.) Since we wish to avoid formulas that we have not derived, we shall not use the relativistic expressions for the energy and momentum of the electron. By applying instead the expressions of Newtonian mechanics, we restrict ourselves to

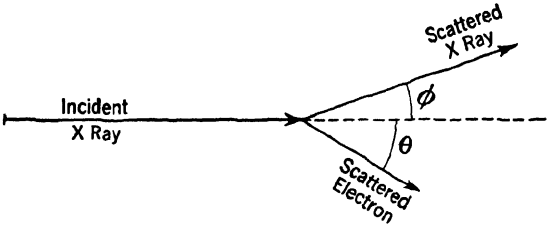


FIG. 19.14. Conservation of momentum at the scattering of an X-ray quantum.

an approximation that is valid only for velocities of the electron small as compared with the velocity of light.

Notation:

ν = frequency of incident X ray
ν' = frequency of scattered X ray
μ = mass of electron
v = velocity given to the electron
ϕ = angle between incident and scattered X ray (see Fig. 19.14)
θ = angle between incident X ray and scattered electron

The conservation of energy is stated in *one* equation since the energy is a scalar quantity.

$$h\nu = h\nu' + \frac{\mu v^2}{2} \tag{I}$$

The conservation of momentum is stated in *two* equations since the momentum is a vector and the law of conservation applies to each of the components; no third component must be considered since the process of scattering takes place in a plane (Fig. 19.14).

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\phi + \mu v\cos\theta \tag{II}$$

$$0 = \frac{h\nu'}{c}\sin\phi - \mu v\sin\theta \tag{III}$$

Which quantities should we consider as known and which as unknown? The fundamental constants h, μ, and c are known once and for all. Furthermore, the experimental physicist knows the frequency ν of the incident X ray and the direction ϕ at which he observes the scattered X ray. Thus the three unknowns ν', v, and θ are to be computed from the three equations. In order to compare the result of the theory with Compton's experiment we are not interested in the velocity v and the angle θ of the scattered electron. So we solve the equations for the wave-length shift $\lambda' - \lambda$. This, unfortunately, is an awkward problem, the solution of which is carried through in Prob. 19.1. The result is

$$\lambda' - \lambda = \frac{h}{\mu c}(1 - \cos \phi)$$

(The rigorous, relativistic treatment leads to the same final formula.) This simple result states that the wave-length shift $\lambda' - \lambda$ depends only on the angle ϕ, not on the wave length of the incident X ray. For the observation of the scattered ray in the direction normal to the primary ray, the wave-length shift always has the value $h/(\mu c) = 0.0242 \times 10^{-8}$ cm. The final formula of the theory successfully predicts the observed shift of the spectral line. The fact that the scattered light contains the unshifted line in addition to the shifted line is explained by the assumption that many firmly bound electrons cannot be considered as free and hence scatter the light as parts of the much larger mass of the atom. The same theory when applied to a much larger mass leads to a negligible shift. If this idea is correct, one should expect a higher intensity of the nonshifted line for the heavy atoms, which have plenty of firmly bound electrons. This has actually been observed. On the other hand, the lightest atoms like lithium scatter X rays with nearly the whole intensity in the shifted line.

This argument explains at the same time why visible light fails to show Compton scattering; there are no electrons bound with an energy small as compared with the energy of the quanta of visible light.

On the other hand, visible quanta have a chance for another division of their energy when scattered from molecules; they may transfer a part of their energy and so start molecular vibration. This describes the Raman effect discussed in Sec. 17.7.

Compton's theory predicts that in each scattering process an electron is ejected. With the Wilson cloud chamber (discussed in Sec. 21.2*a*) such "recoil electrons," ejected by X rays from gaseous atoms, have actually been observed. We shall not discuss the complicated detail because the evidence is not so straightforward as the observation of the wave-length shift.

The excellent agreement of Compton's theory and his observations provides a striking confirmation of the theory postulating that light consists

of quanta endowed with a certain energy and momentum. The same fundamental idea leads to a theoretical derivation of the *radiation pressure.* Such a pressure was predicted by Maxwell (1874) on an entirely different basis. From his electromagnetic theory he derived the result that radiation, at normal incidence, exerts a pressure on a reflecting surface, amounting to twice the energy density of the radiation. This very small pressure has been measured by Lebedew (1901), Nichols and Hull (1903), and Gerlach and Golsen (1923). How is the radiation pressure treated in the quantum theory of light? Here our theoretical picture is that, at the reflecting surface, each quantum bounces back, reminding us of the treatment of the pressure exerted by a gas on a surface. The computation is

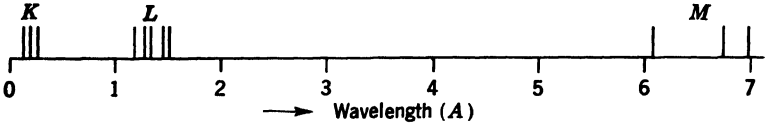


FIG. 19.15. X-ray spectrum of tungsten (omitting the weaker lines and those of longest wave lengths).

given in Prob. 19.2 where the result of the quantum theory is found to agree with the result of Maxwell's theory.

19.2. Properties of Atoms as Revealed by X Rays. In our discussion of X rays we have so far described experimental results and referred to the theory of light quanta. We have not yet made use of the picture of the atom as consisting of a nucleus surrounded by shells of electrons. The contribution of the X-ray line spectra is important for the analysis of the electronic structure and our knowledge of the periodic table. This is the subject of the present section. We shall pay particular attention to the X-ray spectra of the heavy elements in which the simplest conditions prevail.

a. Emission Spectra; Moseley Diagram. It is a striking fact that X-ray line spectra are ever so much simpler than optical spectra. While we had to omit the description of the more complicated optical spectra, it will be easy to describe X-ray spectra. We shall omit only the detail of their fine structure. A heavy element, serving as the target in the X-ray tube, emits an X-ray spectrum which consists of several series of lines. Each series converges toward high frequencies as far as one can tell, considering the fact that each series consists only of a few lines, not infinitely many lines as the series of optical spectra. The various X-ray series of tungsten are sketched in Fig. 19.15. The series located at the highest frequencies is called the "K series," next comes the L series, etc.

Moseley, in 1913, investigated the relation between the X-ray spectra of the various heavy elements. In optical spectra, there is no simple relation whatever between the spectra of atoms adjacent in the periodic table.

(Here we mean neutral atoms, not atoms compared with ions as in Sec. 16.1*b*.) However, in X-ray spectra Moseley discovered a simple relation, which is evident in the graphical representation of the spectra (Fig. 19.16). The X-ray spectra of all elements closely resemble each other; with increasing atomic number they are systematically shifted to higher frequencies. In X-ray spectra, there is no trace of the periodicity that is strikingly demonstrated by the optical spectra and chemical prop-

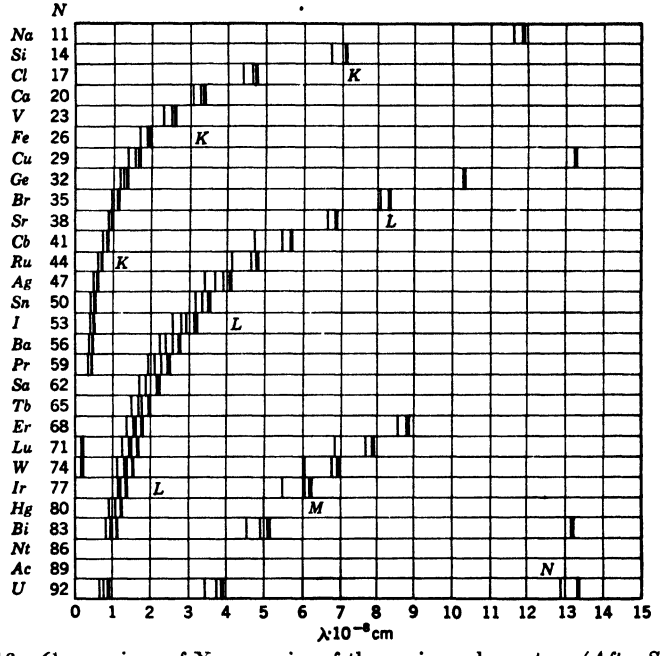


FIG. 19.16. Comparison of X-ray series of the various elements. (*After Siegbahn.*)

erties of the elements. When tracing any one X-ray line, *e.g.*, the first line of the K series, called K_α, through the table of elements, Moseley found the simple relation

$$\nu = \tfrac{3}{4}cR(Z-1)^2 \tag{19.4}$$

where c = velocity of light

R = Rydberg constant (the same as in the Balmer formula of the hydrogen spectrum)

Z = atomic number

When $\sqrt{\nu}$ is plotted against Z, this relation is represented by a straight line. Such straight lines for various X-ray spectral lines are shown in Fig. 19.17. This diagram, called the "Moseley diagram," is of outstanding importance, not only for our knowledge of X-ray spectra, but beyond that for our knowledge of the periodic table. First of all, the diagram tells us that, in a way, our knowledge of the chemical elements is complete.

No new element can be fitted between two of the known elements because this would disrupt the smooth straight lines of the diagram, which obviously represent a law of nature. However, this argument leaves unknown whether or not new elements may be found beyond the heaviest element known at the time of Moseley, *i.e.*, No. 92, uranium.

Historically it is better to say that Moseley discovered a gap in the table of elements by kinks in his straight lines which, however, disappeared

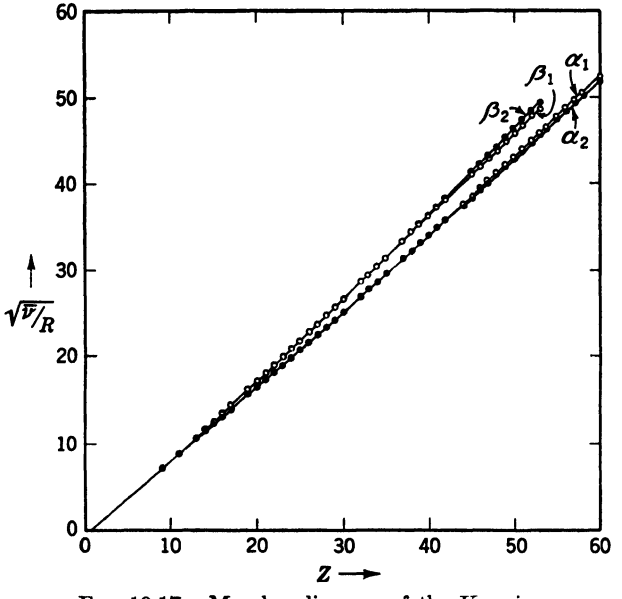


FIG. 19.17. Moseley diagram of the K series.

when he assumed the existence of an element, $Z = 43$, unknown heretofore, discovered many years later. Furthermore, Moseley had to reverse the order of nickel (atomic weight, 58.69) and cobalt (atomic weight, 58.94) in order to obtain smooth lines. He confirmed two similar rearrangements previously proposed by the chemists (see Sec. 18.1). These exchanges of order seem less objectionable nowadays than they may have appeared in 1913 because now we know that any chemical atomic weight is not characteristic of an individual atom but of a mixture of "isotopes" (see Sec. 20.2), the concentrations of which are determined by unknown nuclear processes.

The X-ray spectrum of an element is the same for the solid, the liquid, and the gas; it is even independent of the formation of chemical compounds. In this respect, too, X-ray spectra are much simpler than optical spectra.

Moseley's diagram accurately predicts the X-ray spectra of the few ele-

ments still unknown. Therefore, since Moseley's time, any claim of a discovery of a new element has had to be substantiated by the X-ray spectrum. Only if the element is being produced by artificial transmutation (Chap. 22) in quantities too small for the spectroscopic test are other arguments acceptable.

b. Theory of Shells of Electrons. How do these observations of X-ray spectra fit into the theoretical picture, worked out on the basis of the periodic table, consisting of the nucleus surrounded by shells of electrons (Sec. 18.8)? Our answer will begin with a qualitative picture; then we shall try to estimate the frequencies on the basis of Bohr's theory. Historically, the early exploration of X-ray spectra had the benefit of the interpretation by Bohr's theory which became known only one year after the discovery of X-ray diffraction.

The K series contains the highest frequencies, *i.e.*, the largest quanta emitted. Hence they are attributed to the electrons closest to the nucleus. These are the two electrons of the innermost shell, which, because of this relation to the K series, is called the "K shell" (see Fig. 18.2). With increasing atomic number the K series of the various elements are shifted to higher frequencies because the increasing nuclear charge provides a larger force binding all external electrons.

The corresponding idea applies to the higher series. An atom that has just emitted the line K_α has now the vacant place in the L shell. (The same vacancy may be created instead when it happens that the impinging free electron knocks out one of the L electrons.) If now one of the M electrons drops into the L shell the first line L_α of the L series is emitted, etc. The diagram (Fig. 19.16) indicates that only for the heaviest elements has the N series been observed. For this and the still higher series, the technique of observation is difficult since they are strongly absorbed by air.

The theory accounts for the fact that X-ray spectra fail to show a periodicity. Since all *inner shells* are complete, their only change with increasing atomic number consists of an increasingly tight binding. The periodicity is a feature of the *external shells*, which are responsible for the optical and chemical properties of the elements.

The theory of electron shells predicts a relation closely resembling the "combination rule" (Sec. 15.5*d*) of the optical spectra. When a K electron is knocked out and an M electron falls into the empty place, the line K_β is emitted. When instead an L electron goes into the K shell and next an M electron into the L shell, the same total change of the configuration takes place in two successive steps; hence the total change of the energy is the same. Consequently, the frequencies should bear the simple relation $\nu_{K\beta} = \nu_{K\alpha} + \nu_{L\alpha}$. The experiments confirm this prediction. Another combination rule will be discussed in the section on absorption spectra (Sec. 19.2*c*).

When we attempt a quantitative prediction of an X-ray line spectrum on the basis of Bohr's theory, we can expect only an approximation since the situation is much more complicated than in the hydrogen atom. We try to compute the first line of the K series by simply applying Bohr's theory to an electron which falls from the second to the first orbit ($n = 2$ to $n = 1$) in the electric field of the nucleus of atomic number Z. For this line Bohr's theory predicts the frequency

$$\nu = cRZ^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$
$$= \tfrac{3}{4}cRZ^2$$

This crude approximation approaches Eq. (19.4), discovered empirically by Moseley, surprisingly well since for heavy atoms there is little difference between $Z - 1$ and Z. The factor $Z - 1$ instead of Z is explained by the fact that the electron considered is not confronted with a nucleus alone but with a nucleus whose charge is slightly "screened" by one or several of the innermost electrons. (The outer shells are not expected to affect the result since an electrically charged sphere does not produce an electric field within its interior.)

The success of Bohr's theory in predicting Moseley's empirical formula may well be counted as an additional confirmation of the statement that the atomic number Z equals the nuclear charge. Altogether, the picture of the shells of electrons, introduced for the interpretation of optical spectroscopy and chemistry, gives an excellent account of X-ray spectra.

c. Methods of Observation. Following our treatment of optical spectra, we shall next compare the various methods of observation, excitation by electron impact, absorption, and fluorescence. In all these experiments we shall notice great differences between X-ray spectra and optical spectra which again are fully explained by the theory of electron shells.

By the method of *controlled electron impact* we can excite the first line of the principal series of an *optical* spectrum separately, *e.g.*, the line 2,537 of mercury by electrons of an energy of 4.88 ev. Nothing of the kind can be done with an *X-ray* spectrum, *e.g.*, the line K_α. This line is emitted only when the impinging electron has enough energy to *knock out* a K electron, *i.e.*, the energy computed from the *series limit* of the K series. Then the whole K series appears at once, combined with all the other series. Any series of lower frequency, *e.g.*, the L series, can be excited without the K series, by an electron impinging with an energy computed from the limit of the particular series.

This is exactly what the theory predicts. We cannot expect to raise a K electron to the L orbit because this orbit has no vacant place. Because of the closed nature of the shells, we must completely knock out

K electrons in order to give rise to the emission of the K series and all other series.

In a gaseous atom, theoretically, one may distinguish between knocking out a K electron and raising it to an excited level outside the external electrons. However, this distinction, amounting to a few electron volts, is not noticeable experimentally since we are dealing with energies of many thousand electron volts.

Correspondingly, by knocking out L electrons, which requires much less energy, we give rise to the radiation of the whole L series and the series of lower frequencies. In any case, the excitation consists of ejecting an electron from a closed shell, in other words, ionizing the atom.

The *X-ray absorption spectra* fit equally well into the theoretical picture. To begin with, we must make sure that X-ray spectroscopy permits a definition of the absorption coefficient better than that which we discussed and criticized above (Sec. 19.1*d*). In that primitive method a measurement is made of the hardness of a composite X ray which in general contains spectral lines of several frequencies. The ambiguity disappears when we measure the absorption coefficient of an X ray of one frequency as is possible by the following procedure. In a turning-crystal spectrometer we measure the intensity I_0 emitted at a certain X-ray frequency in terms of the current generated in the ionization chamber. Next, when placing the absorber somewhere between the X-ray tube and the slit, we measure the smaller intensity I. By varying the thickness d of the absorber, we verify that the transmitted intensity I as a function of d is expressed as

$$I = I_0 e^{-\mu d}$$

The constant μ so measured, called the "absorption coefficient," is characteristic for the absorber and the frequency. The absorption of X rays by a certain substance is described by the curve representing the absorption coefficient μ as a function of the frequency ν or the wave length λ. As discussed in Sec. 19.1*d*, the absorption coefficient of an element at any wave length is best described by the "mass absorption coefficient" $\mu_m = \mu/\rho$, where ρ = density of the element (see Prob. 19.3).

The results of this method of measurement are X-ray absorption spectra which differ from the optical absorption spectra (Sec. 17.5*a*) in a way that is readily understood on the basis of the theory. We remember that the optical absorption spectrum, *e.g.*, of sodium vapor (Fig. 17.7), shows all lines connected with the normal state of the atom, *i.e.*, the principal series, and a continuous range of absorption beyond its convergence limit, decaying toward high frequencies. In an X-ray absorption spectrum, the series itself is absent; only the continuous absorption beyond its limit shows up. This is illustrated by Fig. 19.18 in which we schematically compare

the emission spectrum and the absorption spectrum of the same heavy element. Each continuous absorption range starting at the frequency of a series limit gradually decays toward higher frequencies. The explanation of these absorption spectra agrees entirely with the argument just given for excitation by controlled electron impact. Since the shells do not contain vacant places, incident X rays (as well as electron impact) fail to *raise* an electron, for example from the K to the L shell. The only possible effect of incident X rays consists of *removing* an electron; this process gives rise to absorption beyond the convergence limit. It may happen to the K shell as well as to any other shell.

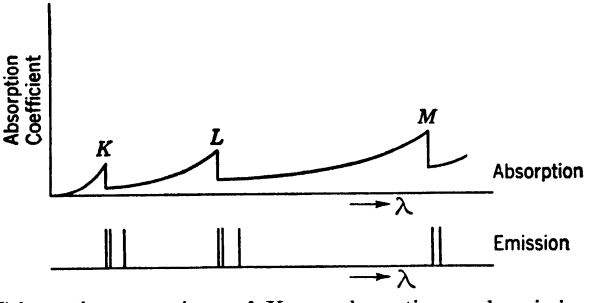


FIG. 19.18. Schematic comparison of X-ray absorption and emission spectra of a heavy element (omitting the structures of the lines and edges). Each absorption edge coincides with the short wave-length limit of an emission series. The sharp lines show up only in emission.

The theory of electron shells predicts a special combination rule (Sec. 15.5*d*). As an example we shall use the line K_α. In the *initial* state of its emission process, an electron is missing in the K shell, in the *final* state it is missing in the L shell, hence the quantum $h\nu$ of the line K_α measures the energy difference between these two atomic states. On the other hand, the K absorption limit is a measure of the energy required to remove an electron from the K shell, the L absorption limit has the same significance for the L shell. Consequently the difference between the two limits should equal the frequency of the line K_α. Observation confirms this theoretical prediction.

The location of the various absorption limits all over the table of elements can be visualized in Fig. 19.16, which shows all the series, each of them represented by only two or three lines. In the absorption spectra all sharp *spectral lines* are absent; but each series limit is conspicuous as the starting point of a *continuous spectrum* which extends toward short wave lengths with gradually diminishing intensity. From this survey we derive the answer to specific questions. For example, when operating an X-ray tube with a tungsten target on 70,000 volts, we excite the tungsten K_α line (0.21A) with considerable intensity. How is this line absorbed

by the various elements, considering equal numbers of absorbing atoms? Light elements are quite transparent because their K series, as far as one can identify them, are located at much longer wave lengths. Thus the diagram explains the great transparency of the tissue of the animal body consisting largely of carbon, oxygen, nitrogen, and hydrogen. Furthermore, it explains the fact utilized in the measurement of the X-ray dose by the ionization chamber, that air shows about the same ionization as animal tissue (Sec. 19.1*d*). Bones absorb considerably more because they contain the heavier element calcium. Elements like barium, located at the beginning of the sixth period to which the target material, *i.e.*, tungsten, belongs, show intense K absorption spectra whose strongest sections, near the limits, coincide with the line K_α of tungsten. Tungsten and its immediate predecessors show much weaker absorption of the same line because here only the latter part of the L absorption is effective. The absorption becomes again stronger for the heaviest elements because their L series limits come closer to the spectral line considered.

For long wave lengths, say 20A, all elements except the very lightest ones are opaque. For very short wave lengths, like those of gamma rays emitted from radioactive elements (wave lengths of the order 10^{-2}A), all elements are transparent, the lighter elements more so than the heavier ones. For still shorter wave lengths, however, something unexpected happens. An entirely different process, pair production, to be explained in the chapter on artificial transmutation (Sec. 22.5), is responsible for an increase of the absorption coefficient in the very extreme energy range of quanta of 1 million electron volts or more (Fig. 22.10).

Now we are able to predict that in X-ray *fluorescence* the same contrast should show up between optical and X-ray spectra as in absorption. Although in sodium vapor the first line of the principal series excites fluorescence of the same wave length, we cannot do the corresponding experiment with the line K_α of a heavy element. However, when we irradiate a heavy element with a line that is strongly absorbed (*e.g.*, barium with the line K_α of tungsten) then we ionize its K shell and the whole K series and all other series of the element that is irradiated appear in fluorescence; *i.e.*, they are emitted in all directions. The corresponding statement applies to the other series, in close analogy to excitation by electron impact discussed above. Here Stokes' law is valid as well as in optical fluorescence (Sec. 17.6). Fluorescence represents X radiation produced by absorption of X radiation. Hence absorption of X rays does not necessarily indicate that radiant energy is *lost* as such; partly it may be only *deflected* into other directions and *deteriorated* into smaller quanta. Only that part of the absorbed quantum that goes into kinetic energy of the liberated electron is really *lost* as radiant energy.

d. Report on Further Developments. Our description of X-ray spectra,

in emission and absorption, was somewhat simplified. Many X-ray lines show a fine structure. Furthermore the absorption edges, except for the K absorption, show structures, *e.g.*, the L absorption a subdivision into three separate limits (Fig. 19.19).

In our discussion of optical spectra and the periodic table it was briefly reported (Secs. 16.1*e* and 18.9) that the theory of the fine structure of spectral lines requires a more detailed picture of the atom involving more quantum numbers. It is highly satisfactory to note that the same system of quantum numbers, which was introduced for the interpretation of optical spectra and substantiated by their bearing on the periodic table, gives a thorough account of all the detail of X-ray spectra.

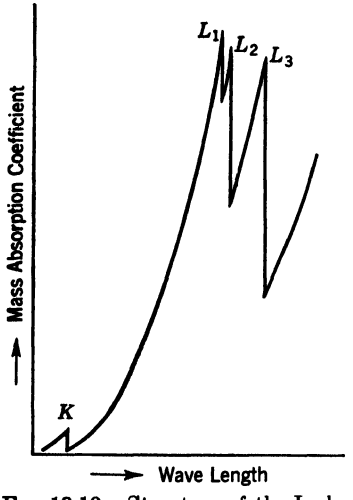


FIG. 19.19. Structure of the L absorption limit of a heavy element.

We limited ourselves to the consideration of the X-ray spectra of the heavy elements. This is justified by their simple structure as well as by the historical development. There is a wide range of wave lengths between optical spectra and X-ray spectra in which the spectroscopic technique is difficult, partly because the air is opaque, still more so because the crystal grating fails and the ruled grating reflects light only with low intensity. Hence, for many years there was a wide gap between the ranges explored in optical and X-ray spectra; but through the work of Lyman, Millikan, and others, this gap has gradually been closed. In the intermediate wave-length range, the transition is evident from the simple structure of X-ray spectra to the complex structure of optical spectra. For example, it is in accord with the theory that for lighter atoms, or for the higher shells of the heavy atoms, the shells are not completely independent of what happens at the surface of the atom. There the spectrum of an element is, to a certain extent, affected by the state or the formation of chemical compounds.

The simple structure of X-ray spectra discussed above as well as the refinement just mentioned provide overwhelming confirmation of the theory of atoms as constituted of nuclei endowed with positive charges and surrounded by shells of limited numbers of electrons.

19.3. Applications. The medical applications of X rays are known so universally that they will be only briefly mentioned. X rays are used for diagnosis and for treatment. For most purposes of *diagnosis* a potential difference between 50,000 and 90,000 volts generates rays of a sufficient hardness. Bones and metals are easily visible, and the digestive tract

can be made visible by mixing a compound of a heavy element, *e.g.*, bismuth, with the food.

Treatment by X rays depends on the fortunate fact that diseased tissue, like a tumor, is susceptible to destruction to a greater degree than the surrounding healthy tissue. In order to reach a deep-seated tumor with minimum destruction of the skin, very hard X rays, generated by potential differences between 200,000 and 1,000,000 volts, or even more, are applied.

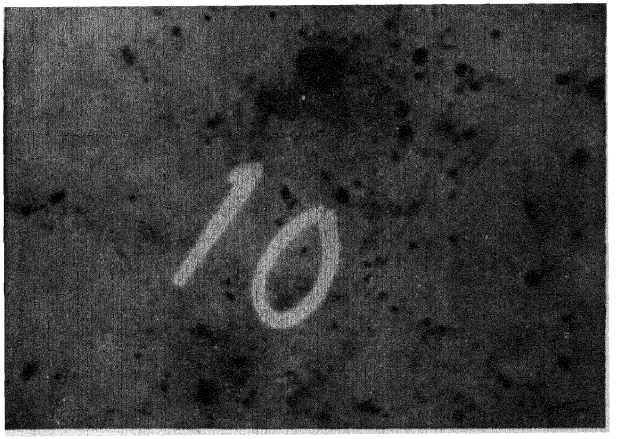


FIG. 19.20. Radiograph of a steel casting showing internal defects. (*Courtesy of Dr. G. L. Clark.*)

For this purpose some hospitals are equipped with special X-ray apparatus operated with Van de Graaff electrostatic generators.

Testing of materials represents another important application of X rays. For example, in X-ray pictures of heavy steel plates defects may show up which reduce their strength (Fig. 19.20).

The structures of complex organic molecules may be analyzed by X-ray diffraction since such molecules show regularities in their structures similar to the regularities in crystals. Thus atomic distances within organic molecules are being determined.

SUMMARY OF CHAPTER 19

1. *Properties of X Rays.* Roentgen discovered that glass and metals when hit by fast electrons emit rays which penetrate through black paper or any light material and produce light on a fluorescent screen. These he called X rays.

Other outstanding effects of X rays are as follows: They affect the photographic plate. They are diffusely scattered by all substances. They ionize

air. They are absorbed, in general by heavy elements more strongly than by light elements.

The dose of X rays is measured by the rate of discharge of a condenser containing air between the plates.

Polarization of X rays may be produced by scattering and tested by a second scattering process (Barkla).

Von Laue discovered that X rays diffracted by the atoms of a crystal interfere with each other, giving evidence of the wave nature of X rays. Since constructive interference depends on the wave length, a spectrum is produced. The wave lengths are of the order 1A, *i.e.*, about 1/5000 of the wave length of visible light, and are measured by Bragg's turning-crystal spectrometer.

Since the index of refraction for X rays of glass, crystals, and metals is slightly smaller than unity, total reflection takes place within a small angle near grazing incidence. This observation makes X rays accessible to spectral analysis by a ruled grating. The combination of this experiment with diffraction by a crystal grating leads to a new determination of the electronic charge ϵ. The result agrees with the result of the oil-drop experiment.

A heavy target bombarded by fast electrons emits two types of spectrum superimposed: a sharp line spectrum characteristic of the material of the target (discussed in Sec. 19.2) and a continuous spectrum. The continuous spectrum has a sharp high-frequency limit ν_l depending only on the voltage V accelerating the electrons, not on the target material. The frequency ν_l can be computed from the equation $h\nu_l = \epsilon V$. The limit is explained by the complete conversion of the electronic kinetic energy ϵV into energy of a quantum $h\nu_l$. This process is the reverse of the photoelectric effect produced by X rays.

The Compton effect is observed when X rays of a sharply defined wave length λ are scattered by a light substance. The spectrum of the scattered rays contains the same wave length λ and a new, longer wave length λ', the difference $\lambda' - \lambda$ depending only on the angle at which the scattering is observed. The shifted spectral line is explained by an application of the "corpuscular" theory of light describing the scattering process as a collision between the quantum and an electron belonging to the scattering material.

2. *Properties of Atoms as Revealed by X Rays.* The characteristic line spectrum of a heavy element consists of a few series called the "K" series at the highest frequency, the L series, etc., each series consisting of only a few lines. Comparing the emission spectra of the heavy elements, Moseley discovered a linear relation between $\sqrt{\nu}$ and the atomic number Z. For example, all first lines of the K series of the various elements are described by the equation

$$\nu = \tfrac{3}{4}cR\,(Z - 1)^2$$

The Moseley diagram representing these relations proves that our knowledge of elements is complete except, possibly, at the end of the periodic table.

X-ray spectra do not depend upon the state of an element nor the formation of compounds. All observations on line spectra are satisfactorily explained by the theoretical picture of the atom consisting of a nucleus and shells of electrons. See the survey given in Table 19.1. Altogether, the X-ray line spectra provide a strong confirmation of the theoretical picture of an atom consisting of a nucleus surrounded by shells of electrons (see Table 19.2).

Table 19.1. *Comparison of Optical Spectrum and X-ray Spectrum*

	Optical spectrum	X-ray spectrum
Spectrum is due to	An *outer* electron	An *inner* electron (normally all available places occupied)
Excitation by controlled electron impact	An *outer* electron raised to higher orbit. Single line (*D* line of Na) excited by excitation potential computed from λ of this line	An *inner* electron knocked out. No individual excitation of lines. Whole series excited by excitation potential computed from λ of series limit
Absorption of radiation	All lines connected with normal state and continuous spectrum beyond series limit	Only continuous spectrum beyond series limits of K, L, etc., series
Radiation.....	The electron just excited falls to lower level	One of the electrons of one of the next shells falls into the vacated place of the inner shell. *Example:* Line K_α due to L electron falling into K shell

Table 19.2. *Properties of Outer and Inner Shells and of the Nucleus*

Chemical and spectroscopic properties	Depend on state and formation of compound; *periodic*	Due to outer shell
X rays	Largely independent of state and formation of compound; *nonperiodic*	Due to inner shells
Isotopes, radioactivity, transmutation	Independent of state and formation of compound; *non periodic*	Due to nucleus

PROBLEMS

19.1. *Compton effect.* Solve Eqs. (I), (II), and (III) given in the text for the wavelength shift $\lambda' - \lambda$ which is observed by Compton. Apply the following procedure:

a. Introduce λ and λ' instead of ν and ν'. The equations so produced are called (IV), (V), and (VI).

b. In order to eliminate the unknown θ, write Eqs. (V) and (VI) such that the members containing θ are on one side. Square and add these equations.

c. As the resulting equation contains h^2/λ^2 and h/λ'^2, simplify it by squaring and subtracting Eq. (IV) (after transferring the members containing λ and λ' to one side).

d. Since we restrict our consideration to velocities v of the electrons small as compared with the velocity c of light, neglect $v^2/(2c^2)$ as compared with 1.

e. In order to eliminate the unknown v, divide Eq. (IV) into the last equation. Express $\lambda' - \lambda$ in terms of the universal constants and the angle θ.

19.2. *Radiation pressure* (*difficult problem*). Prove that the pressure exerted by radiation at normal incidence on a reflecting surface equals twice the energy density of the radiation. Using the data of Prob. 11.3, compute the force exerted by yellow light emitted from a source of 1,000 candlepower on a mirror (area $A = 5$ cm^2) placed in a position normal to the rays at a distance of 2 m from the source. Express the force in ergs and gram weights.

Notation:

c = velocity of light
M = mass of plate
A = area of plate
n = number of quanta per cm^2 and sec.

HINT: (*a*) *Compute the radiation pressure.* (1) Following the procedure of the kinetic theory of gases write the equation for the conservation of momentum for the reflection of one quantum (C = velocity given to the mass M). (2) Write the corresponding equation for the total area A when hit by n quanta per cm^2 and sec. (3) Express the pressure as in Chap. 3. (*b*) *Compute the energy density.* Consider a stream of quanta of cross section A traveling during the time interval τ. (1) Compute the energy traveling during τ through A. (2) Compute the volume occupied by this energy. (3) Compute the energy density. (*c*) *Compare the results* derived under (*a*) and (*b*). (*d*) *Introduce numerical values.*

COMMENTS: The numerical result makes it evident that the measurement of the radiation pressure is very difficult.

19.3. *Absorption of X rays.* Given the mass-absorption coefficient $\mu_m = \mu/\rho$ of mercury for the wave length 0.098A: $\mu_m = 3.31$ cm^2/g. Compute the ratio of transmitted to incident intensity I/I_0 for the following cases: (*a*) a layer of liquid mercury, 1 mm thick, density 13.55 g/cm^3; (*b*) the same, 3 mm thick; (*c*) a 1/10 molar solution in water of mercuric nitrate, $Hg(NO_3)_2$, in a layer 5 cm thick (the molar solution contains 1 mole in 1 liter of the solution). Assume that the solution occupies as much space as the water alone; the absorption by the atoms other than Hg is negligible; (*d*) monatomic mercury vapor, 1 atm at 357°C, in a layer 30.0 cm thick.

19.4. *Heating of target.* For a demonstration experiment, an X-ray tube is at your disposal with a copper target. All you can measure from the outside is the volume of the target as 3.0 cm^3. You want to operate your tube at 20,000 volts and 10 mamp. In order to judge whether you can risk the experiment without cooling the target, compute the time it will take for the target to reach a temperature of 200°C starting from room temperature (20°C). Suppose that the target does not give off an appreciable amount of energy during the experiment. You will find the other necessary data in any textbook of physics.

19.5. *Total reflection.* For crown glass the index of refraction is given in the text as $n = 1 - 1.64 \times 10^{-6}$ (Sec. 19.1*g*). Calculate the small angle of grazing incidence in air that limits total reflection.

HINT: Notice that conventionally in optics the critical angle β of total reflection is measured between the ray and the normal on the surface while in X rays the angle θ is

measured between the ray and the surface. Apply the law of refraction and approximations for small angles.

19.6. *Screens.* You are asked to build a screen protecting you from the highly penetrating line K_α of tungsten. The absorption coefficients μ of aluminum and lead are, respectively, 0.688 and 41.8. What percentage of the intensity will pass through plates 1, 2, 4, mm thick of aluminum and lead, respectively? What thickness of aluminum is equivalent in absorbing power to 2 mm lead?

19.7. *Bragg spectrometer.* Given the crystal constant of rock salt, $d = 2.820$A. In the Bragg spectrometer the first order reflection of a spectral line is observed at an angle $\theta_1 = 15°53'$. Calculate its wave length λ and the angle θ_2 of the second order.

19.8. *Continuous X-ray spectrum.* With the turning-crystal spectrometer we measure the continuous X-ray spectrum excited by a potential difference of 75,000 volts. Compute the short wave-length limit of the spectrum and the adjustment of the spectrometer with which we observe this limit in the first order (rock-salt crystal, $d = 2.820 \times 10^{-8}$ cm).

19.9. *Compton effect.* Calculate the wave-length shifts $\lambda' - \lambda$ predicted by Compton's theory for the angles 0, 45, 90, and 135 deg. For the primary line molybdenum K_α, $\lambda = 0.707$A, compute the shifted wave lengths λ' and the corresponding angles θ' to be observed in the Bragg spectrometer equipped with a calcite crystal ($d = 3.029$A). Compare with Fig. 19.12.

PART VI
NUCLEAR STRUCTURE

In preparation for the discussion of optical spectra, the periodic table, and X-ray spectra we had to insert a chapter on nuclei (Chap. 14) reporting Rutherford's discovery of the *nuclear atom* and the ensuing measurement of *nuclear charges.** The conclusion that the nuclear charge equals the atomic number has been amply confirmed by other arguments (Secs. 15.6*a*, 16.1*b*, 19.2*a*). Furthermore, it may seem that we know the *nuclear masses* (Sec. 9.2), with particularly great accuracy the *relative* masses being measured as atomic weights. We shall find, however, that we must revise our understanding of the significance of the atomic weights.

To what extent do nuclear properties affect the electronic system as discussed in the preceding chapters? In the study of optical spectra and X-ray spectra we had little interest in any nuclear property other than the *nuclear charge*. The *nuclear mass* is simply assumed to be very large in comparison to the electronic mass; it is exceptional that in Bohr's theory of the relative motion of the nucleus a very small effect is explained by taking into account the finite value of the nuclear mass. (Nuclear masses have noticeable effects on molecular spectra, which we have not studied in detail.) In chemistry, of course, the relative nuclear masses, *i.e.*, the atomic weights, play a major part. Since the nucleus is exceedingly small as compared to the electronic structure, other nuclear properties have only very minor effects on atomic spectra and the chemical behavior of elements. This applies to *nuclear magnetic moments*. Finally, the possible *instability* of a nucleus, one of its very important properties manifest in its disintegration or transmutation, is not noticeable at all in the study of the electronic structure. For these reasons, nuclear physics is a field largely independent of the physics of the electronic structure, much more independent than, for example, X rays are of optical spectra.

In Part VI we shall first study the separation of elements into isotopes. This applies to all elements, stable and unstable. Next we shall study natural radioactivity, which is due to the spontaneous disintegration of some elements occurring in nature. Finally, we shall discuss the wealth of new observations discovered since physicists succeeded in breaking up nuclei by high-energy projectiles, thus transmuting elements and even creating new elements heretofore unknown. This new technique opens up a vast new field of physics. Moreover, the new observations profoundly modify what seemed to be firmly established fundamental laws of physics.

*A student beginning the study of nuclear physics should first read Chap. 14.

CHAPTER 20
ISOTOPES

20.1. Apparatus. The discovery of isotopes was the result of a refined technique in positive-ray analysis (Sec. 8.3). J. J. Thomson's parabola method discussed above gave the first, rather vague, evidence of the new phenomenon (1913) while modern apparatus using the same method gives clear-cut evidence (Fig. 8.10). Owing to the need for accurate determination of specific charges, such instruments have been vastly refined. They are called "mass spectrographs" because they collect ions of the same mass along sharp lines on photographic plates and thus produce pictures

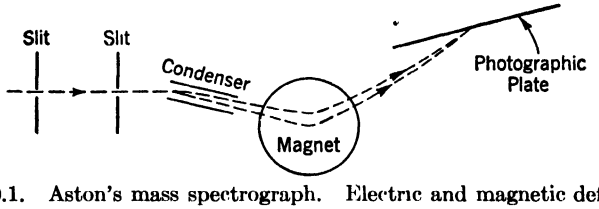


FIG. 20.1. Aston's mass spectrograph. Electric and magnetic deflection.

resembling optical spectra. We shall describe two types, that of Aston and that of Dempster.

Aston's mass spectrograph is sketched in Fig. 20.1. The positive ions, which originate in a low-pressure discharge (not on the diagram), acquire high velocities in the strong electric field located in front of the cathode (see Sec. 17.2*a*). Although most ions hit the metal of the cathode, others pass through a canal that is drilled through the metal. Since these ions which form the positive ray are not all produced at the same distance from the cathode and so fall through various potential differences, they acquire velocities covering a wide range. In Aston's instrument the positive ray, first narrowed down by two parallel slits, is deflected in one direction by an electric field, then in the opposite direction by a magnetic field. (These fields are indicated in the figure by a pair of condenser plates and the circular cross section of a pole piece.) This combination of fields separates the ions constituting the ray according to their values of specific charge, ϵ/μ. Each type of ion, characterized by its ϵ/μ, forms a sharp straight line on the photographic plate. The technical progress due to Aston's method is evident when we compare it with Thomson's parabola method. There the length of each parabola shows the wide velocity range

of the ions constituting the positive ray. This spread of ions with equal ϵ/μ requires a much longer exposure time than in Aston's mass spectrograph where ions of different velocities are focused, *i.e.*, concentrated on one narrow and short "spectral line." The diagram explains this focusing effect qualitatively. While the *electric* field deflects the slow ions more than the fast ones, the *magnetic* field, acting in the opposite sense, makes the same distinction between slow and fast ions and so finally combines

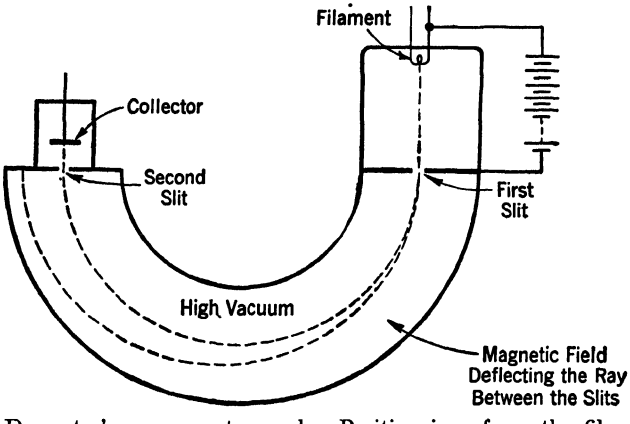


FIG. 20.2. Dempster's mass spectrograph. Positive ions from the filament are accelerated toward the first slit and bent on a circular path by a magnetic field acting between the slits.

at the photographic plate the ions of one value of specific charge, though they are of different velocities.

Simpler is the principle of the mass spectrograph designed by Dempster (Fig. 20.2) who independently made the discovery to be discussed. It was reported in Sec. 8.2*b* that glowing filaments, impregnated with certain salts, give off positive ions, a large fraction being alkali ions. By the use of this source of ions, Dempster's instrument is applicable to different materials and so supplements that of Aston. In high vacuum these ions are subjected to electric and magnetic fields in the same way as described for electrons (see Sec. 8.2*b*). First the ions are accelerated toward a plate by the potential difference V. Those ions which pass through a narrow slit cut into the plate (the first slit) enter another evacuated chamber in which they are subjected to a uniform magnetic field directed perpendicularly to their path. The force exerted by this field on the moving charges bends their path into a circle. After passing around one-half of its circumference the ray is incident on another plate into which a second slit is cut. But only for a special adjustment of all variables will the ray pass through the second slit and be incident on some recording device, *e.g.*, an isolated metal plate connected with an electroscope. The electric charge

per second carried by the ray is measured by the rate of charge of the electroscope. In the figure two rays are shown with slightly different values of ϵ/μ, one of them passing through the second slit and hitting the recording device.

The theory of the instrument was given in Sec. 8.2*b*. The specific charge of the particles recorded is easily computed from

$$\frac{\epsilon}{\mu} = \frac{2V}{H^2r^2} \tag{8.11}$$

In most cases we are dealing with singly charged positive ions. The radius r of the circular path is given by the rigid construction of the apparatus, and the magnetic field H is kept constant. By variation of the accelerating voltage V the various rays can have the radii of their respective circular paths so adjusted that these rays pass successively through the second slit. For every such value of the voltage V we compute the mass μ of the particles in the corresponding ray from the last equation. Next we may compute their atomic weight m from the equation $m = N \times \mu$ [N = Avogadro's number; Eq. (2.3)]. Conversely, Aston, knowing the atomic weight or molecular weight m of the ray, could predict the position of the line on the photographic plate. Hence the outcome of the experiment is apparently fully predictable.

20.2. Whole-number Rule. In our discussion of the results we shall follow the work of Aston. He started with an accuracy in his measurements of one-tenth of 1 per cent. Continuing the work of Thomson, he applied his mass spectrograph to neon gas (atomic weight, 20.20). The unexpected result of this experiment was that at the spot of the photographic plate computed for the atomic weight 20.20 no trace of a ray showed up, thus indicating that such atoms, although apparently well known, do not exist at all. Instead there were revealed on the plate two types of atom, unknown heretofore, with whole-number atomic weights, namely, 20.00 and 22.00. (See the mass spectrum of Fig. 8.10, taken by the parabola method; it even shows a faint trace of the very rare Ne 21.00.) Their intensities are observed as 9 for the ray 20.00 and 1 for the ray 22.00. Thus the average atomic weight results as $(9 \times 20.00 + 1 \times 22.00)/10 = 20.20$, just the well-known value of the "chemical atomic weight" of neon. This observation leads to the conclusion that neon gas is a mixture of two kinds of atom with different masses that cannot be distinguished by their chemical and spectroscopic properties. Hence to both types of atom we must attribute the same nuclear charge, *i.e.*, the same position in the periodic table of elements. Aston gave to these different types of atom of the same element the name "isotopes" meaning atoms having the same position in the periodic table.

When applying the same analysis to other elements, Aston found the

same result over and over again. For example, chlorine (atomic weight, 35.46) consists of the isotopes 35.00 and 37.00 in such a proportion that their average is 35.46. Figure 20.3 shows the more complex mass spectra of tin and xenon. The general law, called the whole-number rule, states that *each chemical atomic weight that deviates from a whole number is due to a mixture of isotopes, each of them with a whole-number atomic weight.* Only hydrogen noticeably deviates from this rule; its atomic weight = 1.008 is due to the individual hydrogen atoms (see Sec. 20.5).

Aston's discovery is of such fundamental importance that it necessitates a new definition of an element. We now define elements and isotopes as follows: *Elements* are the ultimate constituents beyond which matter cannot be analyzed by chemical processes (or can be analyzed only to a very small extent). *Isotopes* are the ultimate particles into which elements can be analyzed by the determination of ϵ/μ for charged particles, as in the mass spectrograph. Analysis by the mass spectrograph shows that atoms of the same element may differ by their nuclear masses, although they have the same nuclear charge. However, atoms of the same isotope have the nuclear charge and mass in common.

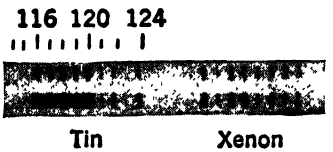


FIG. 20.3. Mass spectra of tin and xenon. (*After Aston.*)

It had been known for a long time that many elements have whole-number atomic weights, when that of oxygen is defined as 16.0000. Examples are helium (4.00), fluorine (19.00), and sodium (23.00). These elements are not analyzed into several isotopes (except possibly into one isotope of major abundance and one or several very rare isotopes). In some cases the same integer serves as atomic weight for several elements. For example, the atomic weight 40 is found among the isotopes of argon, calcium, and potassium. Such atoms of the same atomic weight but different atomic numbers are called "isobars."

The discovery of isotopes makes it evident that the chemical atomic weight of an element is not the property of individual atoms but represents an average. This makes less objectionable the chemist's rearrangement, in the periodic table, of certain pairs of atoms in a way later supported by the Moseley diagram (Secs. 2.2 and 19.2*a*). Some justification can be found in the consideration that the relative abundances of the various isotopes, *e.g.*, of argon and potassium, are determined by vaguely known nuclear processes (see Sec. 23.3*b*).

20.3. Structure of Matter. As early as 1815, Prout had noticed that the atomic weights show a marked preference for whole-number values. He had suggested the important conclusion that the atoms of all elements are built of the same fundamental particle, presumably the lightest atom, hydrogen, with the atomic weight 1. Thus carbon would contain 12 of

these particles, nitrogen 14, oxygen 16, etc. This hypothesis became untenable as more accurate values of the atomic weights became known, and many deviations from the simple rule were found. Aston's discovery revives the whole-number rule and so gives striking evidence in favor of the hypothesis that all matter is constituted of one or a few fundamental particles. The great progress due to this idea is evident when we compare it with the older idea of the nature of matter. In chemistry, the infinite variety of all substances is analyzed into elements. Here we assume 96 different types of atom. The discovery of isotopes seems to complicate our picture greatly because so many elements, in turn, are analyzed into different types of atom, the isotopes. Now we seem to have several hundred different types of atom. The great simplification, finally, comes in through the whole-number rule, which indicates one or a few fundamental particles as building blocks of all matter.

What is the fundamental particle? The obvious guess attributing this role to the hydrogen atom leads into a difficulty since the atomic weight of hydrogen is the one that noticeably violates the whole-number rule by its value 1.008. Hence 4 hydrogen atoms are heavier than 1 helium atom (atomic weight, 4.00). This deviation is reconciled with the idea that 1 helium atom is constituted of 4 hydrogen atoms by invoking Einstein's principle of the equivalence of mass and energy (Sec. 8.4). We applied this principle first to an interpretation of the discovery that electrons of very high kinetic energy show an increase of mass. Next, tentatively, we applied the same principle to various problems. In Prob. 9.9 we argued that we must expend energy in order to separate a hydrogen molecule into its two constituent atoms. Hence the pair of atoms represents energy stored and should be *heavier* than the molecule. It is true that the numerical computation led to a result far below the accuracy of the best measurement. Here we are confronted with a similar case as 4 hydrogen atoms are *heavier* than 1 helium atom. We may assume that 1 helium atom can be taken apart into 4 hydrogen atoms. But here, different from the dissociation of molecules, the change of *nuclear* structure which takes place requires energy of an entirely different order of magnitude. This explains why in the atomic weights of helium and hydrogen the deviation from the factor 4 is easily noticeable.

Accepting this hypothesis, we compute the energy *spent in the disintegration* of one helium nucleus. (In Probs. 9.10 and 9.11, as a good approximation, we computed the energy relation between helium and hydrogen considering *neutral atoms*.) Since the helium nucleus has only half the charge supplied by 4 protons (Secs. 14.2 and 15.6), we cannot expect 4 protons to form a helium nucleus. The discovery of the neutron (see Sec. 22.2) led to the assumption that all composite nuclei are constituted of protons and neutrons; *e.g.*, the helium nucleus consists of 2 protons and

2 neutrons. With the accurate values of the atomic weights of the neutron, hydrogen, and helium, reported in Sec. 22.2*c* and in Appendix 5, the energy spent in the separation of a helium nucleus into 2 protons and 2 neutrons results to 28.2×10^6 ev (not very different from the approximate result obtained for neutral atoms). This is nearly seven million times the energy of dissociation of the hydrogen molecule H_2.

It is not claimed that this argument represents an experimental confirmation of Einstein's principle. That would be the case only if we were able to perform an independent measurement of the energy predicted by the principle. Later, discussing nuclear reactions, we shall find processes in which all energies are accessible to measurement. They will provide a test of the principle (Sec. 22.7). It is a fascinating idea that the same vast amount of energy is *gained in the combination* of 4 hydrogen atoms forming 1 helium atom. It has been computed that the energy gained, if we should so combine all hydrogen atoms contained in a glass of water, would be sufficient to drive a transatlantic liner across the ocean (see Prob. 9.11). But it must be remembered that this result is based solely on atomic weights and their interpretation on the basis of Einstein's principle. There is no laboratory experiment known in which the combination of all hydrogen contained in a glass of water is actually performed or which would at least show some promise that it can be performed practically. We shall come back to this process in the chapter on energy production in nuclear reactions (Sec. 23.3).

Studying nuclear reactions (Chap. 22), we shall find that, within nuclear physics, the energy of separation of helium represents a very high value. This indicates a very high stability of the helium nucleus. (We are familiar with the idea that the stability of a structure is expressed by the energy required to break it up, Sec. 18.3.) This stability, here derived from the atomic weights, is confirmed by other observations. In the chapter on the scattering of alpha particles (Sec. 14.1), we argued that they are identical with helium nuclei. They are projectiles that are able to break up other nuclei; but no observation is known in which an alpha particle itself goes to pieces. It is a curious coincidence that helium has the most stable *electronic* structure (Sec. 18.3) as well as the most stable *nuclear* structure of all elements.

The conventional notation gives both, the mass number as a *superscript after* the chemical symbol and the atomic number as a *subscript before* this symbol. For example, the two isotopes of neon are written ${}_{10}Ne^{20}$ and ${}_{10}Ne^{22}$. This notation makes it evident that 4 protons ${}_1H^1$ have the same mass but twice the charge of a helium nucleus ${}_2He^4$. There is no such difficulty in the relation between helium and some heavier elements. Two helium nuclei ${}_2He^4$ form the beryllium isotopes ${}_4Be^8$, three of them form carbon ${}_6C^{12}$, four of them oxygen ${}_8O^{16}$, five of them the neon isotope ${}_{10}Ne^{20}$.

Although in the chapter on Isotopes we apply Einstein's principle only to the *mass defects*, *i.e.*, to small quantities of the order of a few thousandths of a proton mass, a convenient standard is obtained by computing the "atomic mass unit," *i.e.*, the energy equivalent of the mass belonging to a unit atomic weight (see Prob. 20.5). The result is 931 Mev. However, the application of this unit does not imply that the exchange between mass and energy has ever been observed in such large quantities. *Million electron volt*, abbreviated Mev, is the conventional energy unit in nuclear physics. It is applied as well to the energies of charged particles accelerated by high voltage as to any other energy, *e.g.*, of quanta or nuclear reactions.

Positive-ray analysis may impress the student, to begin with, as a remote field of physics without any general interest just indicating the nature of the rays as consisting of charged atoms and molecules. Here the great importance of this field becomes manifest. Positive rays give us a more profound understanding of the nature of matter by revealing the fact that the great variety of the different elements known in chemistry are actually built of one or a few building blocks. Moreover, the example of hydrogen and helium shows that positive-ray analysis, interpreted by Einstein's principle of the equivalence of mass and energy, gives evidence of the relative energies of nuclei. When accepting Einstein's principle, we discard the principle of conservation of mass which through centuries had been accepted as one of the cornerstones of physics and chemistry. We applied Einstein's principle only to the slight *excess beyond unity* evident in the atomic weight of hydrogen. One may go a step farther and assume that *all matter* is an accumulation of energy. Then the principle of conservation of energy fully replaces the two old principles, which seemed to be independent: that of mass and that of energy. No exception has been found, however, to the principle of conservation of electric charge.

20.4. Deviations from the Whole-number Rule. The whole-number rule is the outcome of the high technical development of the mass spectrograph. The further development of this instrument enabled Aston to measure the relative weights of isotopes with still higher accuracy. In this way he discovered that all isotopes deviate from the rule by noticeable amounts. Because of the great significance of these deviations as indicating nuclear energies, many of them, in particular those of the light elements, have been determined with a special mass spectrograph of high precision designed by Bainbridge. We shall mainly apply his numerical results.

Figure 20.4 demonstrates the accuracy of Bainbridge's results. The O atom and the CH_4 molecule, although differing in their atomic weights only in the higher decimal places, appear widely separated. The same is

true for the ordinary hydrogen molecule and the heavy hydrogen atom, which we shall discuss in the next section. Defining the atomic weight of oxygen O = 16.00000 the atomic weight of helium becomes He = 4.00216. Whoever has tried to improve the accuracy of a measurement will appreciate this success leading to three more significant figures. The accuracy is so high that one must take into account the fact that the positive-ray method furnishes the atomic weight of a *charged* atom like He^+ which is less than the atomic weight of the *neutral* atom by the contribution of 1 electron, *i.e.*, 0.00554.

Now we find that the mass of 4 helium atoms (4He = 16.00864) exceeds the mass of 1 oxygen atom (O = 16.00000). Each one of the two systems

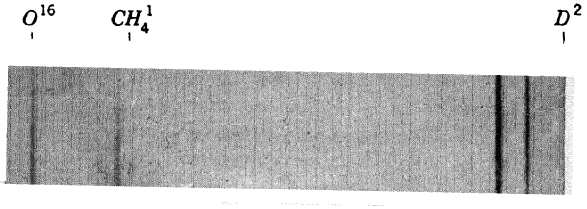


FIG. 20.4. Mass spectrum. The molecule CH_4 and the atom O have both the same mass number 16; the light hydrogen molecule and the deuterium atom have both the same mass number 2. The mass defects are evident. (*Courtesy of K. T. Bainbridge.*)

has 8 external electrons. Therefore, the larger mass of the four heliums must be attributed to their nuclei, not to external electrons. Consistently, we explain it by the same idea by which we correlated 1 helium and 4 hydrogens, *i.e.*, the equivalence of mass and energy. The corresponding computation leads to the result that an energy of 8.04 Mev is required to separate an oxygen nucleus into 4 helium nuclei.

Aston applied his analysis to all elements accessible to his method. All show deviations from the whole-number rule. So here is the strange situation of a vast array of atomic weights, stretching from 1 to 242, all figures very nearly being whole numbers, but all deviating from whole numbers in the third and higher decimal places. The number before the decimal point, indicating the multiple of fundamental building blocks, was called by Aston the "mass number" a ($a = 4$ for helium). The deviation from the whole number, $m - a$, is called the "mass defect" (m = atomic weight, for helium 4.00216). He plotted the quotient $(m - a)/a$, called the "packing fraction," against the mass number a. His results are given in the curve of Fig. 20.5, which shows no trace of periodicity as should be expected since we attributed the periodicity of the table of elements to the external electronic structure. It is a striking fact that a smooth curve, although branching on the side of the light elements, represents all packing fractions. In this respect the nuclei show a much simpler regularity than the electronic structures.

The zero value attributed to the packing fraction of oxygen has no physical significance since it is due to the arbitrary definition of its atomic weight as a whole number. Only the difference between the values belonging to two elements has significance. This difference furnishes the energies *spent* or *liberated* by the various nuclear separations. (This application of the curve will be demonstrated by Probs. 20.4, 22.4 to 22.6, and 22.8). Our computation makes it evident that energy is *liberated* when four $_2He^4$ form $_8O^{16}$, or two $_8O^{16}$ form $_{16}S^{32}$. In general the formation of a nucleus with a smaller packing fraction liberates energy. The same

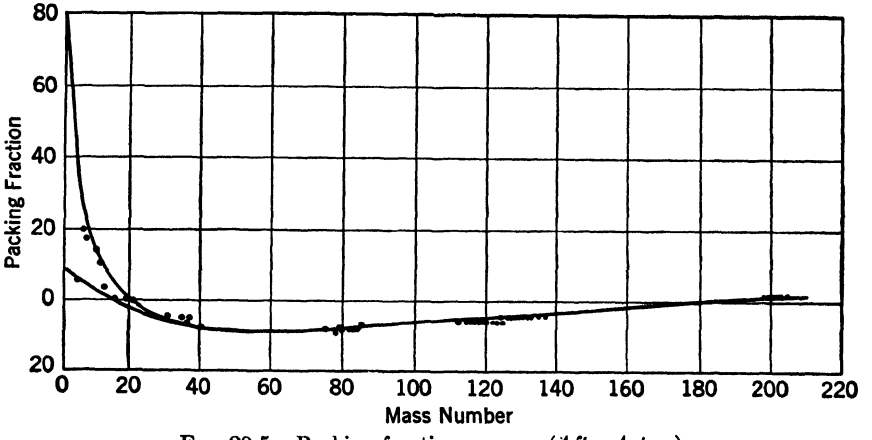


FIG. 20.5. Packing-fraction curve. (*After Aston.*)

idea applies to the right wing of Aston's curve. There the situation is complicated by the fact that a heavy element, *e.g.*, the uranium isotope $_{92}U^{235}$, cannot simply split into two lighter elements like $_{36}Kr^{84}$ and $_{56}Ba^{138}$. Although their nuclear charges add up to 92, the sum of their mass numbers, 222, is deficient as compared with the mass number 235 of U. We found a related difficulty in the relation between $_1H^1$ and $_2He^4$ (see Sec. 20.3). Later we shall solve this difficulty by assuming neutral particles of the atomic weight 1, called "neutrons," as essential building blocks of all atoms heavier than $_1H^1$ (Sec. 22.2).

Einstein's principle of the equivalence of mass and energy predicts a certain change of packing fraction to occur in the emission of an alpha particle from radium. The radium atom contains energy stored up like a charged gun. Therefore, the radium atom should have a larger mass than the fragments into which it splits. Unfortunately the atomic weights of radium and the "daughter element" radon are not known with an accuracy sufficient to check the principle.

Great practical interest is connected with the question: How can we *gain* energy? In other words, which are the nuclear processes in which energy is *liberated*? The general answer is closely connected with the slope

of the curve of packing fractions. The high values of the *left* wing indicate that the lightest atoms as compared with their heavier neighbors contain stored energy. Hence energy is *liberated* by the *combination* of the light atoms. On the other hand, the packing fractions increasing toward the *right* wing indicate that the heavy atoms *liberate* energy when changing to lower-weight atoms, *i.e.*, when *disintegrating*. This argument agrees with the well-known fact that the heaviest elements disintegrate spontaneously (Chap. 21). We shall study an application of this curve when computing the energy liberated by uranium fission (Sec. 22.8, Prob. 22.7).

The deviations from the whole-number rule represent a case in which the painstaking exploration of the higher decimal place results in a great new discovery which is not anticipated in the less accurate figures.

20.5. Abundances of Isotopes. The atomic weights of the *chemical elements* (with very few exceptions) are as sharply reproducible as the accuracy of the measurements permits. Therefore, before the discovery of isotopes, they were considered to be fundamental constants. Now we know that an important factor determining a chemical atomic weight is the relative abundance of the isotopes which, by a refined technique, we may well alter. The fundamental significance is now attributed to the atomic weights of the individual *isotopes*, as discussed in Sec. 20.4. It is a striking fact that, with few exceptions, for each element the relative abundance of the isotopes is the same once and for all. As a matter of fact, the measurement of the relative abundance combined with the atomic weights of the isotopes provides a very accurate determination of the chemical atomic weight. The relative abundance is measured by the currents registered in the ionization chamber. Figure 20.6 shows the relative abundance of the mercury isotopes.

Are the relative abundances so measured characteristic only for the earth? The little material that may serve to answer this question is derived from the investigation of meteorites, which presumably are members of the solar system, too. They show the same relative abundances as the elements known in the laboratory.

A striking exception to the rule is given by lead. Figure 20.7*a* shows the isotopic constitution of "ordinary" lead, *i.e.*, the lead found in many ores. Entirely different is the constitution of lead found associated with radioactive elements. As we shall see in the next chapter, these elements decompose in many steps which end with lead as the stable product. Figure 20.7*b* shows the constitution of lead found at Katanga in the Belgian Congo, one of the rich sources of uranium and radium. Katanga lead shows a striking preeminence of the isotope 206 which has only a rather low abundance in ordinary lead. We shall come back to this fact when discussing the radioactive series (Sec. 21.4). We must conclude that, in the early geological period in which the minerals were formed, a certain

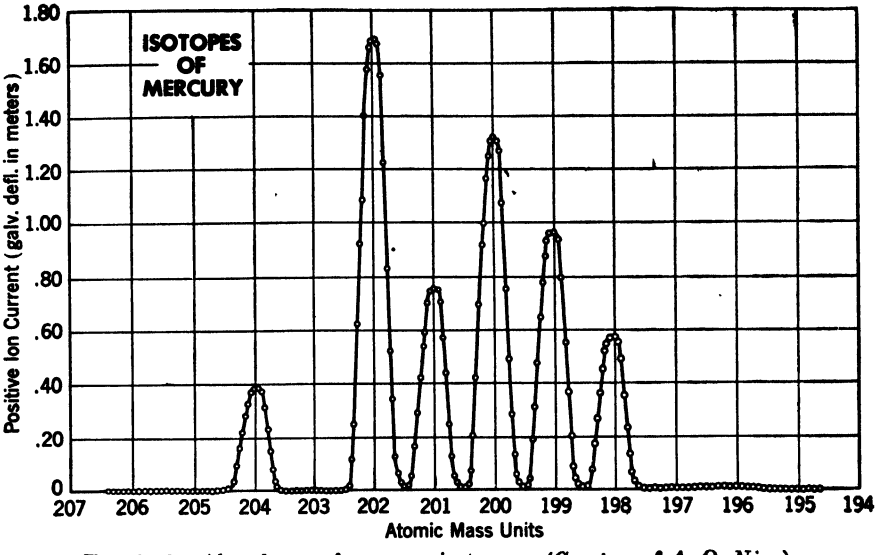


FIG. 20.6. Abundance of mercury isotopes. (*Courtesy of A. O. Nier.*)

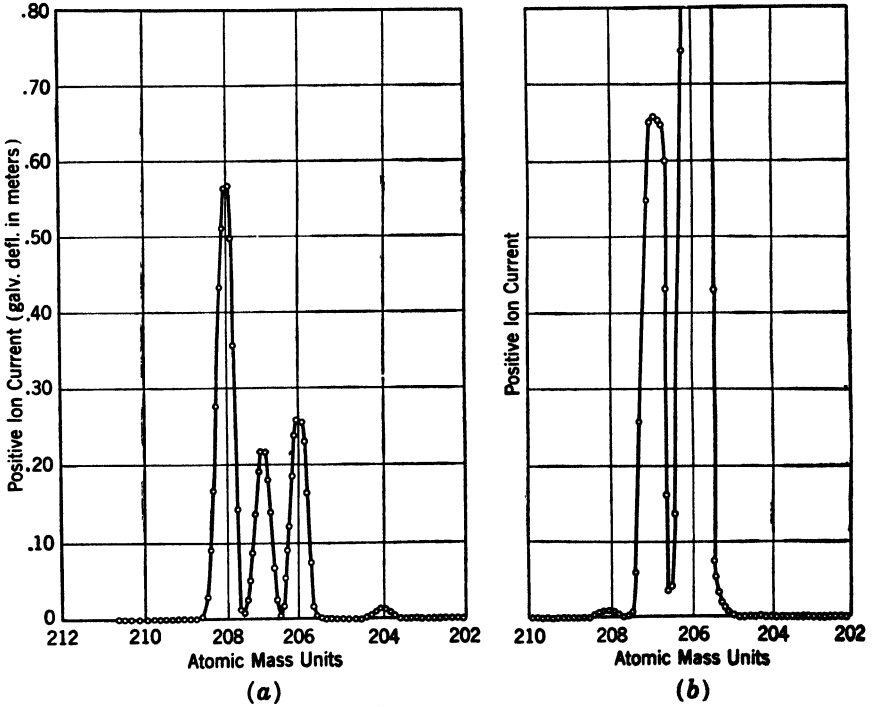


FIG. 20.7. Abundance of the isotopes of lead. (*Courtesy of A. O. Nier.*) (*a*) Ordinary lead; (*b*) Katanga lead.

isotopic constitution prevailed all over the whole material now accessible to our investigation. This constitution remained unchanged through the ages except for the few elements that are spontaneously disintegrating and so giving rise to the gradual formation of elements like Katanga lead.

In many elements, in addition to the well-known isotopes, rare isotopes have been discovered. The most important example is the rare heavy isotope of hydrogen ${}_1H^2$, frequently called "deuterium"; its nucleus is called the "deuteron." Its existence was inferred by a slight discrepancy between the values of the atomic weight of hydrogen determined by chemical methods and by the mass spectrograph. However, the mass spectograph used was not so sensitive that it showed the heavy isotope. Urey, Murphy, and Brickwedde (1932) went through a laborious procedure intended to increase the concentration of the heavy isotope if present at all. They relied on the fact predicted by the theory that a light atom should evaporate more readily than a heavy atom. Hence they evaporated a large quantity of liquid hydrogen and searched the residue for heavy hydrogen. They investigated the line spectrum which, for the heavy isotope, should show all Balmer lines slightly displaced to shorter wave lengths as predicted by Bohr's theory of the relative motion of the nucleus (Sec. 15.6*b*). Actually, the displaced lines appeared and proved the existence of a new isotope in the element hydrogen, which had seemed so thoroughly explored. Heavy hydrogen has a relative abundance of 1/4,500. Its effect on the chemical atomic weight is small but just noticeable. However, the striking deviation of the chemical atomic weight of hydrogen from unity (Sec. 20.3) is not due to the presence of deuterium but is a property of the most abundant isotope ${}_1H^1$.

Many other rare isotopes have been found. For example ${}_6C^{13}$ (abundance 0.7 per cent) is responsible for the fact that the atomic weight of carbon 12.01 slightly exceeds a whole number. Nitrogen has a rare isotope ${}_7N^{15}$. Oxygen has two rare isotopes, ${}_8O^{17}$ (0.04 per cent) and ${}_8O^{18}$ (0.20 per cent). This fact causes a curious ambiguity in the definition of our standard. The chemist attributes the atomic weight 16.0000 to the chemical element containing all three isotopes. On the other hand, the mass spectroscopist attributes the value 16.00000 to the most abundant isotope, the only isotope recorded on most mass spectra. Hence he attributes to the mixture the atomic weight 16.0044 (Prob. 20.6). For this reason the atomic weights derived from mass spectra must be corrected in order to make them comparable to those determined by chemical methods. For most purposes it is not necessary to take into account this correction.

In this section we restrict ourselves to the consideration of the isotopes found in nature. In the chapter on the transmutation of elements we shall study many new isotopes produced in the laboratory. We reported only the numerical values of the relative abundances. What processes are responsible for determining these abundances remains a mystery. In

the section on energy production in stars (Sec. 23.3) we shall find a partial answer to this question.

20.6. Separation of Isotopes. For many purposes of research and practical application (see Sec. 20.8) a separation of isotopes in larger quantities is desired. It is true that the *mass spectrograph* provides a complete separation; but it yields only small quantities. This, at least, was considered to be a fact before the Second World War. In the meantime, the rare uranium isotope $_{92}U^{235}$ (abundance 0.7 per cent) has been separated by the mass spectrograph in quantities not announced but sufficient to destroy a city.

Fractional distillation of hydrogen has been mentioned as increasing the abundance of the heavy isotope in the residue. A complete separation of the neon isotopes has been accomplished by *gaseous diffusion*. When a steady stream of mercury vapor is maintained in a glass tube and neon gas is diffusing against the stream, the lighter isotope passes at the higher rate because of the larger speed of its atoms (Sec. 3.2). In order to apply diffusion to the isotope separation of solid elements, gaseous compounds are formed, like UF_6 for the separation of the uranium isotopes (Sec. 23.1). Related to this method is the separation by the *flow of gas through a porous clay pipe*. In order to explain this process, we go back to the well-known determination of the density of a gas by "effusion." A very small hole is drilled through the wall of a glass bulb containing two gases. If the hole is small as compared to the mean free path, we predict the rate of escape of one or the other gas by considering the molecular collisions with the wall. Any molecule that happens to hit the hole escapes. Light molecules, since endowed with higher speed than heavy ones [see Eq. (3.5)], hit the wall more frequently and so have a priority for escape. Light hydrogen will escape more readily than heavy hydrogen. The residue will show an increasing concentration of heavy hydrogen.

The separation of light and heavy hydrogen is comparatively easy since the mass ratio of the two isotopes is as large as 2:1. Even in nature the relative abundance of the two is not strictly constant, and their physical properties are noticeably different. For example, heavy water, *i.e.*, water built of 2 heavy hydrogen atoms combined with 1 ordinary oxygen atom, has a melting point 3.8°C higher than ordinary water. Much more difficult is the isolation of the rare isotopes C^{13}, N^{15}, and O^{18}. Their great importance will be discussed in Sec. 20.8.

20.7. Nuclear Magnetic Moments. The magnetic moment of a nucleus is a property that gives important evidence concerning its structure. As briefly mentioned in Sec. 16.1*c*, the hyperfine structure of spectral lines allows a rather indirect determination of some nuclear magnetic moments. One may predict that *nuclear* magnetic moments are of a much smaller order of magnitude than *electronic* magnetic moments since quantum theory postulates angular momenta in multiples of $h/2\pi$, and the same value of

angular momentum would impart a much slower rotation to the relatively large mass of a nucleus than to that of an electron.

More direct methods for the measurement will be only briefly reported. They are based on the fact that, in a stable molecule like hydrogen or water or paraffin, the *electronic* structure has no resulting magnetic moment since all moments of the individual electrons (orbital and spin moments) cancel each other. Hence only the *nuclei* are responsible for the resulting magnetic moments of the substances. As the simplest example, let us consider hydrogen. Suppose that hydrogen nuclei are subjected to an external, constant magnetic field H. Quantum theory predicts that each hydrogen nucleus, representing a tiny magnet (magnetic moment $= M$) has two quantized orientations, parallel or antiparallel to this field (see Sec. 16.1*c*). These two positions differ by a certain energy that is computed as the energy required to turn a magnetic needle of the moment M in the magnetic field H from the parallel into the antiparallel position. The computation (see Prob. 20.8) gives this energy as $2MH$. The nucleus may change its orientation between these two quantized values by emission or absorption of light. The frequency ν of this light is computed from Bohr's quantum condition as $h\nu = 2MH$.

It is estimated that this frequency belongs to the radio-frequency range. Here the experimental problem of observing an absorption spectrum cannot be solved with the familiar technique (Sec. 17.5) since no spectrographs are available. Most of the accurate information that we now have on nuclear magnetic moments is due to Rabi and his collaborators (beginning 1936) who used their elegant method of molecular beams. Omitting the description of their experiment, we give an outline of the device recently used by Purcell, Torrey, and Pound (1945) and its application to the hydrogen nucleus. A small coil of wire, which is part of a resonance circuit (frequency 29.8×10^6 cycles/sec) surrounds the sample to be tested, *e.g.*, paraffin which provides a great density of hydrogen atoms. (It turns out that the carbon atoms contained in the paraffin are ineffective.) Thus the hydrogen nuclei are subjected to alternating magnetic fields of the high frequency just given. This coil is put into a constant magnetic field H which, as explained, imparts quantized orientations and thus a characteristic frequency ν to the nuclei. If this frequency coincides with the high frequency of the circuit, the nuclei absorb energy. This explains the observation which shows that, at a special value of the constant field, in this case $H = 7{,}000$ oersteds, the material in the coil affects the phase and amplitude of the high-frequency current. For these values of frequency and magnetic field the above equation yields a value for the magnetic moment of the proton as

$$M = 1.406 \times 10^{-23} \text{ erg/oersted}$$

As expected, this value is of a smaller order of magnitude than Bohr's magneton (Sec. 15.5*f*). For nuclear magnetic moments, the conventional unit is the "nuclear magneton," defined as Bohr's magneton multiplied by the mass ratio of electron and proton. In this unit the magnetic moment of the proton is 2.79. The new method described here is applied to the precise measurement of the magnetic moments of many nuclei. The resulting values are characteristic for the individual isotopes of an element; *e.g.*, protons and deuterons have different magnetic moments.

20.8. Applications. Rare isotopes find important applications as "tracers" in physical, chemical, and biological research. This will be illustrated by an example. Suppose we want to trace the distribution in the animal body of a certain protein, occurring in the food. This protein is prepared with carbon that contains an artificial extra abundance of the heavy isotope C^{13}, and the food containing this protein is fed to mice. After a certain time, the mice are killed and the carbon, extracted from the various organs, is analyzed in the mass spectrograph. One or the other organ may show an extra high abundance of the heavy isotope and so indicate that this organ is a preferred consumer of the protein under investigation.

Here, as in all similar experiments, we rely on the fact that the various isotopes of one element show the same chemical properties since these are determined by the *electronic structure*, common to the isotopes, but not by the *nuclear masses*. Hydrogen represents the only case in which this assumption may be questioned since, in a reaction, the mass ratio 2:1 of the isotopes may give a slight priority to one or the other isotope. The experiment discussed above gives only a special example of a highly developed field, which makes the mass spectrograph indispensable in biological and medical research.

SUMMARY OF CHAPTER 20

By positive-ray analysis, Aston (1921) discovered that neon (atomic weight, 20.20) does not contain individual atoms with the atomic weight 20.20 but consists of a mixture of two types of atom with the whole-number atomic weights 20.00 and 22.00 and the relative abundance 9 and 1. This gives the average atomic weight 20.20 in agreement with the well-established chemical value. In general, any element with an atomic weight deviating from a whole number is analyzed into several types of atom, each of whole-number atomic weight. They are called "isotopes." A slight exception is given by hydrogen whose atomic weight 1.008 belongs to the individual atoms. Isotopes of the same element have the same nuclear charge, the same chemical and spectroscopic properties (with minor exceptions), but different nuclear masses.

This discovery revives Prout's hypothesis stating that all atoms are built of one or a few fundamental particles, the outstanding particle presumably being the hydrogen atom. Its slight deviation from the whole-number rule is interpreted on the basis of Einstein's principle of the equivalence of mass and energy. It is assumed that a large amount of energy is required to split 1 helium atom into 4 hydrogen atoms and that this energy stored in the hydrogen atoms makes them appear heavier. The energy of separation of the helium atom so computed is about seven million times the energy of dissociation of a hydrogen molecule. In this computation all atoms are assumed to be neutral. However, 4 protons cannot simply form a helium nucleus since they possess two times the required charge. Therefore, one must assume that the helium nucleus contains 2 protons and 2 neutrons.

A further improvement of the technique results in atomic weights given by six significant figures. In most atomic weights the third figure after the point shows a deviation from the whole-number rule. Aston plotted the packing fraction $(m - a)/a$ (a = atomic weight; m = mass number = nearest whole number to the atomic weight) against the atomic weight a. Thus he found a simple curve without a trace of the periodicity evident in chemistry and spectroscopy. From the data given by Aston's curve energies of separation (*e.g.*, $O \rightarrow 4He$) can be computed. The curve gives evidence of the instability of elements, the lightest elements tending to combine, the heaviest elements tending to disintegrate with energy liberated by both processes. The conventional notation gives the atomic number and the mass number as, for example, ${}_2He^4$.

The elements have well-defined chemical atomic weights. This fact indicates that the relative abundances of the isotopes are once and for all the same. A notable exception is given by lead found in uranium minerals, presumably present as the end product of radioactive decay.

Many elements have rare isotopes. Examples are ${}_1H^2$, ${}_6C^{13}$, ${}_7N^{15}$, ${}_8O^{17}$, ${}_8O^{18}$. Here only stable isotopes are considered, not the radioactive isotopes to be discussed in Chap. 22.

The isotopes of an element may be partly or wholly separated. Rare isotopes are valuable as tracers in physical, chemical, and biological research.

Nuclear magnetic moments are measured by subjecting a substance that has no resulting *electronic* magnetic moment to an external magnetic field. This causes quantized orientations of the nuclei, which differ by sharply defined energies. Transitions between such quantized states are produced by quanta of the corresponding energy, *i.e.*, by radiation of the radio-frequency range.

PROBLEMS

20.1. *Mass spectrograph.* In Dempster's mass spectrograph an ion beam is bent into a circle of 5.00-cm radius by a magnetic field of 3,840 oersteds. What voltages must be applied to accelerate the following types of singly charged ion to such a velocity that they are recorded? (*a*) $_3Li^6$; (*b*) $_3Li^7$; (*c*) $_{19}K^{39}$; (*d*) $_{19}K^{41}$. See Appendix 5.

20.2. *Mass spectrograph.* In Dempster's mass spectrograph (Fig. 20.2) ions belonging to an impurity are accelerated by a potential difference of 772 volts and, after passing the slit, bent by a magnetic field $H = 3{,}840$ oersteds into a half circle of 5.00-cm radius. What is the nature of these ions? Assume singly charged ions.

20.3. *Resolving power.* In one of Dempster's mass spectrographs, (Fig. 20.2) positive ions, after being accelerated by an electric field, are bent by a magnetic field of 3,840 oersteds into a half circle of 5-cm radius. Discuss the resolving power of this instrument on the following basis: Suppose that the first slit is 0.5 mm wide and that each positive ray, when incident on the second slit, has the same width. Furthermore, suppose that, at the place of the second slit, Dempster is able to resolve rays that do not overlap and even are separated. This means that some "darkness" exists between such rays. For this to occur, they must be more than 0.5 mm apart (measured from the middle of one ray to the middle of the other). Can he resolve lithium isotopes (mass numbers, 6 and 7)? Can he resolve mercury isotopes (mass numbers, 200 and 201)?

HINT: For given values of voltage and magnetic field, two adjacent rays belong to two adjacent isotopes. Both rays emerge from the same (the first) slit. They are separated after passing through one-half circle because their masses differ. When they come near the second slit, they are assumed to have a width of 0.5 mm each. Assume that one ray (*e.g.*, Li^6) just hits the second slit ($2r = 10$ cm, V to be computed). Where does the ray that belongs to the other isotope hit the plate into which the slit is cut? If, for the same voltage, darkness exists between the two rays, these two isotopes can be resolved.

20.4 *Nuclear energy.* How much energy in Mev is liberated when (*a*) three $_2He^4$ form $_6C^{12}$; (*b*) four $_2He^4$ form $_8O^{16}$; (*c*) $_2He^4$ and $_6C^{12}$ form $_8O^{16}$? The answer to (*c*) serves as a check for the answers to (*a*) and (*b*).

20.5. *A standard energy equivalent.* Compute the energy equivalent of the mass of unit atomic weight.

20.6. *Energy equivalent of* 1 *kg.* Suppose that the *total mass* of 1 kg is transformed into energy. How large is this energy (in kwhr)? The answer about equals the energy produced by all electric power plants of the United States (as of 1939) running for 2 months (H. D. Smyth).

20.7. *Scale of atomic weights.* Compute the atomic weight of natural oxygen (abundance of isotopes, see Appendix 5) in the "physical scale" in which the atomic weight of the most abundant isotope is defined as exactly 16.

20.8. *Work required to turn a magnet.* A magnetic needle is turned in a magnetic field starting from its stable position (parallel to the field) into the opposite position. By integration, compute the work required in terms of the field strength H, the pole strength m, and length l of the needle.

HINT: Obtain the expression for ΔW = work required to turn the needle by the small angle $\Delta\alpha$. Take α as the variable of integration and integrate. (ml is called the "magnetic moment" M of the needle.)

CHAPTER 21

NATURAL TRANSMUTATION AND RADIOACTIVITY

Natural radioactivity was discovered more than half a century ago by A. H. Becquerel. This discovery, together with those of X rays and of free electrons, marks a turning point in the history of atomic physics. Two difficulties retarded the exploration of this new field: (1) Only exceedingly weak samples of active material were available at the beginning. (2) Since radioactivity was completely foreign and even contradictory to all that was known of physics and chemistry, there was no theory whatever to guide the exploration; it developed only gradually, guided by the experiments. Although historically these great difficulties made the progress devious, we can well go through arguments more straightforward than those of history since we have grams of radium as well as the theory of the nuclear atom at our disposal.

21.1. Discovery and Fundamental Properties. The discovery of X rays (1895) suggested a relation between visible fluorescence and emission of X rays which are both emanating from the glass wall of Roentgen's discharge tube. As Becquerel (1896) explored such a relation using uranium salts, he found a new penetrating radiation that is permanently given off by uranium minerals. Against any expectation, this radiation is independent of any treatment of the mineral with light, X rays, cathode rays, or any other supply of energy.

The uranium minerals were then subjected to a painstaking chemical analysis by Pierre and Marie Curie. Many kinds of chemical separation were applied. After each separation, the products were tested, the inactive part discarded, and the active part further analyzed. The result was that there are several active elements, prominent among them being one associated with barium and thus recognized as an alkaline earth. By fractional crystallization the inactive barium was gradually removed. The progress of the purification was tested by two criteria: the appearance of an atomic spectrum hitherto unknown and, more conclusive, the increase of the activity of the sample. We continue with the words of Mme. Curie:

> After a long effort I succeeded in obtaining radium as a pure salt in a quantity sufficient for the determination of the atomic weight. So I assigned to it its place in the periodic table of elements.

The atomic number, 88, of radium, found by Mme. Curie was later confirmed by its X-ray spectrum. Soon thereafter it was found that many other heavy elements show more or less strongly a similar activity. Radium is conspicuous by the strength of this new effect. The outstanding effects produced by radioactive elements are as follows:

1. They permanently emit radiations of various grades of penetrating power; each species (later we shall say each radioactive isotope) has its characteristic radiation. We have already studied alpha rays (Chap. 14). In the next section we shall find two more types of ray, still more penetrating than alpha rays. All these rays blacken photographic plates and ionize air.

2. All radioactive elements are continually creating small quantities of new elements. An example is radium, which continually generates small quantities of helium and radon (abbreviated Rn), both rare gases. Helium, of course, is well known chemically. Radon, however, is found only as a product of radium. It is chemically identified as a heavy rare gas. As such, it belongs to number 86 of the periodic table, preceding radium, which is an alkaline earth, by two numbers. (No sufficient quantities of radon are available for producing a measurable X-ray spectrum and so identifying the new element.)

3. A tube containing radium always has a temperature slightly higher than the surroundings.

The conclusion, unheard of at the time of the discovery, is reached that we must assume a hidden source of energy to be responsible for the effects observed. In order to judge this mysterious energy, we compare the decomposition of radium with a chemical decomposition as follows: (1) While the disintegration of radium into helium and radon goes on spontaneously all the time, nobody has ever succeeded in combining radon and helium and so producing radium in the same way in which any chemical molecule can be synthesized. (2) The disintegration is an intrinsic property of the radium atom and is entirely independent of anything we can do to it like heating it or bombarding it with electrons or combining it chemically with any other substance. (3) The energy content of radioactive rays, amounting to several Mev, contrasts with all known chemical energies that are only about one-millionth of this value. (4) In the disintegration process new elements are created.

All these facts prove that the spontaneous disintegration of radium bears no relation to a chemical process. Radium is not the only element that shows this activity. Many other heavy elements do the same to various extents. In particular, each radon atom, itself a product of a decomposition, in turn decomposes with the emission of another alpha particle and so creates more helium.

The experimental facts described, which are entirely different from any-

thing observed in other fields of physics and chemistry, force us to assume a process within atoms hitherto unknown. We assume that *radium, as well as other radioactive elements, has an intrinsic probability, which we cannot affect at all, to disintegrate into other elements* (Rutherford and Soddy, 1902). In some elements this probability is so high that only minor concentrations of the element can accumulate as in the case of radon. In other elements, as in radium itself, it is so low that, within days or a few years, the mass of the element does not appreciably decrease.

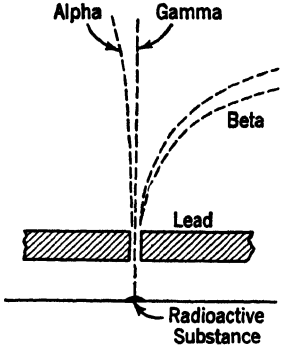


FIG. 21.1. Schematic drawing showing the separation of the three types of radioactive ray by a magnetic field deflecting a bundle of rays that have passed through a lead diaphragm.

The creation of new elements can occur only by a splitting of the nuc eus. Hence we must conclude that in the radium nucleus, as in an explosive, energy is stored which, at the explosion, spontaneously breaks it up into a helium and a radon nucleus. Since the atomic numbers of radium, radon, and helium are 88, 86, and 2, respectively, we notice the conservation of the *nuclear charge*. The *atomic weight* of radon cannot be determined accurately, but we can predict it as the difference of those of radium and helium, *i.e.*, $226 - 4 = 222$. The energy exchange in the disintegrations of radioactive elements is of the order of several Mev. The corresponding change of mass may be computed on the basis of Einstein's principle as pointed out in Sec. 20.4. The change of mass shows up only in the higher decimal places of the atomic weight and is by no means large enough to affect the mass number.

In the next sections, we shall explore the three outstanding aspects of radioactivity: (1) the nature of the various rays emitted, (2) the rate at which they are emitted expressed by the half-life of the parent substance, and (3) the chemical transmutations caused by the emission of the rays.

21.2. Radioactive Rays; Methods of Observation. The nature of the radioactive rays is brought out in the experiment schematically represented by Fig. 21.1. A pencil of radiation that is subjected to a magnetic field perpendicular to its direction is separated into three rays. One of them is positively charged and only slightly deflected; this is the alpha ray discussed above. Another ray, called "beta" ray, is deflected in the opposite direction and so indicates a negative charge. Finally, the third type of ray called "gamma" ray is not deflected at all by electric or magnetic fields; it has all the properties of a very hard X ray, in particular its very high penetrating power. Thus there exist two corpuscular rays and this additional ray which must be supposed to have a quantum structure like the X rays. Various devices, the most important ones based on the

ionization of gases caused by these rays, have been built for their detailed investigation. We shall illustrate all these devices by the effects they show when alpha rays are used. Afterwards we shall describe the effects of beta and gamma rays.

a. Alpha Rays. We anticipated the discussion of alpha rays (Chap. 14) in order to have the background for Rutherford's theory of the nuclear atom, which is based on observations of the scattering of alpha particles. Here we summarize their properties.

It is *observed* that alpha particles accumulating in a glass tube represent helium gas. We *conclude* that the alpha particle is essentially identical with a helium atom; hence its mass is $\mu = 6.64 \times 10^{-24}$ g. We assume that the charged particle when traversing matter gradually is losing its kinetic energy and may pick up the electrons needed for its neutralization so that finally it represents an atom of helium that does not show any symptom of its origin.

It is *observed* that the alpha particle is positively charged and has a specific charge $\epsilon/\mu = 4.82 \times 10^3$ emu/g. Combining this figure with the preceding result, we *conclude* that its absolute charge is $\epsilon = 3.20 \times 10^{-20}$ emu. As this is twice the electronic charge, we further conclude that alpha particles are identical with doubly positively charged helium ions.

It is *observed* that alpha particles penetrate gold foil, 2,000 atoms thick. We *conclude* that gold and other matter have their mass concentrated in very small nuclei and that the alpha particle itself is a very small projectile, presumably a helium nucleus.

For many years the outstanding method of observing and counting alpha particles has been the laborious observation of *scintillations* on a fluorescent screen. Rutherford made some of his greatest discoveries by counting scintillations. Now we ask: Does each incident alpha particle produce an observable scintillation? This question is answered by combining two measurements as follows: Using the same alpha ray, the scintillations per second are counted and, independently, the number of particles arriving is measured by the total charge they convey to an insulated condenser plate. Both measurements lead to the same figure. Thus their combination proves that each alpha particle produces an observable scintillation.

Another outstanding property of alpha rays is their limited range. A radium sample that produces ample scintillations when close to the screen, becomes ineffective beyond a well-defined distance. The range of alpha rays so determined is a characteristic property of the emitting atom; *e.g.*, in 1 atm of air the range of alpha rays from radium is 3.39 cm.

In most devices we use the ionization of air in order to explore the radiation. The simplest apparatus is the *ionization chamber*, a closed chamber containing a charged condenser connected to an electroscope. For the observation of alpha rays the radioactive sample is placed inside the chamber

or in front of a very thin window. It is easy to measure the *over-all effect* by the decay of the charge on the electroscope. The ionization due to one *individual particle* can be measured in a similar device if the short burst of electric current, due to the effect of the particle, is amplified. This permits the counting as well as the differentiation between more or less heavy bursts of ionization and is of great value for distinguishing the various particles.

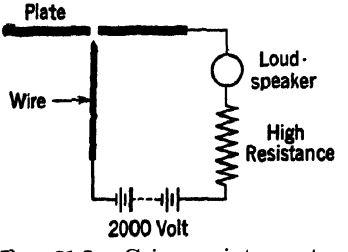


FIG. 21.2. Geiger point counter; discharge in air between point and plate.

A very useful device, simple enough for students to use though highly developed for research purposes, is the *Geiger counter* (1908). In this counter an electric discharge through air or another gas at atmospheric pressure or, in most cases, at a lower pressure is used. A simple construction is shown in Fig. 21.2. The discharge takes place between a plate through which a small hole (a few millimeters in diameter) is drilled, and a pointed wire which is placed with its point opposite the hole. A self-maintained discharge between the wire and the plate requires for its start a minimum potential, say, of 2,000 volts. The potential applied is kept a little below this threshold so that ordinarily no current is flowing. Only when an alpha particle shoots through the air between the wire and the plate does the ionization start the discharge, which lasts for only a very short time since the voltage drop in the high series resistance causes so great a loss of potential difference between plate and wire that the discharge goes out automatically and the device is ready to receive the next alpha particle. Each burst of electric current shows up, *e.g.*, in a string galvanometer. More conveniently it is amplified and operates either a loud-speaker or a mechanical counting device. Thus the counting of alpha particles, which by the scintillation method is fatiguing work, is wholly mechanized. The "point counter" here described serves for alpha or beta rays which, with special devices, may be distinguished from one another. The range of alpha particles can be demonstrated.

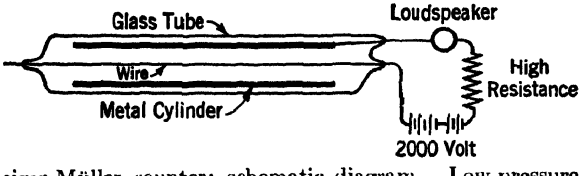


FIG. 21.3. Geiger-Müller counter; schematic diagram. Low-pressure discharge between a wire and a coaxial metal cylinder.

A more reliable device is the *Geiger-Müller counter* (Fig. 21.3; 1928). It consists of an electric discharge tube with a thin axial wire as the cathode

and a concentric metal cylinder as the anode; the tube is filled with air or argon or alcohol vapor of several centimeters pressure. The electrical connections are essentially the same as in Fig. 21.2.* The much larger sensitive volume is the outstanding advantage of the Geiger-Müller counter over the point counter. Although constructed for the counting of gamma rays, it counts beta and even alpha rays equally well if provided with a sufficiently thin window. Modern improvements of the counters have led to electric circuits of great complexity, all planned to increase the maximum rate at which the counter may serve. For this purpose, first, the duration of each burst of electric current must be reduced. Next, since the mechanical recorder has some unavoidable inertia, an intermediate circuit is built that has the function of feeding only each second burst into the recorder. By combination of two or more such devices one can have the recorder show only one response, say, for each 64 particles incident on the counter tube. This makes possible the recording of thousands of counts per second. Another development, the combination of several counters to "coincidence counting," will be discussed in the section on annihilation (Sec. 22.5) and applied to cosmic ray investigations (Chap. 24).

The author assumes that, at the present stage of the discussion, the reader needs no further experimental proof of the atomic structure of matter and the consistency of our argument. However, one piece of additional evidence must be discussed since alpha rays permit the determination of Avogadro's number by the most direct method imaginable, *i.e.*, the direct counting of the atoms contained in 1 gram atom of helium. Using a small mass of radium we count the alpha rays emitted per second. (We observe the rays emitted into a small solid angle and compute the total number.) On this basis we compute the number emitted per year from 1 g of radium. Each alpha particle counted represents 1 atom of the helium gas slowly emanating from the radium. In addition the total volume of the helium emanating from 1 g of radium in 1 year is measured. Thus we compute the number of helium atoms per cubic centimeter and, since the atomic weight is known, the number of atoms in 1 gram atom, which is Avogadro's number. For the numerical values see Prob. 21.1. The result agrees with the results of other determinations within the limit of experimental error.

The *Wilson cloud chamber* (C. T. R. Wilson, 1911) is another device utilizing the ionization of air. It supplies surprisingly detailed information of a different kind. It is a familiar view that, on a perfectly clear day, a light cloud hangs around the top of a high mountain. The condensation of water is explained as follows. Air is lifted by the wind as it approaches the slope of the mountain. Thus the air expands and also cools since it does

*For technical circuits see J. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, 1938.

mechanical work in the process of expansion. If, before the expansion, the content of water vapor is slightly below saturation it may happen that, after the expansion and cooling, the saturation limit is passed and condensation takes place. This is made evident by the cloud. Similar is the process going on in Wilson's cloud chamber. Figure 21.4 shows a simple chamber. A glass cylinder is closed on one side by a glass plate, on the other by a piston. The cylinder contains air and a few drops of liquid water, which readily provides water vapor at the saturation pressure. To begin with, the piston is pushed in, compressing the air. A short time is allowed to provide saturation of water vapor. Next, by the release of the piston, a sudden expansion of the air in the chamber is produced. The corresponding cooling brings the water vapor, mixed with the air, beyond the saturation point so that condensation of water follows and is seen as cloud formation.

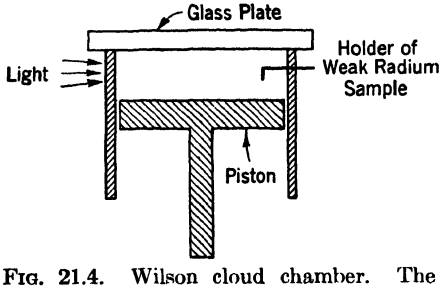


FIG. 21.4. Wilson cloud chamber. The space above the piston contains air saturated with the vapor of water or alcohol. Electrodes for the electric field sweeping out the ions are not shown.

It is known that condensation occurs with preference on dust particles and on ionized molecules. At the first expansions, the inevitable dust present in air causes a cloud to form all over the chamber. This is easily swept out by an electric field since the dust particles and the little water droplets carry electric charges. (The electrodes needed for sweeping are not shown in the figure.) Now the chamber is ready for the main experiment. When a weak radioactive sample carried by a metal wire is introduced, the cloud formed after the expansion sticks to the ionized air molecules and so indicates the path of the alpha particles (Fig. 21.5). Although these clouds drift away very soon, the paths of the particles can for a moment be clearly seen or photographed. Striking is the straight character of each ray, its well-defined end, and the uniform length of all rays called their "range." The range of the alpha ray is characteristic for the emitting atom. In the figure the rays from two radioactive elements, each with its characteristic range, are superimposed. This direct observation of the range confirms what we mentioned above as a result of the study of scintillations.

We want to correlate the observation of tracks by the cloud chamber with Rutherford's theory of the scattering of alpha particles. Rutherford and his coworkers investigated the scattering by the simple technique of counting scintillations (Chap. 14). He explained the high penetrating power of the rays by the hypothesis of the nuclear atom. This leads to

the assumption of two different types of collision process suffered by alpha particles when passing, for example, through gold foil. We distinguished them on the basis of the laws of mechanics. The alpha particle bounces off when colliding with a *nucleus* since this is much heavier than the alpha particle. However, the particle continues in a straight path when colliding with an *electron* and throws this light body out of the way. These two types of collision are beautifully demonstrated by cloud chamber pictures.

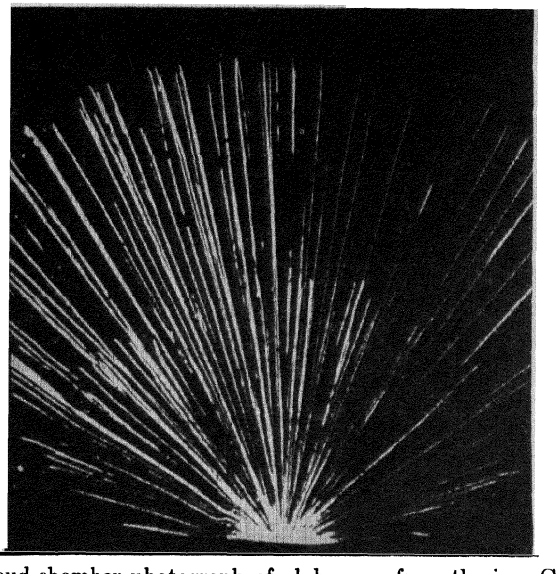
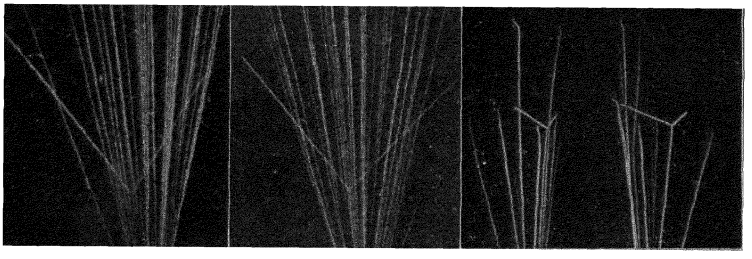


FIG. 21.5. Cloud-chamber photograph of alpha rays from thorium C and C′. Each group has its characteristic range. (*Courtesy of C. T. R. Wilson.*)

Figure 21.5 shows a group of alpha rays, all shooting in straight lines. Each water droplet of the apparently continuous track indicates one collision of the alpha particle *with an electron.* That is one ionization process. This is so common an event that the high density of the droplets gives the impression of a continuous cloud in the shape of the track. Figure 21.6 shows the rare collisions of alpha particles *with nuclei.* In the cloud chamber, in contrast to the case of the gold foil, the atoms of the gas are not necessarily heavier than the alpha particle. Figure 21.6*a* shows the scattering in helium, *i.e.*, by nuclei of masses equal to those of the particles. The two tracks so produced, that of the original alpha particle deflected by the collision and that of the "recoil nucleus," are both well defined. In gases heavier than helium, like oxygen (Fig. 21.6*b*), the track of the recoil nucleus is very short as would be expected since the alpha particle keeps most of its energy because of its smaller mass.

We must study in detail all the information we can derive from the

tracks observed in a cloud chamber because in artificial transmutation (Chap. 22) a greater variety of particles are being generated and *identified* by their cloud chamber tracks and, moreover, reveal their *kinetic energies* by these tracks. Figure 21.6 shows that fast nuclei of various kinds are produced by the impacts of alpha particles. The velocity of the alpha particle originating, say, from radium, is known once and for all, having been determined by electric and magnetic deflections. We compute the velocity given to the target particle on the basis of the velocity of the impinging particle, the masses of both particles, and the angles observed in the cloud chamber. This is a familiar problem of elementary mechanics.



(*a*) (*b*)

FIG. 21.6. Collisions of alpha particles with nuclei. (*a*) With helium; (*b*) with oxygen. (*Courtesy of P. M. S. Blackett and Proceedings of the Royal Society.*)

If we want to avoid the complication due to the occurrence of various angles, we select only tracks due to head-on collisions, easily recognized by the direction of the target particle which is thrown along the same line in which the alpha particle travels. This simple case is covered by the theory given in Prob. 14.1. The result is, for example, that the proton picks up a velocity $8v/5$ while the alpha particle, after the impact, continues its path in the original direction with the velocity $3v/5$ (v = velocity of the incoming alpha particle). By such experiments we compare the tracks due to the various particles at various kinetic energies.

Two outstanding features of the tracks are noticed. The average density of the track is characteristic for the type of the particle, *e.g.*, 100,000 ions per centimeter for alpha particles, about one-quarter of this value for protons, about 1/100 of the same value for beta particles. It is immaterial that these figures are not sharply defined since in any experiment there is not much choice among the various particles.

It is true that at atmospheric pressure the density is so high that the droplets, each representing 1 ion, cannot be counted. But the counting is easily done at lower pressures, and the figure for 1 atm is computed as inversely proportional to the pressure.

For proton rays as for alpha rays, the range is a well-defined function of their kinetic energy. This relation is studied by observing artificially

accelerated protons so that the range observed may serve for a determination of the kinetic energy. For equal energy, the range of protons is about four times as long as that of alpha particles.

We may check this determination of the nature and velocity of any particle by applying a strong magnetic field in a direction perpendicular to the direction of its path. Since we know the velocity (derived from the range), the magnetic deflection leads to a determination of ϵ/μ for the particle which, in turn, reveals its nature and so provides a check of the argument. Figure 21.7 shows the magnetic deflection of alpha particles in a field of 43,000 oersteds.

Summarizing, we notice the great variety of observations to be made with the cloud chamber. It reveals the nature of particles, their velocities, and a great deal of detail of the collision processes between particles.

The processes by which X rays and alpha rays are losing energy when traversing matter are widely different, as is evident from the description of their absorption. The fall in intensity of X rays is described by an exponential law $I = I_0 e^{-\mu d}$ (Sec. 19.1*d*) stating that there is *no well-defined limit* of the thickness through which X rays may penetrate. On the other hand, Fig. 21.5 strikingly shows that all alpha rays emanating from the same element have about the same range; the absorber takes away all particles belonging to the ray *after they have traversed the same distance.* These contrasting observations are explained by the different processes of absorption. An X-ray quantum spends its whole energy *in one process,* either the photoelectric effect or the Compton effect. Within each centimeter of path length in the absorbing medium, this process has a certain probability and removes a certain fraction of all quanta from the ray (see Prob. 17.5). Thus mathematically the intensity of the X ray decays following an exponential law and never reaches exactly zero. Hence we describe the absorption by an *absorption coefficient.* On the other hand, the individual alpha particle spends its energy *in many processes,* in each one of them ionizing a molecule. Thus it gradually is losing its initial kinetic energy which is equal to several Mev. This is not noticeable on the photograph of Fig. 21.5 except by the sudden end of each track. The distance within which several hundred thousand ionization processes take place is about the same for all particles. This explains why we describe their absorption by *their range,* not by an absorption coefficient. The gradual loss of velocity of the individual alpha particle along its track becomes evident in a strong magnetic field deflecting the particle (Fig. 21.7). The radius of curvature R depends on the magnetic field by the relation $R = \mu v/\epsilon H$ (see Sec. 8.2*a*). In the experiment represented by the figure, ϵ/μ and H are constant. Hence the radius R is proportional to the velocity. The figure shows that the rays, coming from above, are increasingly curved, hence show smaller values of R, toward the ends of their ranges.

Another difference between X rays and alpha rays is obvious, consider-

ing their nature. The X-ray quantum when absorbed disappears. The alpha particle when slowed down picks up electrons and continues its life as a helium atom.

When studying light or X rays, we get used to the fact that the *observation* shows something *continuous*, like the light emitted from a lamp. Only an elaborate theoretical argument makes us believe that the process involved, the emission of light quanta, is *discontinuous*. In the Geiger counter, however, the discontinuity of radioactive radiation is strikingly evident by the discrete kicks of the loud-speaker. Still more striking is the aspect in the cloud chamber which shows the individual alpha-ray tracks, their lengths, their deflections by a magnetic field (Fig. 21.7) and, as we shall study in detail, the fate of the alpha particles in various collision processes. The high energy of radioactive rays is required to produce these clearly visible tracks of individual particles.

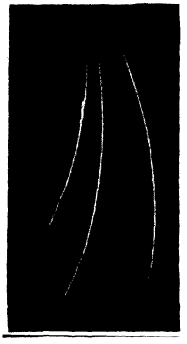


FIG. 21.7. Curved tracks of alpha rays in a magnetic field of 43,000 oersteds. (*After Kapitza.*)

b. Beta Rays. Figure 21.1 illustrates an experiment that shows that alpha, beta, and gamma rays are all three present among the rays coming from a composite source. When we apply chemical separation to a composite source, as first was done by the Curies, we find that each radioactive element emits either an alpha or a beta ray (with a very few minor exceptions in which both alpha and beta rays come from the same element). This makes the separate study of beta rays simple. As we shall see later, many beta emitters are produced by artificial transmutation. Gamma radiation is commonly associated with the emission of alpha or beta rays.

By magnetic deflection the beta ray indicates its negative charge. The combination of magnetic and electric deflection enables us to determine its specific charge, ϵ/μ, and velocity. The numerical value of the specific charge identifies the ray as consisting of free electrons. Their velocities are high, in some cases even closely approaching the velocity of light. Beta rays of a sufficient density produce fluorescence of a screen as is well known to everybody who has seen a cathode-ray oscilloscope. The cathode ray is of the same nature as the beta ray, although of lower kinetic energy of the individual particles, and produces a bright fluorescence. However, *individual* beta particles, different from alpha particles, fail to show up by *individual* scintillations. To determine the law of decay of a beta radiator (see Sec. 21.3) the *ionization chamber* and electroscope are used a great deal. Because of the high penetrating power of the beta ray, the chamber may be closed by a thin aluminum window.

The *penetrating power* of beta rays is not so well defined as that of

alpha rays as we shall see when observing their tracks in the cloud chamber. Nevertheless one can determine rather well the thickness of the aluminum sheet that completely shields the ionization chamber from the effect of the beta rays coming from one or the other active element. Once the relation between this thickness and the velocity of the rays has been determined (Fig. 21.8), this is a convenient method for the determination of the maximum velocity of a bundle of beta rays.

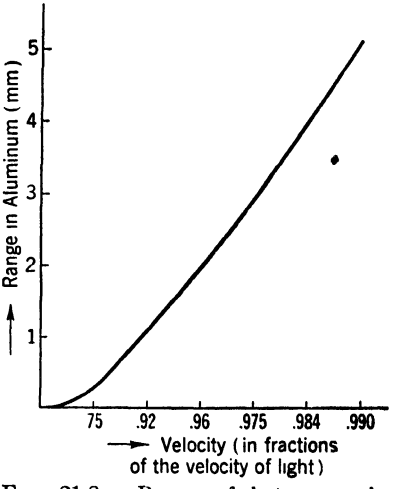


FIG. 21.8. Range of beta rays in aluminum as a function of their velocity.

Much more detail is revealed by a measurement of the velocities in a beta-ray spectrograph (Fig. 21.9). Its construction closely resembles that of a mass spectrograph. But here we know the specific charge, ϵ/μ, of the particles and want only to determine their velocities. A narrow bundle of beta rays, separated out by two slits, enters a magnetic field perpendicular to their path. The field turns each particle in high vacuum on a circular path of the radius $R = \mu v/\epsilon H$ [Eq. (8.7)]. The formula shows that the magnetic field spreads the rays according to their velocities v. After passing through half circles, the rays are recorded on a photographic plate. The unexpected result is that, in many cases, the beta rays coming from an isolated active element have not all the same velocity, but, in most cases, show a *spread of velocity over a wide range* with a well-defined maximum limit, characteristic for the emitter. This is called a "continuous" beta-ray spectrum. Here beta rays differ from alpha rays which, by their uniform range, show that they have *all the same velocity* when emanating from the same emitter. Similarly gamma rays, emitted from the same element, have all the same energy quanta, in other words, a sharp line spectrum (see Sec. 21.2c). Hence the *continuous* beta-ray spectrum is an exceptional observation.

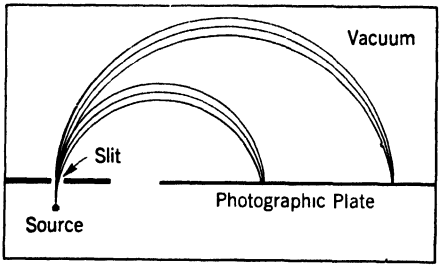


FIG. 21.9. Beta-ray spectrograph. The magnetic field, normal to the plane of the figure, bends the two beta rays shown in the figure on circular paths.

This observed fact is opposed to our idea of sharply defined energy levels. Such levels are evident in the nuclei that are left after the emission of the

beta rays because the subsequent emission processes of alpha or gamma rays are sharply defined and bear no evidence of a continous range of nuclear energy. This dilemma, the observation of a *continuous* spectrum leading to a *sharply defined* energy level, was tentatively solved by Pauli (1931) who postulated that the emission of a beta particle from the nucleus is accompanied by the emission of another particle, called the "neutrino," which escapes direct observation. Pauli assumes that the total energy emitted is sharply defined, only its distribution between the beta particle and the neutrino varies over a continuous range. Thus the high energy limit of the continuous beta-ray spectrum represents the total energy of the emission process. The new particle must be supposed to be neutral and have a mass small as compared to that of the proton, otherwise the displacement law (Sec. 21.4) would fail for beta emission. Furthermore, a charged particle would produce tracks in the cloud chamber. A great effort has been made hunting for this elusive particle. The evidence for its existence, if there is any, is so indirect that we refrain from discussing it.

There are other beta-ray spectra in which *sharply defined* particle velocities are observed. These beta emissions, however, are understood as secondary processes, due to the emission from the nucleus of a *gamma ray* which, in turn, by photoelectric effect ejects an electron from the K or L or M shell of the electronic structure. This more complex process is identified by an energy relation. Radium, for example, although an alpha emitter, emits also a beta-ray spectrum which consists of three sharp lines. The beta ray of lowest energy, called β_1, is ejected presumably from the most firmly bound shell, the K shell. If this is true we expect the relation to apply:

Energy of gamma quantum = energy of β_1 + ionization energy of K shell

Correspondingly, to the next ray, β_2, the relation should apply:

Energy of gamma quantum = energy of β_2 + ionization energy of L shell

By subtraction we find

$$\text{Energy of } \beta_2 - \text{energy of } \beta_1 = \text{energy of K limit} - \text{energy of L limit}$$

The measurement of the beta-ray spectrum checks well with the difference between the K and L ionization limits, which are accurately known from the X-ray absorption spectrum. The corresponding relation holds for the beta rays β_2 and β_3 compared with the L and M limits of the X-ray spectrum. These relations prove that the *sharp line* beta-ray spectra do not consist of electrons ejected from the nucleus but of K or L or M electrons ejected by a gamma quantum, which, in turn, is emitted from the nucleus. This process is called "internal conversion." When the lines of

the beta-ray spectrum are assigned to the various X-ray absorption limits, the energy of the gamma ray can be computed (see Prob. 21.10).

The Geiger counter responds well to beta rays. Its operation differs from that of the ionization chamber in that it exhibits a brief *self-maintained* electric discharge which is only *started* by the incoming particle. Except by special devices, this discharge fails to give evidence whether it is started by an alpha or a beta particle. But by an aluminum window of proper thickness one can screen off the alpha rays and still transmit beta

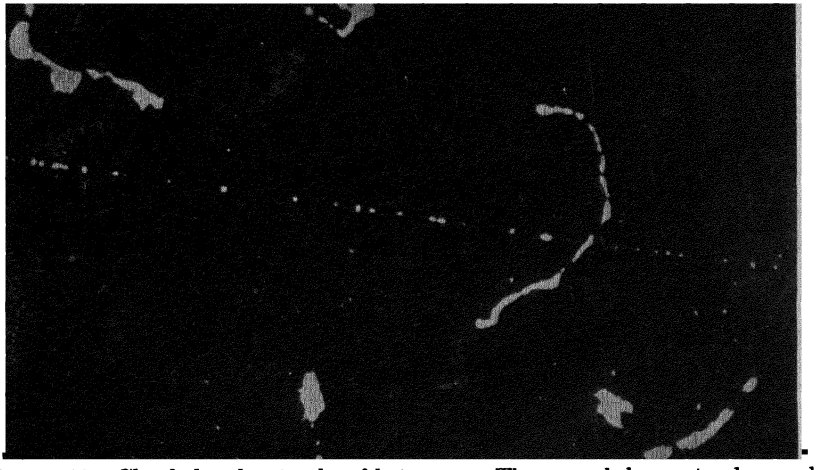


FIG. 21.10. Cloud-chamber tracks of beta rays. The curved, heavy tracks are due to slow beta particles; the straight, light track is due to a fast beta particle. (*Courtesy of C. T. R. Wilson.*)

rays. Finally one can correct for possible gamma rays by inserting a heavier aluminum window, which stops all beta rays but has no noticeable effect on the much more penetrating gamma rays.

Cloud-chamber pictures show other properties of beta rays. Figure 21.10 shows slow beta rays ejected from gaseous molecules by gamma rays and, in addition, one straight track due to a fast beta ray. It is seen that slow beta rays are deflected by collisions much more readily than alpha rays. This has the effect that the range of a beta ray is less well defined than that of an alpha ray (see Fig. 21.5). Since beta rays have ranges much larger than those of alpha rays, it is convenient to measure them in aluminum instead of in air. In spite of the numerous deflections suffered by beta rays once they slow down, one can reasonably well determine a distance beyond which no beta particle reaches; thus the curve of Fig. 21.8 has been obtained. The straight track of the fast electron seen in Fig. 21.10 is less dense than the curved path of the slower electrons. This indicates that the faster electrons have a smaller chance for energy losses.

The high penetrating power of very fast electrons observed in cosmic rays (Chap. 24) is another manifestation of the same fact.

c. Gamma Rays. Gamma rays are similar to X rays and of a different nature than alpha or beta rays, which are the only *material* rays observed in natural radioactivity. Their penetrating power is equal to or greater than that of X rays and, like the latter, they are studied by their effects on photographic plates or in ionization chambers or, most conveniently, with Geiger counters. Since in all such devices both types of ray produce the same effects, we conclude that they are of the same nature. The pene-

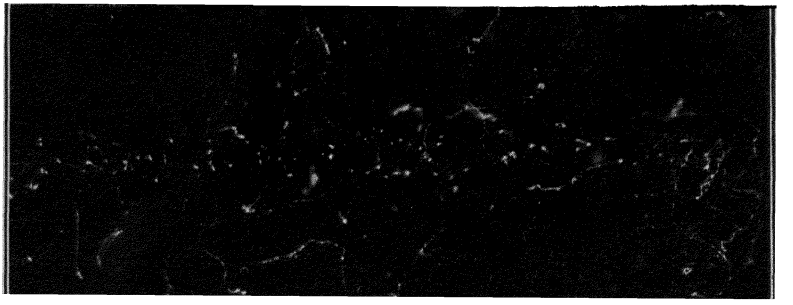


FIG. 21.11. Cloud-chamber tracks due to gamma rays. The tracks show secondary electrons ejected by the gamma rays. (*Courtesy of C. T. R. Wilson.*)

trating power of most gamma rays is the same as that of X rays generated by several million volts.

A difficult experimental problem is presented by the measurement of gamma-ray wave lengths. The wave lengths of the less penetrating gamma rays, measured by Bragg's crystal spectrometer, are of the same order as those of X rays. This instrument, however, is not applicable to harder gamma rays because their wave lengths are short as compared to the grating constant of crystals. In some cases wave lengths of gamma rays are computed from the energies of associated beta rays which are emitted by internal conversion as discussed in the preceding section. A systematic determination of gamma-ray wave lengths is based on cloud-chamber photographs. Figure 21.11 shows the trace of a bundle of gamma rays in air. Because of the high penetrating power of the rays, we are sure that most of their quanta pass through the chamber without producing any effect. The tracks observed are due to the few quanta absorbed; and these quanta show up only indirectly by the secondary electrons that they eject from the air molecules. This effect of gamma rays in the cloud chamber is entirely different from the effect of alpha or beta rays; these latter rays produce tracks that show the paths of individual alpha or beta particles by continuous series of droplets. On the other hand a gamma quantum when absorbed produces 1 high-energy electron whose path shows

up by a cloud. The aggregate of all these secondaries gives the impression of the gamma ray passing through the chamber. But the track of the individual gamma quantum does not show up.

A more detailed scrutiny of the tracks, into which we shall not enter, shows minor differences between the two processes that a gamma ray may produce. Either it ejects an electron from an air molecule by the photoelectric effect and so converts practically its entire energy into kinetic energy of the ejected electron, or, in the Compton scattering, it gives only part of its energy to an electron, the other part to a deteriorated quantum. Although in many individual tracks no clear-cut decision between these alternatives can be made, a laborious statistical treatment of many cloud-chamber tracks of secondary beta rays gives evidence of the energy quantum, hence of the wave length of the gamma ray. The various methods agree in showing that gamma rays have sharply defined wave lengths, characteristic for the emitting nucleus. We compare this time-consuming and inaccurate method for measuring one or two gamma-ray wave lengths with the ease with which optical wave lengths are determined. On a photographic plate (see Fig. 16.3) many hundred sharp optical spectral lines are recorded and measured with high precision and without any ambiguity within a short time. Great progress in our knowledge of the nucleus would result if a gamma-ray spectrograph could be constructed as powerful as a Rowland grating for light. There is no indication, however, that this can be achieved.

Our treatment of alpha, beta, and gamma rays is descriptive and does not lead to a theory of the nucleus as the description of optical spectra culminates in Bohr's theory. There exists no theory of nuclear structure which would lead to as comprehensive a prediction of a simple nucleus as that given by Bohr's theory of the hydrogen spectrum.

The radioactive rays are compared with light and X rays in Table 21.2, given in the summary.

21.3. Half-life. After discussing the *nature* of the radioactive rays, we now study the *rate* at which they are emitted. For each radioactive element the rate of emission is directly proportional to the mass of the sample present. This simple observation indicates that the atoms do not affect each other, *e.g.*, in stimulating the emission of rays.

In most cases the decay of the emitter is conveniently traced by the gradual decrease of the emission. A familiar laboratory experiment is the measurement of the decay of thorium emanation. Here the quantity of the active element is measured by its activity, say, every 20 sec; this can well be done by once admitting a trace of thorium emanation into the condenser of an ionization chamber and next charging the condenser, say, every 20 sec to the same initial potential difference and measuring the rate of discharge by observing the leaf of an electroscope. (Here we dis-

regard the fact that each individual reading covers a time interval of several seconds during which the source may not be exactly constant.)

The observation shows that, for a given radioactive element, it always takes the same length of time, called the "half-life" to lose one-half of its original strength, *i.e.*, to decay to one-half its original amount. Mathematically, this law of decay is expressed in the plot of the activity N (on an arbitrary scale) against the time t. Here we obtain a curve (Fig. 21.12*a*) which is represented by an exponential law

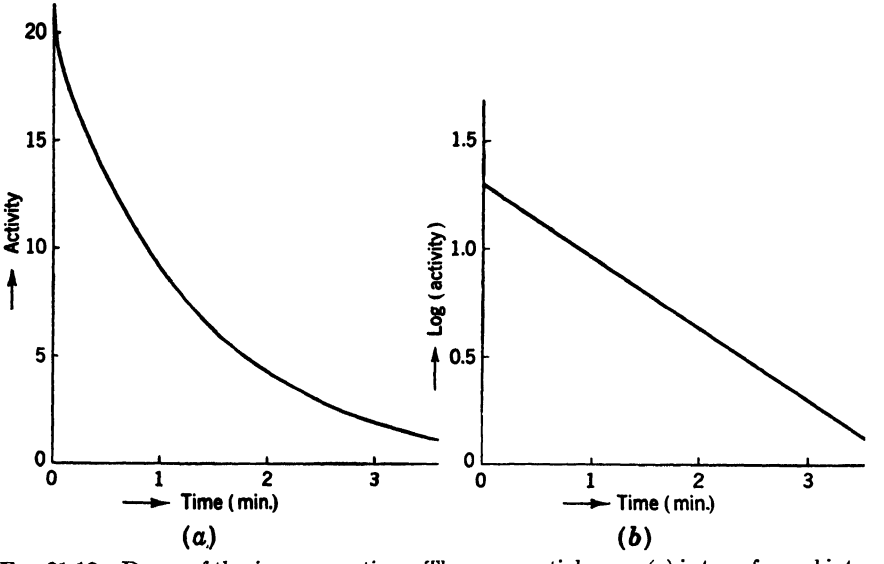


FIG. 21.12. Decay of thorium emanation. The exponential curve (*a*) is transformed into the straight line (*b*) by applying a logarithmic scale.

$$N = N_0 e^{-\lambda t} \tag{21.1}$$

where N_0 = initial activity

λ = empirical factor, called "decay constant"

Instead of plotting N against t we rather plot log N against t as in Fig. 21.12*b*. This has the advantage that the eye can judge directly the straight character of the line while it is unable to judge whether or not a curve is well represented by an exponential function. Moreover, the logarithmic scale readily represents a range of figures much wider than that represented by a linear scale.

The constant λ represents the reciprocal of the time during which the activity N decreases to the fraction $1/e$ of its initial value N_0. The decay constant λ is closely connected with the half-life T. A simple computation, carried out in Prob. 21.2, gives

$$T = \frac{\log_e 2}{\lambda} \tag{21.2}$$

Attention is called to the fact that N_0 does not enter into the expression for T; hence, as stated above, the half-life does not depend on the quantity of the element present.

The observation described by Eq. (21.1) can be derived from the theoretical assumption that each atom has an intrinsic probability of disintegrating within any given time interval, irrespective of the disintegration of its neighbors. On this basis we understand that in any fixed time interval *a certain fraction of the number of atoms* disintegrates. In other words, when we consider a time interval Δt so short that within it the number N of atoms present is appreciably constant, then the number ΔN decaying during Δt is proportional to N and Δt, the constant of proportionality λ being characteristic for the material and entirely independent of the physical conditions. Hence,

$$\Delta N = -\lambda N \, \Delta t \tag{21.3}$$

In Prob. 21.3 it is proved that this fundamental assumption necessarily leads to the observed decay described by Eq. (21.1).

In many observations of radioactive decay, the situation is complicated by the fact that the daughter substance in turn disintegrates and, therefore, does not accumulate without limit.

This is negligible in the case of thorium emanation because the daughter substance has a very much shorter half-life of only a fraction of a second. In this case, apparently, the active atom emits two alpha particles simultaneously. The following daughter substance has a much longer life.

This complication can be avoided completely in the case of radium if the daughter substance, the gas radon, is allowed to escape.

In the laboratory this situation must be carefully avoided, partly for reasons of health, partly because the escaping radon would deposit its daughter products on the walls of the laboratory and render them permanently radioactive.

We consider now the simple case where the daughter substance is allowed to accumulate in the same container with the parent substance, *e.g.*, radon (half-life, 3.82 days) with radium (half-life, 1,590 years). We start from pure radium; the daughter substance radon is generated at the same rate at which the radium decomposes. During the first minutes, the number of radon atoms is so small that their spontaneous decomposition (proportional to this number) is negligible as compared to the rate of their creation. However, when more radon accumulates, the uniform rate of its creation is more and more counterbalanced by the increasing rate of its decomposition. After a considerable length of time, these two rates become practically equal and so define the concentration of radon in "radioactive equilibrium" with radium. No larger concentration of the daughter substance can be created by the parent substance. This equilibrium is

given by the equation stating that the rate of creation equals the rate of decomposition or, considering Eq. (21.3),

$$\lambda_p N_p \, \Delta t = \lambda_d N_d \, \Delta t$$

where the subscripts p and d indicate parent and daughter, respectively. The equilibrium concentration of the daughter element follows as

$$N_d = \frac{N_p \lambda_p}{\lambda_d} \tag{21.4}$$

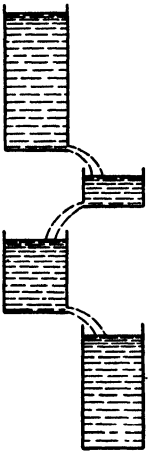


FIG. 21.13. Mechanical model of radioactive equilibrium.

This concentration goes down only very slowly with the decay of the parent substance radium. Hence an observer who paid attention only to the radon, disregarding the presence of the radium, would be misled into believing that radon decomposes with the long half-life of 1,590 years. The last equation is used for the determination of very long half-lives. For example, in uranium minerals radium is observed to be present in the constant relative concentration $\mathrm{Ra/U} = 3.4 \times 10^{-7}$, supposed to be the equilibrium concentration. Since the half-life of radium is 1,590 years, that of uranium is computed to 4.7×10^9 years.

We restricted our consideration of the radioactive equilibrium to the simple case of a parent and a daughter substance. In most cases the daughter substance in turn decomposes into products that are unstable and contribute to the activity observed. A good mechanical picture of radioactive equilibrium is given by several water containers, one placed below the other (Fig. 21.13). Any container except the first receives water in a stream more or less plentiful from its next upper neighbor and delivers it to its next lower neighbor. The last container is closed so that the water accumulates. It represents the stable end product of the decay (see Sec. 21.4). The case of radium and radon (long and short half-lives, respectively) is duplicated when we give a very narrow outlet to the top container and a much wider outlet to the next lower one. The experiment may begin with radium chemically purified, represented by all containers being empty except the highest. When we open its outlet, water will accumulate in its neighbor the water level of which will go up at a uniform rate because, to begin with, the rate of loss is small as compared with the rate of gain. But soon the rate of loss will become larger and slow down the rise of the water level. After some time, this level will reach a stationary state representing the radioactive equilibrium. The condition for this equilibrium states that the rate of gain equals the rate of loss.

Radioactive equilibrium enters into the definition of the unit of radioactivity. This has been chosen largely with the idea in mind of establishing a standard dose for medical purposes. Here radon is more important than radium as we shall see in Sec. 21.6. Hence the activity of a standard quantity of radon is chosen as the unit. *One curie is defined as the activity of the radon which is present in equilibrium with* 1 *g of radium.* More commonly the smaller unit 1 millicurie is used.

Conventionally the same unit is applied to artificially produced radioactive substances. Thus 1 curie is defined as the activity of any substance in which 3.7×10^{10} atoms disintegrate per second. (This is the number per second of radium atoms disintegrating in 1 g of radium or the equilibrium amount of radon.) This number is not necessarily identical with the number of particles emitted per second. For example, pure radon (half-life, 3.8 days) has various daughter products of much shorter half-lives so that each disintegration process of 1 radon atom leads to the emission of 3 alpha and 2 beta particles in rapid succession until an atom of much longer half-life is reached. For all practical purposes, these emission processes occur simultaneously. In experiments with artificial radioactivity (Chap. 22), usually the quantity of the new element produced is so small that it cannot be weighed; nevertheless its activity can be measured in millicuries (Prob. 21.8).

For gamma rays the same unit of dose is used as for X rays, *i.e.*, 1 roentgen (see Sec. 19.1*d*). This unit, however, is not applicable to alpha and beta rays. The two units, 1 curie and 1 roentgen, differ fundamentally. The curie directly defines a property of the radiating element; when its activity (in curies) and half-life are known, one can easily compute the number of atoms present from Eq. (21.3). On the other hand, 1 roentgen is defined on the basis of the arbitrary selection of air as the absorber. This measurement gives no indication of the total energy of gamma radiation present. Hence the curie is of interest for both the physicist and the biologist. However, the roentgen is of no use for research in physics although it gives a satisfactory statement regarding the biological effect of gamma rays.

21.4. Radioactive Series. In radioactive decay the nucleus that emits an alpha or beta particle changes its chemical nature. Our knowledge of these particles and nuclei is so thorough that we can predict the change in the nucleus brought about by the emission. The *alpha particle* carries the mass 4 (in mass numbers) and the positive charge 2 (in electronic charges) away from the parent nucleus. Consequently the daughter nucleus is lighter by mass number 4 and is placed 2 atomic numbers back in the periodic table. The *beta particle*, emitted from the nucleus, carries away no appreciable mass but the negative charge 1, hence leaves a daughter nucleus of unchanged mass number but placed one atomic num-

ber higher in the periodic table. In both cases the change of packing fraction (the higher decimal places of the atomic weight) can be predicted only if we know the kinetic energy of the alpha or beta particle emitted.

The laws here stated, called the "displacement" laws, are represented in the diagram of Fig. 21.14. Here each element, characterized by its *atomic number*, occupies a certain place on the abscissa while its various isotopes, characterized by their *mass numbers*, are displayed along the ordinate. The emission of an alpha particle produces a new atom two places to the left and four places down. (In the diagram only every fourth mass number is plotted.) A beta emission shifts the nucleus only one place to the right. The diagram shows the wide extension of this series of disintegration processes beginning with $_{92}U^{238}$ ending with $_{82}Pb^{206}$ which we have mentioned before as one of the stable isotopes of lead (Sec. 20.5).

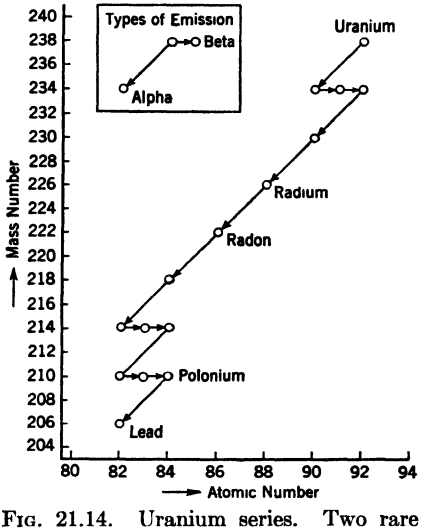


FIG. 21.14. Uranium series. Two rare cases of branching are omitted.

The facts represented in Fig. 21.14 are given in Table 21.1 which includes the half-lives of the various elements covering a range between 10^{-6} sec and 4.7×10^{9} years. (Very short half-lives have not been measured with a watch but estimated from an empirical relation between the half-life and the range of the alpha particle emitted. We omit the discussion of this relation.) Each isotope has its characteristic half-life and, in the great majority of cases, emits either an alpha or a beta particle. There are two exceptional cases of "branching" in which a few hundredths of 1 per cent of the disintegrating atoms chose an alternative way down toward $_{82}Pb^{206}$ (omitted on the diagram and the table).

Our present knowledge of the nuclear charges and the nature of alpha and beta particles makes the displacement laws represented in this diagram quite obvious. At the time of the discovery these laws, independently found by Fajans and Soddy (1913), represented great progress. The experiments required to establish them consist largely of chemical analysis. We have mentioned already the simplest case, the relation between radium and radon. Radium was recognized by the Curies as an alkaline earth. It was found that the emission of an alpha particle leads to a daughter element called "radon," hitherto unknown, chemically identified as a rare gas, hence, in the periodic table, preceding the parent element by two

Table 21.1. *Uranium-radium Series*
(Omitting two rare cases of branching)

Mass No.	Atomic No.	Element	Radiation	Half-life
238	92	Uranium I	α	$4.6 \times 10^9 y$
234	90	Uranium X_1	β	$24.1d$
234	91	Uranium X_2	β	$1.14m$
234	92	Uranium II	α	$2.7 \times 10^5 y$
230	90	Ionium	α	$8.3 \times 10^4 y$
226	88	Radium	α	$1{,}590y$
222	86	Radon	α	$3.825d$
218	84	Radium A	α	$3.05m$
214	82	Radium B	β	$26.8m$
214	83	Radium C	β	$19.7m$
214	84	Radium C′	α	$1.50 \times 10^{-4}s$
210	82	Radium D	β	$22y$
210	83	Radium E	β	$5.0d$
210	84	Polonium	α	$140d$
206	82	Lead		

places. Another example is given by the beta emission from radium D, which is an isotope of lead and generates an element chemically identified as bismuth which follows lead in the periodic table. Thus chemical analysis led to the displacement law. Here an outstanding experimental problem of research in radioactivity shows up, the chemical separation of neighbors or near neighbors in the periodic table. In modern research on the transmutation of elements, this chemical problem plays a major part, all over the periodic table of elements. In many cases this analysis is made difficult by the short half-lives of the elements, which prevents an accumulation of an appreciable quantity. The distinction of the element radium is due to the fact that it has a half-life sufficiently long to permit a weighable accumulation, on the other hand sufficiently short to make its radioactivity strongly noticeable. The results reported above, based on chemical analysis and the properties of alpha and beta particles, may be considered as another powerful confirmation of the law stating that the atomic number equals the nuclear charge.

We have introduced isotopes as the result of investigations with the mass spectrograph (Chap. 20; Aston, 1920). Historically, isotopes were discovered much earlier as the products of radioactive disintegration (Soddy). For example, ${}_{92}U^{238}$, by emitting an alpha particle, changes into thorium ${}_{90}Th^{234}$. Its atomic weight 234 follows from the displacement law and does not agree with the atomic weight 232 of the chemically known element thorium. By such relations the occurrence of many isotopes among the heavy elements has been discovered. A simple relation in

which isotopes are predicted is evident in the disintegration of uranium $_{92}U^{238}$, the parent element of the whole series. By alpha emission it is transmuted into the element of atomic number 90 and mass number 234. The product emits 2 beta particles in succession and so brings the atom back to the atomic number of uranium but to an atomic weight smaller by 4. It follows that here an isotope of the parent element uranium is formed. In general, the sequence of 1 alpha and 2 beta emissions creates an isotope of the parent element with a mass number smaller by 4. Another example of the displacement laws is given by the lead isotope of the mass number 206 which is predicted as the end product of the uranium-radium series and actually found in preferred abundance in the lead associated with uranium minerals (Sec. 20.5, Fig. 20.7).

In addition to the *uranium-radium series* just discussed, two more such series have been known for many years. The *actinium series* begins with the rare uranium isotope $_{92}U^{235}$ and ends with lead $_{82}Pb^{207}$; the *thorium series* beginning with thorium $_{90}Th^{232}$ ends with the heavier lead isotope $_{82}Pb^{208}$. We shall not discuss the detail of these series, which follow the same principles as the uranium-radium series. Recently a fourth series was discovered which does not contain any element of a half-life long enough to make it appear in nature. The series starts from artificially produced plutonium $_{94}Pu^{241}$ (see Sec. 22.8; this isotope originates from $_{92}U^{238}$ by alpha, not by neutron, bombardment); the series ends with the stable bismuth isotope $_{83}Bi^{209}$. It is given the name "neptunium series" after the longest lived member. These new results demonstrate that our knowledge of the radioactive series is limited by our technical ability to isolate short-lived radioactive elements. What we consider to be the first member of a series may well be the daughter of a short-lived element not yet isolated.

All the radioactive isotopes contained in these four series belong to the heaviest elements. This agrees with our discussion of Aston's packing-fraction curve (Sec. 20.4). A large packing fraction, *i.e.*, a high location on the curve, is identified with a large energy stored in the atom. All heavy, radioactive elements are located on the right rising branch of the curve in agreement with the general rule that the most stable configuration is given by the minimum of this curve near the mass number 60. It is a surprising exception that two lighter elements, the rare potassium isotope $_{19}K^{40}$ and the rubidium isotope $_{37}Rb^{87}$, show beta-ray emission. Both have very long half-lives; otherwise they would not be found in nature.

21.5. Report on the Theory of the Nucleus. What are the forces that keep the nuclei assembled? The only force we are sure of is the Coulomb repulsion which tends to disrupt the nuclei. This repulsion explains satisfactorily the scattering of alpha particles even at approaches as close as

about 10^{-12} cm (see Sec. 14.3). Hence, outside of this distance the Coulomb repulsion is the outstanding force acting between nuclei. In order to explain the existence of nuclei of positive charges larger than that of the proton, we must assume that for closer approaches of protons and neutrons new forces of attraction come into play, which are overwhelmingly larger than the Coulomb repulsion acting between the positive charges. Although we do not know these mysterious forces so well that we could theoretically predict nuclear structures, we can describe some experimental facts by a simple mechanical model. In order to explain the method, we compare the emission of alpha particles from radioactive nuclei with a very different process, the emission of electrons from a glowing metal. These electrons are in the low kinetic-energy range of thermal motion, some of them leaving the metal with negligible energy. This is explained by a model (see Fig. 10.2) in which a set of steel spheres contained in a tray with a sloping rim is violently shaken. We may interpret the section of the tray given in the figure as representing the potential energy of a sphere in any position, low at the bottom but having a constant height anywhere outside the tray. In particular, the model represents the energy of liberation of a sphere as the energy required to lift the sphere from the bottom to the rim of the tray. The electron emission is compared with the occasional escape of one of the spheres.

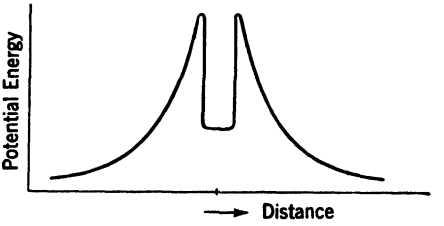


FIG. 21.15. Mechanical model representing the potential energies of nuclear particles.

Alpha rays, on the other hand, are always emitted from a radioactive element with a high kinetic energy characteristic of the element. Correspondingly we invent a mechanical model of the nucleus. The particles constituting the nucleus (called by a common name "nucleons") are pictured as contained in a deep well (Fig. 21.15) in which they perform a random motion.

One may attribute a temperature to the assembly of these particles, but this temperature bears no relation to the temperature of the body measured with a thermometer since no energy exchange takes place between the particles constituting the nucleus and all the atoms constituting the body.

Occasionally, an alpha particle is thrown up to such a height that it escapes over the rim. Outside the nucleus (differing from the electron ejected from the metal) the alpha particle is subjected to the Coulomb repulsion, which gives it the high kinetic energy observed. The potential energy of the alpha particle with respect to the nucleus is highest near the rim and decreases with increasing distance.

In Sec. 15.3 we computed this potential energy for the case of the electron and the nucleus as $-Ze^2/r$. A similar expression, applies to the alpha particle; but here repulsion takes place instead of attraction.

Graphically the potential energy is represented by a curve sloping down from the rim (proportional to $1/r$). Hence in the mechanical picture a particle ejected rolls down the slope and so acquires a high kinetic energy. These slopes surrounding the well make the model appear like a volcano that is occasionally erupting.

How high above the surroundings is the rim of the crater? The kinetic energy of the alpha particles emitted seems to give the direct answer. For example, alpha particles from uranium U^{238} are ejected with a kinetic energy of 4.2 Mev. Here, however, we run into a discrepancy that indicates that our mechanical model is too simple. In our discussion of the size of the nucleus (Sec. 14.3), we learned that the scattering by uranium of alpha particles (coming from an outside source) is correctly described by the theory of scattering for energies of alpha particles as high as 8.8 Mev. We must conclude that the *impinging alpha particles* when approaching the nucleus even with this high energy are repelled simply by the Coulomb force. According to this argument, the height of the rim over the surroundings must be at least 8.8 Mev, hence much higher than indicated by the energy of the *alpha particles spontaneously ejected* from uranium.

This discrepancy is solved by wave mechanics. Here, in contrast with Newtonian mechanics, a particle contained in the crater has a chance to escape even if its energy is not sufficient to lift it over the rim. For any height of the particle *in the well* wave mechanics predicts a certain probability of finding the particle *outside the well.* It is true that this probability is exceedingly small for low heights where the walls are thick. However, wave mechanics predicts that closer to the rim the particle has a noticeable chance to escape through the thin wall. This is commonly referred to as the "tunnel effect." An alpha particle contained in the well may collide very frequently with the walls without escaping. But there is a chance for an occasional favorable hit that leads to escape. These are the alpha particles we observe as emitted from uranium. The same idea applies to the alpha particles bombarding the uranium nucleus from outside in the scattering experiment. Most of these alpha particles bounce off (as a sphere would roll back from a slope like that of Fig. 21.15) and are recorded as scattered. In the same experiment it is not noticeable that a very few alpha particles penetrate as through a tunnel into the interior of the uranium atom. The quantitative application of wave mechanics leads to the prediction of a law correlating the half-life of the nucleus and the range of the alpha particle ejected. This law, which we shall not further discuss, agrees well with the observed facts (Geiger-Nuttall law).

Table 21.2. Comparison of Light, X Rays, and Rays from Natural Radioactive Substances

	Light or X rays	Alpha rays	Beta rays	Gamma rays
Character.	Quanta $h\nu$ (governed by waves of length c/ν)	He^{++} ions = He nuclei	Electrons	Same as X rays, same or shorter wave length
Velocity...	Velocity of light c	Up to 1/15 c	Up to 99.8/100 c	c
Energy of particle or quantum	Visible light: several ev. Technical X rays: $10^4 - 10^6$ ev	Up to 8.8×10^6 ev	Up to 2×10^8 ev	Up to several 10^8 ev
Penetrating power		1/100 mm aluminum	Several 1/10 mm aluminum	Several cm lead
Absorption, observed	$I = I_0 e^{-\mu x}$	Limited range; dense ionization over the full length of range; straight paths except very rare sharp deflections	Limited, not sharply defined range; less dense ionization than by α rays; crooked paths	$I = I_0 e^{-\mu x}$ good approximation
Absorption, theory	Each quantum when absorbed gives away total energy in one process; fraction of energy lost per cm path is constant	Each particle spends its energy on many ionization processes; no deflection in collisions with electrons because of large mass of α particle; very rare sharp deflection in collision with nuclei	Each particle spends its energy on many ionization processes; deflection occurs since β particle is light	Each quantum when absorbed gives away its energy in one of a few processes: ionization (photoelectric effect), Compton effect, or pair production
Relation to emitting atom	Wave length sharply defined characteristic for electronic structure of emitting atom	Energy of α particle sharply defined, characteristic for emitting nucleus	*Continuous* β-ray spectra with sharp high-energy limit are characteristic for emitting nucleus; *sharp line* β-ray spectra represent emission of K or L . . electrons ejected by γ rays from nucleus	Wave length of γ ray sharply defined, characteristic for emitting nucleus

gives evidence of one ionization process. Each kink in an alpha-ray track shows that a collision with a nucleus, a much rarer event, has taken place.

Beta rays consist of fast electrons. They have a higher penetrating power than alpha rays. The beta-ray spectrograph, based on the magnetic deflection, shows that beta rays originating from nuclei have continuous ranges of energy with sharp high-energy limits. There is, however, a special class of beta-ray spectra of sharply defined energy; these consist of "secondary" electrons ejected by gamma rays from the K or L or M shell of the emitter. The cloud chamber shows that the tracks of beta rays are much longer and more crooked than those of alpha rays.

Gamma rays have a penetrating power ever so much higher than that of alpha or beta rays. They are identical with X rays of very short wave lengths.

A comparison of the various rays is given on Table 21.2.

3. The decay of a radioactive element is described by a simple exponential function, characterized by the *decay constant* λ or, instead, the *half-life* T. This is explained by the assumption that each element has an intrinsic probability of disintegration, in other words, that the number ΔN of atoms disintegrating during the short time interval Δt is proportional to the number of atoms N present. If the daughter substance is active itself, it accumulates only to a limited equilibrium concentration. The unit of radioactivity, 1 curie, is defined as the activity of the radon which is in equilibrium with 1 g of radium.

4. The emission of alpha or beta particles is responsible for the *spontaneous transmutation of elements.* Thus uranium ${}_{92}U^{238}$ gradually is transmuted into ${}_{88}Ra^{226}$ and, in many further steps, finally into the stable lead isotope ${}_{82}Pb^{206}$. The emission of an alpha particle produces a new element with an atomic number smaller by 2 and a mass number smaller by 4. The emission of a beta particle increases the atomic number by 1 and leaves the mass number unchanged (displacement laws). These transmutations have led to the discovery of *isotopes* earlier than the mass spectrograph. There are three more radioactive series, the actinium, the thorium, and the neptunium series, all following the same principles.

5. The emission of an alpha particle is represented by a *mechanical model* resembling an erupting volcano. Wave mechanics predicts the tunnel effect, *i.e.*, the passing of the alpha particle through the thin wall of the volcano.

6. *Radioactivity is applied* to the determination of the age of minerals. For medical applications beta rays are most important. Usually they are applied as coming from daughter substances of radon which is sealed into tiny glass needles. Radioactive isotopes serve as tracers.

PROBLEMS

21.1. *Avogadro's number.* A microgram (10^{-6} g) of radium (which is not separated from its products, see Sec. 21.3) emits 14.8×10^4 alpha particles per sec. One gram of radium produces 172 mm³ of helium gas under standard conditions per year. Compute Avogadro's number. Density of helium gas under standard conditions $= 1.77 \times 10^{-4}$ g/cm³.

21.2. *Relation between half-life and decay constant.* A radioactive substance is decaying according to Eq. (21.1). (*a*) Compute the time T during which the initial number N_0 of molecules is reduced to half its value. (*b*) Compute the time T' during which the initial number N_0 is reduced to 90 per cent of its value.

21.3. *Radioactive disintegration (calculus problem.)* A radioactive substance of which N_0 atoms are present at the time $t = 0$ decays such that during the short time interval Δt the number of disintegration processes (counted by scintillations) is ΔN. This is proportional to the number N present at the time t, provided we choose Δt so short that within Δt the total number N does not appreciably change. The factor of proportionality λ, called the "disintegration constant," is characteristic of the substance. Compute the number of atoms N_1 present after a long time interval t_1.

HINT: (*a*) Suppose that the time between $t = 0$ and $t = t_1$ is divided into many equal increments Δt. For an increment Δt write the equation stating the general law, considering that an *increase* of the time leads to a *decrease* of the number N. (*b*)–(*e*) Apply the same method as in Prob. 17.5.

21.4. *Age of rocks.* In a uranium mineral, lead is found predominantly of the isotope 206, indicating the radioactive origin of the lead. The mineral contains 0.093 g lead to 1 g uranium. Compute the age of the mineral. Given, half-life of $_{92}U^{238} = 4.5 \times 10^9$ years. All other elements of the uranium series have much shorter half-lives.

HINT: (*a*) Compute the decay constant λ from the half-life T using the result of Prob. 21.2. (*b*) Compute ΔN = number of lead atoms and N_0 = total initial number of atoms = final number of (lead + uranium) atoms. (*c*) Compute the time t from Eq. (21.1).

21.5. *Number of particles emitted.* Radium has a half-life of 1,590 years. In each disintegration process one alpha particle is emitted. (*a*) What fraction of the radium disintegrates within 1 sec? (*b*) How many alpha particles are emitted per sec from 1 mg of radium? Disregard the alpha particles emitted by the succeeding disintegration processes in the radioactive series. (*c*) What fraction disintegrates within 300 years?

21.6. *Elastic collisions of alpha particles.* An alpha particle (velocity u_1) hits (*a*) a proton, (*b*) a helium nucleus, (*c*) an oxygen nucleus. Consider only head-on elastic collisions. Compute the velocities of the alpha particle itself and the other nuclei after the collision using the results and the notation of Prob. 14.1.

21.7. *Equilibrium concentration of radon.* Compute the number of atoms and the mass of radon in equilibrium with 1 g of radium. Given the atomic weights and half-lives (Ra 226, 1,590 years; Rn 222, 3.82 days).

21.8. *Activity expressed in curies.* After a certain nuclear reaction (see Chap. 22) radioactive sodium $_{11}Na^{24}$ is found with an activity of 0.01 millicurie and a half-life of 14.8 hr. Compute the disintegration constant λ, the number N of sodium atoms present, and their total mass.

21.9. *Number of disintegration processes in a radioactive series.* In the actinium-uranium series $_{92}U^{235}$ gradually disintegrates into $_{82}Pb^{207}$. How many alpha and beta particles are emitted by any atom when going through this series?

21.10. *Sharp-line beta spectrum.* The beta spectrum of radium consists of three sharp lines with the energies 87,500; 170,000; and 184,000 ev, respectively. Assume that these lines are due to internal conversion of a gamma-ray quantum liberating an electron from the K or the L or the M shell. The respective energies of liberation are given by the X-ray absorption limits as 97,500; 17,200; and 3,500 ev. (It is assumed that the alpha emission associated with the gamma emission produces a radon nucleus; hence these energies are taken for radon instead of radium although this distinction is hardly noticeable.) Compute the energy and wave length of the gamma ray.

COMMENT: The consistency of the result, within the limit of error, confirms the explanation of the beta rays as due to internal conversion.

CHAPTER 22

ARTIFICIAL TRANSMUTATION AND RADIOACTIVITY

During the Middle Ages the search for gold was an outstanding incentive for research in chemistry. The conversion of a common metal into gold was the chief aim of many medieval alchemists. This problem has been solved only within the past decades though at a scale too small to satisfy the fantastic hopes of the alchemists and with an effort and technical development far surpassing anything they could imagine. In the present chapter we shall follow the historical development and begin with discoveries made without the modern machines for the production of high-energy particles. Then we shall describe these machines and the wealth of new results obtained by their application until, finally, in uranium fission, we shall come to the controlled production of nuclear energy. In exploring this complex field, we keep in mind the same idea that guided us through all the preceding discussions. We shall not accept merely on authority new conjectures like those of the mysterious properties of neutrons and fission but shall present systematically the experimental evidence and the arguments leading to such new concepts. Modern arguments are likely to be more involved than those of fifty years ago, not so much by the application of mathematics as by the complicated set of experiments and interpretations required to elucidate what happens in the nucleus. In several cases we shall follow the arguments given in the original papers.

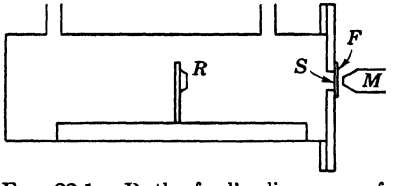


FIG. 22.1. Rutherford's discovery of the artificial transmutation of nitrogen; chamber filled with nitrogen. *S*, silver foil; *F*, fluorescent screen; *M*, microscope; *R*, sliding holder of radium sample.

22.1. Discovery. In his numerous observations of alpha rays and their ranges (Sec. 21.2*a*) Rutherford (1919) occasionally found a very rare type of scintillation when the chamber was filled with nitrogen (Fig. 22.1). As the source *R*, emitting alpha rays, is gradually moved away from the fluorescent screen *F*, the abundant scintillations stop abruptly at the well-defined distance of 7 cm (which includes the air equivalent of the silver foil). Nevertheless some *very rare* scintillations continue for a distance as large as 40 cm. Cloud-chamber pictures, too, show occasional tracks of

abnormal lengths generated by alpha particles impinging on nitrogen nuclei (Fig. 22.2).

What is the *nature* of these rays of long range and what is their *origin*? The standard procedure (Sec. 8.2) for a determination of the specific charge and velocity cannot be applied to these rays because it applies only to rays that originate from a well-defined spot like a glowing filament while these new rays start anywhere in the volume of the chamber. Therefore,

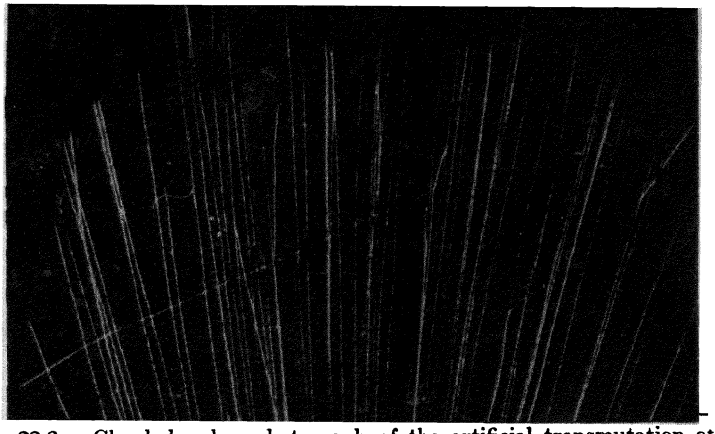


FIG. 22.2. Cloud-chamber photograph of the artificial transmutation of a nitrogen atom by an alpha particle. (*Courtesy of P. M. S. Blackett and Proceedings of the Royal Society.*)

a less straightforward line of argument must be used. The rays are recognized as consisting of *fast protons* (1) by their long range and (2) by their cloud-chamber tracks which are less dense than those of alpha rays (Sec. 21.2*a*). By experiments with artificially produced fast protons a relation between the range of protons and their initial velocity has been found (Sec. 21.2*a*). Hence the range observed in Rutherford's experiment can be taken to indicate the velocity. This complicated argument is confirmed by the deflection of the rays in a strong magnetic field. Here the cloud-chamber tracks indicate the positive charge of the particles and confirm the value of ϵ/μ as that of protons when their velocity is derived from their range as just mentioned. Thus there is no doubt about the *nature* of the rays; they consist of fast protons generated somehow by alpha rays passing through nitrogen.

Regarding the *origin* of the rays, one may suspect that the nitrogen contains traces of gaseous hydrogen as an impurity and that these rays of long range are due simply to impacts of alpha particles on hydrogen nuclei (similar to that shown in Fig. 21.6*a*). This trivial explanation, however, cannot be correct for two reasons: (1) The same alpha rays when

passing through *hydrogen* produce proton rays of much shorter range, only up to 28 cm instead of the 40 cm characteristic for the new rays observed here (both figures for rays ejected forward). (2) The ordinary elastic collisions, like collisions between billiard balls, necessarily cause the particle to be ejected with a *forward* component whereas the cloud chamber shows the surprising fact that in nitrogen some of the protons are ejected *sideways* and even *backward* (Fig. 22.2). These arguments prove that the protons ejected are not due to hydrogen present as an impurity but to a fundamentally new process.

We continue by quoting Rutherford's paper (1919):

> From the results so far obtained it is difficult to avoid the conclusion that the long-range atoms arising from collisions of alpha particles with nitrogen are not nitrogen atoms but probably atoms of hydrogen . . .. If this be the case, we must conclude that the nitrogen atom is disintegrated under the intense forces developed in a close collision with a swift alpha particle, and that the hydrogen atom which is liberated formed a constituent part of the nitrogen nucleus . . .. The results as a whole suggest that, if alpha particles—or similar projectiles—of still greater energy were available for experiment, we might expect to break down the nuclear structure of many of the lighter atoms.

Since the proton is observed with considerably higher kinetic energy than it could receive in an ordinary collision with an alpha particle, one must assume that the alpha particle and the nitrogen nucleus form a "complex" containing, as internal energy, most of the kinetic energy of the impinging alpha particle. (Not all the kinetic energy of the alpha particle is transferred to internal energy because of the conservation of momentum; see Prob. 22.7.) This energy content immediately breaks up the complex into ${}_8O^{17}$ and ${}_1H^1$. Since the probability of this process is very small indeed, the amount of hydrogen produced is far below the chemically detectable limit. Only one alpha particle in a million gives rise to the ejection of a proton.

What happens to the alpha particle and the nitrogen nucleus in this collision? The cloud-chamber picture gives the answer (Fig. 22.2). It shows only two tracks after the collision process: the light track of the proton and a heavy track that must be attributed to the other nuclear masses sticking together. Simple arithmetic shows that ${}_7N^{14}$ combining with ${}_2He^4$, after losing ${}_1H^1$, forms ${}_8O^{17}$, *i.e.*, the nucleus of a rare isotope of oxygen. For the sake of computation it is convenient to introduce an intermediate particle called the "compound nucleus" which would result if the projectile ${}_2He^4$ and the target ${}_7N^{14}$ should actually stick together. This would be the rare, fluorine isotope ${}_9F^{18}$ which, instead of having a stable nucleus, would have a nucleus endowed with high energy and thus would immediately split into ${}_1H^1$ and ${}_8O^{17}$.

In summary then we have the result that a fast *helium* nucleus colliding with a *nitrogen* nucleus may produce a transmutation, knocking out a *hydrogen* nucleus and combining itself with the residual to form *oxygen* ${}_8O^{17}$. Rutherford made this great discovery also with a strikingly simple technique involving the painstaking scrutiny of scintillations.

Rutherford and his collaborators extended the search for nuclear transmutations to other elements which they subjected to bombardment by alpha particles. Most of the lighter elements show corresponding effects. It is easily understood why the effect cannot be obtained with heavier elements. Their nuclei, because of the higher positive charges, repel the alpha particle, itself a positively charged body, so strongly that the approach is never close enough to lead to a nuclear reaction. This is a general limitation on the effect of charged projectiles on nuclei, the heavy nuclei being protected by such an electrostatic barrier.

22.2. Neutrons. *a. Discovery of Neutrons.* In 1932 and 1933 four important discoveries, initiating a new epoch in nuclear research, followed each other within a short period. They are the discoveries of the neutron, the positron, artificial radioactivity, and nuclear transmutations by high-energy particles generated in machines.

The discovery of the neutron by Chadwick (1932) is a direct outgrowth of the above-mentioned research into nuclear transmutations by alpha-particle bombardment. Beryllium, when bombarded by alpha particles, gives off a highly penetrating radiation (Bothe, 1930) which at first was considered to be identical with gamma radiation known in 1930 to have by far the greatest penetrating power. In the following year Irène Curie Joliot and F. Joliot made the striking observation that the ionization chamber in which the "beryllium rays" are recorded shows an *increased* effect when paraffin or other matter containing hydrogen is placed, like an absorber, in front of the window of the ionization chamber. They interpreted this effect by assuming that the beryllium rays have the unexpected power of ejecting fast protons from the paraffin and that these, in turn, enhance the ionizing effect observed in the chamber. For the process of ejection they assumed that gamma-ray quanta constituting the beryllium ray exert a Compton effect on the protons contained in the paraffin. It is true that the original theory of the Compton effect has been introduced for a different problem, the collisions of quanta and *electrons*. But there is no reason why the same theory should not apply to the collisions of quanta and *protons*.

The starting point of Chadwick's discovery was an intrinsic contradiction to which this interpretation leads. The difficulty becomes evident from quantitative considerations as follows. The "recoil protons" are observed to be ejected with a kinetic energy of 5.7 Mev (inferred from their range in air). How large then is the gamma-ray quantum which,

by Compton effect, would transfer so much energy to the proton? The answer is derived from the theory of the Compton effect simplified by the special assumption of a head-on collision, in other words, of a collision in which all motion occurs in a straight line. This computation (see Prob. 22.1) gives the maximum kinetic energy transferred to the mass m by the quantum $h\nu$ as

$$W_{\max} = \frac{2h\nu}{2 + mc^2/h\nu}$$

For our special case the energy of the quantum $h\nu$ is computed as 55 Mev. The numerical value of this energy is unexpectedly large and difficult to reconcile with the energies stored in light nuclei according to Aston's curve of packing fractions. Here we shall not discuss Chadwick's detailed estimates.

The contradiction, however, becomes manifest when we perform the same experiment and computation for the case of *nitrogen* instead of hydrogen. Here the range of the nitrogen "recoil ions" produced by the beryllium radiation indicates their kinetic energy as about 1.2 Mev. The corresponding energy of the hypothetical impinging gamma-ray quantum is computed as 90 Mev. This is the same quantum which when passing through *hydrogen* seems to contain only 55 Mev. In order to avoid this contradiction, Chadwick adopted an entirely different hypothesis about the nature of the radiation. He continued as follows:

> If we suppose that the radiation is not a quantum radiation, but consists of particles of mass very nearly equal to that of the proton, all difficulties connected with the collisions disappear, both with regard to their frequency and to the energy transfer to different masses. In order to explain the great penetrating power of the radiation we must further assume that the particle has no charge. We may suppose it to consist of a proton and an electron in close combination, the "neutron" discussed by Rutherford in his Bakerian Lecture of 1920.

Next, on the basis of the observation just cited, Chadwick computed for this hypothetical neutron the mass and velocity that would give the observed energy transfer in the two collisions reported. The result of the computation (to be performed by the reader, see Prob. 22.2) is

$$\text{Mass of neutron} = 1.16 \times \text{mass of proton}$$

This result satisfactorily proves that the contradiction mentioned above is removed when the highly penetrating "beryllium radiation" is assumed to consist of neutral particles of nearly the mass of the proton. This then was the discovery of the neutron.

The great penetrating power of the neutron is explained by its lack of charge, which makes it wholly insensitive to the close approach of an electron or any nucleus, in contrast to the alpha particle which, at some

distance from a heavy nucleus, is deflected by the strong Coulomb repulsion (Chap. 14). In our schematic way, the production of neutrons is written as

$$ {}_4\mathrm{Be}^9 + {}_2\mathrm{He}^4 \rightarrow ({}_6\mathrm{C}^{13}) \rightarrow {}_6\mathrm{C}^{12} + {}_0n^1 $$

As in a preceding example the "compound nucleus" ${}_6\mathrm{C}^{13}$ is not observed but only computed as the unstable particle which immediately splits up.

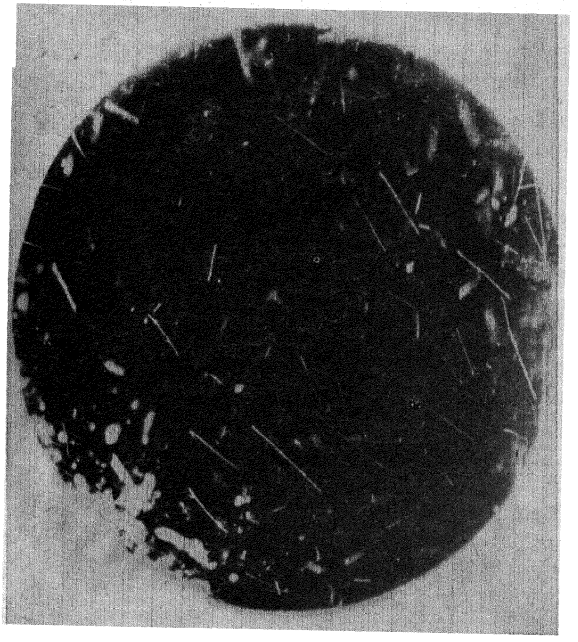


FIG. 22.3. Tracks of recoil protons. The protons are hit by neutrons coming from a source at lower right corner. (*Courtesy of P. I. Dee and C. W. Gilbert.*)

The cloud-chamber photograph (Fig. 22.3) confirms the assumption that the neutrons kick the protons, and the proton tracks cause the ionization measured. When the cloud chamber is filled with CH_4 and subjected to neutron bombardment, the short, straight tracks of recoil protons show up and their preference for a forward velocity is noticeable. (The neutrons come from the lower right corner.)

Comparison of cloud-chamber photographs shows a striking contrast between the various types of radiation. Alpha and beta rays, protons, all other nuclei, and electrons form "ionizing radiations"; for these the whole track of the individual particle is visible. On the other hand, neutron rays and gamma rays are called "nonionizing radiations" since most of them pass unnoticed through the cloud chamber. Gamma rays will only occasionally ionize a molecule and are then noticed by the crooked

tracks of the secondary electrons so produced (Fig. 21.11). Very different is the picture due to a beam of neutrons passing through a hydrogen (or methane-)-filled cloud chamber (Fig. 22.3). Only the tracks of the recoil protons appear while the neutrons, kicking the protons and bouncing off, do not leave tracks.

In surveying the discovery of neutrons, we remark that Chadwick's argument is more involved than any preceding argument we have discussed in that it presupposes cloud-chamber measurements and their interpretation, the laws of impact as applied to atoms, and the theory of the Compton effect. Chadwick's discovery turned out to be most fruitful and is amply confirmed by the numerous effects ascribed to neutrons, finally leading to uranium fission (Sec. 22.8).

b. Neutrons as Building Blocks. The ejection of neutrons from nuclei suggests the hypothesis that the neutron is one of their common constituents. If so, all nuclei may be thought of as consisting of protons and neutrons, the number of protons being identical with the atomic number, and the sum of protons and neutrons representing the mass number. (Other arguments leading to the same hypothesis are concerned with the magnetic moments of the constituent particles, which we shall not discuss.) The alpha particle, because of its great stability (Sec. 22.4), would presumably play the part of an intermediate building block in which 2 protons and 2 neutrons are firmly bound together. This picture agrees well with the nuclear reaction that has led to the discovery of the neutron; ${}_4Be^9 + {}_2He^4$ may form 3 alpha particles sticking together as ${}_6C^{12}$ and 1 neutron which is thrown out.

The isotopes of all elements are represented conveniently in a diagram wherein the number of neutrons (mass number − atomic number) is plotted against the number of protons. (This is similar to the diagram plotting the mass number against the atomic number, Fig. 21.14). Figure 22.4 shows this diagram for the light elements. Many stable, light nuclei are located on the 45-deg line, indicating equal numbers of neutrons and protons, like ${}_1H^2$, ${}_2He^4$, ${}_6C^{12}$, ${}_8O^{16}$, ${}_{10}Ne^{20}$. The heavier elements, however, contain more neutrons than protons. The most common isotope of the heaviest element known in chemistry, ${}_{92}U^{238}$, has 146 neutrons and only 92 protons. One may suppose that here the strong electric repulsion tending to break up the protons is overcome by a binding force due to the neutrons, which is not known in detail. This diagram is commonly used for representing the results of artificial transmutations. The reader will easily find on the diagram the steps representing spontaneous alpha or beta emission or, say, the neutron ejection from a beryllium atom which, in the same process, combines with an alpha particle.

The simplest nucleus beyond the proton is the deuteron. Here the nuclear binding force is explained by the "exchange force" acting between

a proton and a neutron (Heisenberg). The theory predicts that, when a proton and a neutron are close together, the charge cannot be attributed to one or the other partner but may be found near either one of them

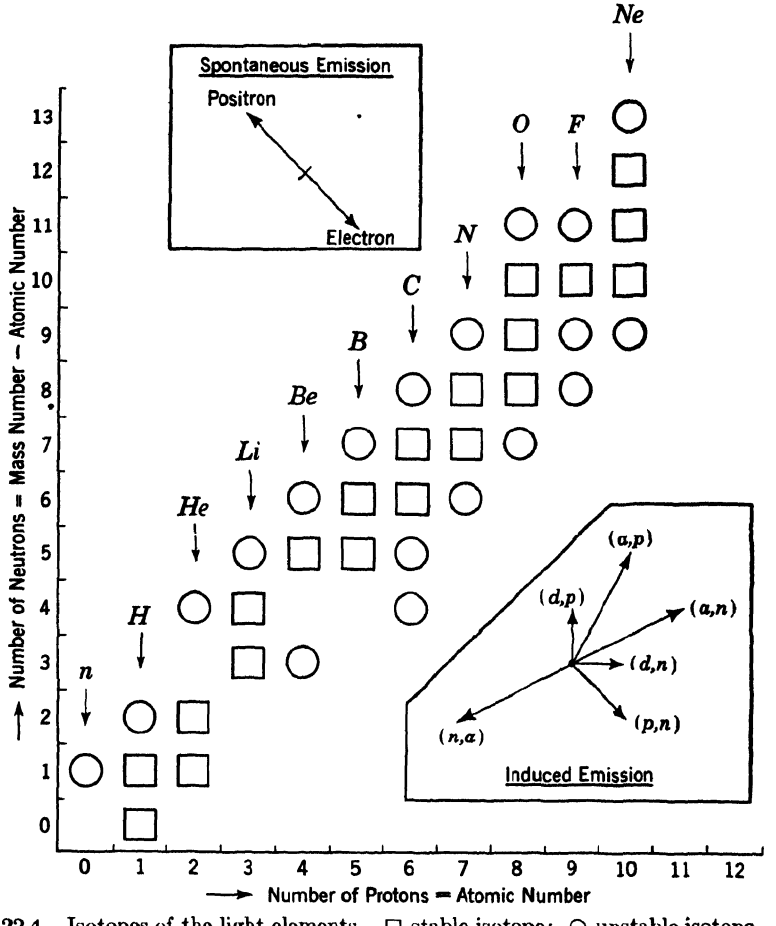


FIG. 22.4. Isotopes of the light elements. □ stable isotope; ○ unstable isotope. The unstable isotopes *below* the stable ones are *positron* emitters; those *above* the stable ones, *electron* emitters.

with equal probability; hence, on the average, it cannot be told which particle is the neutron and which the proton. Furthermore, it is theoretically predicted that this easy exchange is responsible for a force holding the proton and neutron together. This argument explains the formation of the deuteron and plays a part in heavier nuclei. Recent experiments on the scattering of neutrons by protons (not to be discussed here) confirm this theoretical picture.

c. Atomic Weight and Binding Energies. How can we determine the atomic weight of the neutron more accurately than it was crudely done above on the basis of collision experiments? The chemical methods fail because we cannot produce neutrons in bulk. The method of electric and magnetic deflections fails also because the neutron is not affected by such fields. Instead, its atomic weight has been determined by a thorough examination of the deuteron, *i.e.*, the heavy hydrogen nucleus, in which 1 proton and 1 neutron are bound together. The atomic weight of the deuteron and the proton are known with very high accuracy by Bainbridge's analysis carried out with the mass spectrograph. The difference between the two gives the value of *nearly one* for the neutron; but this value is inaccurate because the atomic weight of the deuteron is reduced by E/c^2 where E is the energy of formation (Sec. 20.4). In other cases (Prob. 20.4) we computed the energy E from the masses of the partners and the resulting nucleus; here, on the other hand, the mass of one partner is the unknown and what we need is an independent determination of the energy of formation E.

This is supplied by a new observation. It has been found that gamma rays when passing through a cloud chamber filled with deuterium produce characteristic single tracks of a well-defined length. They are explained as follows. The deuteron consists of a proton and a neutron bound together. Assuming that the gamma-ray quantum separates the deuteron into its constituents by "nuclear photoelectric effect," we expect to see the track of the proton only since the neutron is nonionizing (see Sec. 22.2*a* and Fig. 22.3). Nevertheless, the track of the proton gives evidence as well of the neutron which shoots away invisibly in the opposite direction. (Only these two particles must be considered in the conservation of momentum since the momentum $h\nu/c$ of the gamma quantum is negligible.) The numerical data are as follows (see Prob. 22.3): The energy of the gamma-ray quantum emitted from thorium C'' is known to be 2.65 Mev. This energy is partly consumed for the disintegration of the deuteron; in addition, it produces a proton track in the deuterium-filled cloud chamber which, by an extra calibration, indicates a proton energy of 0.25 Mev. The invisible neutron is supposed to carry away the same energy. Hence the energy of disintegration E of the deuteron follows from the energy balance

$$\text{Quantum} = E + 2 \times \text{kinetic energy of proton}$$

E becomes 2.15 Mev. This figure enables us to state the mass balance for the disintegration process, keeping in mind that we *add* energy to the deuterium in order to take it apart.

$$\text{Mass of } {}_1H^2 + \frac{E}{c^2} = \text{mass of } {}_1H^1 + \text{mass of } {}_0n^1$$

It is convenient to rewrite the same equation in terms of atomic weights, remembering that 931 Mev is the energy equivalent of 1 atomic weight unit. The atomic weights taken from Appendix 5 (including a minor correction) give an atomic weight of the neutron = 1.00894. (On the basis of this result the lack of stability of the neutron is computed in Prob. 22.4.)

Once we know the atomic weight of the neutron, we can compute the energies of its binding to other nuclei from the packing fractions of the various isotopes. The smallest energy of binding (1.6 Mev) is found in beryllium when we compare $_4Be^8$ and $_4Be^9$. This low value explains the fact that beryllium, under alpha bombardment, gives a more copious supply of neutrons than any other element. In the heavier nuclei the binding energy of a neutron is of the order of 5 Mev.

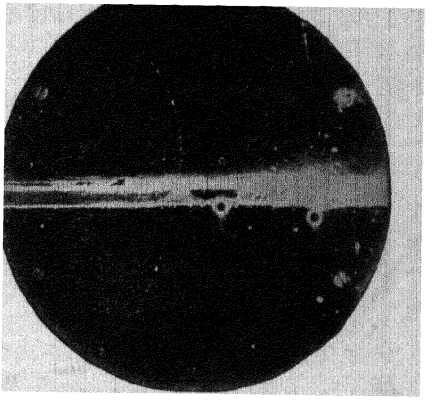


FIG. 22.5. The discovery of the positron by C. D. Anderson. (*Courtesy of C. D. Anderson.*)

22.3. Positrons. Before studying neutron reactions and artificial radioactivity, we complete our survey of the elementary particles. We study next the discovery of the positron which originated from an entirely different group of experiments. In Chap. 24 we shall discuss cosmic rays. These are highly penetrating rays of unknown origin traveling through the cosmos, producing secondary particles in air and, in particular, in heavy materials like the wall of a cloud chamber. Figure 22.5 shows a famous cloud-chamber photograph from which C. D. Anderson (1932) inferred the existence of a new particle. When the picture was taken, there was a magnetic field perpendicular to the face of the chamber bending the tracks of the particles. The new particle traverses a 6-mm-thick lead plate placed across the chamber, and so gives evidence of an extraordinary energy. The photograph also shows that the magnetic field curves the track more strongly above than below the lead plate. This indicates that the particle above the plate is slower than below. Since the lead plate can only slow the particle down, this must be assumed to come from below and to be a secondary liberated from the bottom of the cloud chamber by a cosmic ray. The density of the cloud track and the penetrating power through metals are the same as for very fast electrons.

The strangest feature of the track is that the sense of its curvature combined with the direction of the magnetic field (directed into the paper) indicates a *positive charge*. Thus this simple picture represents the im-

portant discovery of a positively charged particle having the same ionizing power as the electron. This particle is called the "positron." When we attribute to it the specific charge of the electron, its initial kinetic energy amounts to 63 Mev. Another very significant photograph is shown in Fig. 22.6; here a cosmic ray ejects both electrons and positrons from the same spot of the wall, both producing tracks of equal density but oppositely curved. As a final convincing proof of the existence of positrons, it was soon found that artificial transmutation generates radioactive isotopes of many elements, which give rise to a copious supply of positrons (see Sec. 22.4).

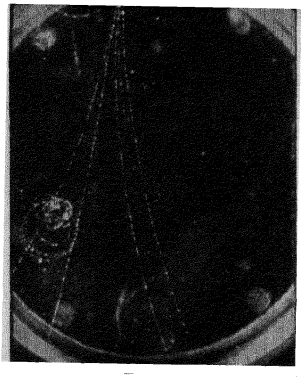


FIG. 22.6. Production of two positron-electron pairs in the wall of the cloud chamber. (*Courtesy of C. D. Anderson and S. H. Neddermeyer.*)

With the discovery of the positron we are embarrassed by having too many elementary particles at our disposal. We may assume the *neutron* and *positron* to be elementary and the *proton* to be a combination of the two. Or else, we may take the *proton* and *negative electron* as elementary; then their combination would give the *neutron*. We have no way of deciding between such alternatives. One cannot even be sure whether such a distinction has any significance since a combination or separation of these various particles may well occur within a nucleus built of protons and neutrons when it emits either an electron or a positron. Thus this emission would be comparable to the emission of a light quantum from an atom since this quantum is also not supposed to exist as such in the atom.

Since we have unambiguous evidence for positrons and electrons, we may ask, for the sake of symmetry, whether the well-known proton has its counterpart in a *negative proton*. No conclusive experimental evidence of such a particle has been published.

22.4. Artificial Radioactivity; Neutron Reactions. Artificial radioactivity has been discovered by the same type of experiment that Rutherford performed to produce the first artificial transmutation, *i.e.*, bombardment of light elements with alpha particles. Later the experiments were vastly extended by using as projectiles neutrons, which themselves were produced by alpha-particle bombardment. At about the same time the machines to be discussed in the next sections produced a wealth of new radioactive isotopes due partly to the use of other projectiles, partly to the use of projectiles with higher energies than those available in natural radioactivity. Here we shall describe at some length examples of the methods for analyzing these reactions and their products. Later, in dis-

cussing the work done with the cyclotron, we shall only summarize the results.

Irène Curie Joliot and F. Joliot (1934) discovered that several light elements, after being bombarded with alpha particles, remained radioactive after the bombardment; their activities follow the same exponential law of decay as those of natural radioactive elements. An example is aluminum $_{13}Al^{27}$ which, *at the time of alpha-particle bombardment*, gives off neutrons (observed in a boron-lined ionization chamber, see below). Simple arithmetic suggests the following nuclear reaction:

$$_{13}Al^{27} + {}_2He^4 \rightarrow ({}_{15}P^{31}) \rightarrow {}_{15}P^{30} + {}_0n^1$$

where the compound nucleus $_{15}P^{31}$ serves only for an intermediate step of the computation. But here, in contrast with the bombardment of beryllium (Sec. 22.2*a*), it is found that *the piece of metal remains radioactive after the bombardment* and decays with a half-life of 2.5 min. The magnetic deflection of the particles emitted shows that they are positrons. Chemical separation of aluminum and phosphorus leads to a fraction containing the phosphorus in which all the activity is concentrated and so confirms the reaction scheme suggested.

Here we meet again the chemical problem that plays so great a part in nuclear research, the separation of neighbors or near neighbors in the table of elements. Special techniques had to be developed because only an exceedingly small fraction of the atoms of the original element suffer transmutation.

The emission of positrons from the radioactive isotope $_{15}P^{30}$, which is produced here, changes it into a stable isotope, namely $_{14}Si^{30}$. The Joliots, discovering more processes of the same kind, produced several artificially radioactive isotopes of the light elements.

A much greater variety of such isotopes covering the whole periodic table has been produced by neutron bombardment (Fermi and collaborators, 1935). Instead of giving the long list of all neutron reactions, which may be found in special treatises, we shall discuss one reaction in detail in order to make clear the observations and arguments that lead to the final reaction scheme.

Pure aluminum, $_{13}Al^{27}$, is bombarded by neutrons generated in a radium-beryllium source as described in Sec. 22.2*a*. The electroscope shows that the piece of metal stays radioactive when the neutron source is removed and that it decays with a half-life of 14.8 hr. The activated metal is subjected to various chemical separations which separate any adjacent element from aluminum. Thus it is found that the active element is not aluminum itself but sodium. Since sodium has an atomic number (11) smaller by 2 than that of aluminum (13), we infer the ejection of an alpha particle. This process must be connected with a loss of mass number by 4, thereby leading to the mass number 24 of the active sodium. Now we are

able to write the nuclear reaction introducing, for the sake of convenience, the compound nucleus as an intermediate body

$$_{13}Al^{27} + {}_{0}n^{1} \longrightarrow ({}_{13}Al^{28}) \longrightarrow {}_{11}Na^{24} + {}_{2}He^{4}$$

Conventionally this scheme is written in the abbreviated form

$$_{13}Al^{27}\ (n, \alpha)\ {}_{11}Na^{24}$$

writing in the parentheses first the projectile, then the particle knocked out. The process is called a "neutron-alpha reaction."

A separate problem is presented by the properties of the radioactive $_{11}Na^{24}$. With a half-life of 14.8 hr it emits electrons and so changes into the element with a nuclear charge larger by one, $_{12}Mg^{24}$. This final product is known as a stable magnesium isotope In all later investigations of the neighbors of sodium, a half-life observed as 14.8 hr (combined with electron emission of a certain penetration) served, without further chemical analysis, as an unambiguous test for the presence of $_{11}Na^{24}$.

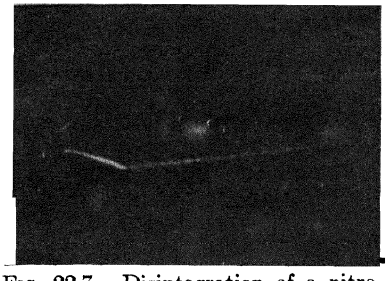


FIG. 22.7. Disintegration of a nitrogen nucleus by a neutron (no track) into an alpha particle (long track) and a boron nucleus (short track). (*Courtesy of N. Feather and Proceedings of the Royal Society.*)

The neutron-alpha reaction does not necessarily generate a *radioactive* isotope. For example, the reaction $_{5}B^{10}$ (n, α) $_{3}Li^{7}$ results directly in the formation of a *stable* isotope. This reaction, having a high yield, is of practical interest since it is commonly used as a test for neutrons. A "boron-lined" ionization chamber responds to neutrons by the emission of alpha particles which, in turn, produce ionization. This device is particularly effective for slow neutrons (see below).

In another type of neutron reaction a proton is ejected instead of an alpha particle. In the same experiment one or the other reaction may be induced by neutron bombardment. In aluminum just considered, under neutron bombardment, the alternative reaction is

$$_{13}Al^{27}\ (n, p)\ {}_{12}Mg^{27}$$

The probabilities of the various reactions depend upon the neutron velocity. The product nucleus is heavier than all stable magnesium isotopes. After a certain half-life it changes by electron emission into the stable $_{13}Al^{27}$.

Figure 22.7 shows typical cloud-chamber tracks due to neutrons impinging on nitrogen. The neutrons themselves, coming from below, do not leave tracks. Nevertheless their momenta show up in the fact that the two particles produced in the nuclear reaction have upward components of momentum. (If the impinging neutron should have no momentum,

the two particles formed in one reaction would part along a straight line.)

The most important neutron reaction is *neutron capture*. Here simply an isotope of higher mass number is generated, which may be stable or unstable. This reaction which is most probable for slow neutrons may occur with aluminum, too. By the capture of the neutron, its binding energy becomes available and thus provides energy for the emission of a gamma ray. Hence the reaction is written

$$_{13}Al^{27} (n, \gamma) {}_{13}Al^{28}$$

The product nucleus $_{13}Al^{28}$ is radioactive, emitting an electron and so changing into the stable silicon isotope $_{14}Si^{28}$. Electron emission is typical for the product of neutron capture if the nucleus so produced has a neutron in excess of a stable number. One may visualize that in this unstable nucleus a neutron, after a certain lifetime, spontaneously changes into a proton by ejecting an electron that is observed.

In many other cases the product of neutron capture fails to show any radioactivity. Then one must conclude that one stable isotope has been transformed into another stable isotope of the same element with an increase of mass number by one. In such cases the binding energy of the neutron which is made available by its capture is emitted as a gamma-ray quantum. An intermediate case is given by the natural radioactivity of potassium which stands isolated among the lighter elements not being a member of one of the radioactive series (Sec. 21.4). It may have been induced in preterrestrial times by the reaction

$$_{19}K^{39} (n, \gamma) {}_{19}K^{40}$$

The product $_{19}K^{40}$ is an electron emitter of such a long half-life (of the order 10^9 years) that a very small abundance has survived up to the present time.

Neutron capture differs from other neutron reactions in that *slow neutrons* are most effective. We can predict how to produce slow neutrons. The discovery of neutrons (Sec. 22.2*a*) is based on the fact that the neutrons, ejected with high speed from the radium-beryllium source, readily transfer their kinetic energy to protons. Hence, when passing through a thick layer of water, the neutrons finally slow down to the average kinetic energy associated with room temperature. Such "thermal neutrons" are still effective for neutron capture and in most cases even much more effective than fast neutrons. For example, neutron capture by silver is forty times as effective for thermal neutrons as for fast neutrons. Uranium fission will present another example of the high activity of thermal neutrons (Sec. 22.8).

Neutron capture may serve to remove free neutrons that are produced in large quantities in the cyclotron or the pile (see below). The protons,

e.g., in water, which effectively *slow down* neutrons, may finally *capture* them in the reaction ${}_1H^1$ (n, γ) ${}_1H^2$, producing deuterons and emitting a gamma ray. This process, however, has only so small a probability that the neutron, after being slowed down, may make, say, a hundred collisions with protons before capture occurs. The most efficient trap for thermal neutrons is cadmium. Its technical importance will be mentioned in the discussion of the uranium pile (Sec. 23.2).

After discussing the outstanding neutron reactions [schematically called (n,α), (n,p), and (n,γ)], we compare the two processes by which we have learned to induce radioactivity, alpha and neutron bombardment. Neutrons are the much more efficient projectiles because, even when slow, they are able to approach any nucleus, light or heavy, without having to overcome the Coulomb repulsion. Alpha particles, on the other hand, are so strongly repelled by the heavier nuclei that particles emitted from naturally radioactive sources (energy < 9 Mev) fail to produce reactions in elements heavier than calcium (atomic number, 20). Another difference is due to the type of radioactivity induced. Neutron bombardment produces *electron* emitters (except if the impinging neutron knocks out two of the bound neutrons), while alpha bombardment leads in some cases to *electron* emitters, in other cases to *positron* emitters. What is the general rule predicting the type of emission? The tendency is the same as mentioned before, *i.e.*, toward the ultimate formation of the most stable configuration. In the diagram of Fig. 22.4 the unstable isotopes are indicated by circles. The diagram represents *electron* emission by a transition to a neighbor *downward to the right* and *positron* emission correspondingly *upward to the left.* Hence all products of neutron bombardment, being located *above* the stable isotopes come *down* by *electron* emission. However, an example of *positron* emission is given by ${}_{15}P^{30}$ which is located *below* the stable isotope.

Also consistent with the above scheme for the formation of stable isotopes is the ability of the nucleus to capture one of the K electrons instead of emitting a positron. By either of these processes, the nuclear charge is reduced by one. K-electron capture is made evident by the subsequent X-ray emission caused by the empty place in the K shell. Heavy nuclei show K-electron capture in preference to positron emission since their large nuclear charges are responsible for a close approach of the K electrons; correspondingly, light nuclei prefer positron emission. The tendency toward the most stable configuration will also decide the alternative between electron or positron emission in the numerous cases of artificial radioactivity induced in the cyclotron and other machines (Sec. 22.6).

22.5. Annihilation of a Pair; Pair Production. One may ask: Why are not positrons observed more often? The answer is that they readily combine with electrons when passing through matter. In this process a large

amount of energy becomes available, and one may guess that this energy will be transformed into radiation. The energy available is simply computed on the basis of Einstein's principle assuming that, in addition to the kinetic energy of the two particles, twice the mass of the electron is exchanged into energy. This "annihilation" contributes an energy of 1.02 Mev. Theoretically, however, one should not expect to observe only one gamma-ray quantum of this energy for the following reason. Suppose that 1 positron and 1 electron, both with negligible kinetic energy, come together. Since they do not have any appreciable linear momentum, their exchange into a gamma-ray quantum, which has a momentum $h\nu/c$, would

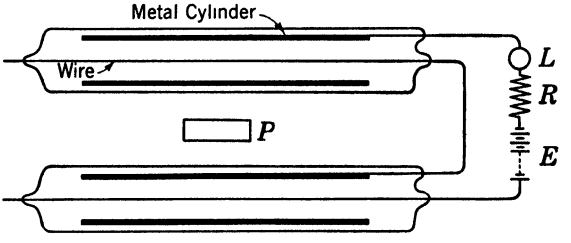


FIG. 22.8. Coincidence counter; schematic diagram of two Geiger-Müller counters connected in series. L, loud-speaker; R, high resistance; E, source of 4,000 volts; P, positron emitter. Coincidences are due to two gamma-ray quanta emitted by the annihilation of a positron-electron pair.

violate the law of conservation of momentum. However, the momentum is conserved when the total energy available is divided up into two equal quanta emitted in opposite directions. What appears to be a bold speculation, here finally leads to the prediction of a gamma radiation that can easily be checked by observation. Actually, when positrons are incident on matter, gamma radiation of the predicted energy is observed and found to be independent of the target element. Thus, these gamma rays give evidence of annihilation of a pair. As a matter of fact gamma radiation of just 0.51 Mev is observed, indicating that annihilation is most probable for *slow* positrons and electrons.

Another experimental test of this speculation lends itself to a laboratory experiment. It is based on "coincidence counting," the essential idea of the apparatus being the combination of two Geiger-Müller tubes in series, as in Fig. 22.8.* When only one tube is made conducting by a gamma-ray quantum, the other tube still blocks the current. Only when both tubes are made conducting simultaneously will the loud-speaker or the mechanical recorder respond. (This may be accomplished, for example, by a cosmic ray that is hard enough to shoot through both counters;

*The technical circuits, which are much more involved, are given in the book of J. Strong, see footnote, Sec. 21.2*a*.

see Chap. 24.) In our experiment, coincidences are counted when the positron source is placed *between the counters* so that both will be triggered by the two quanta emitted in opposite directions. Cu^{64} may serve as the positron emitter. Some of the positrons are annihilated by electrons within the piece of metal. The experiment actually shows the predicted coincidences and so confirms the occurrence of annihilation.

While, in the annihilation process just described, mass is transformed into radiation, in the reverse process radiation is transformed into mass. This process, the *production of a positron-electron pair* by a gamma-ray quantum, has also been observed. It does not happen without the presence of matter and it turns out that heavy matter is most effective in pair production. According to the preceding argument, the gamma ray must have a minimum energy of 1.02 Mev. An example is given by the cloud-chamber tracks of Fig. 22.9. They are caused by a hard gamma-ray quantum, itself nonionizing, which in the air of the chamber produces a positron-electron pair. The momentum of the quantum coming from below is responsible for the upward momenta of the two particles generated.

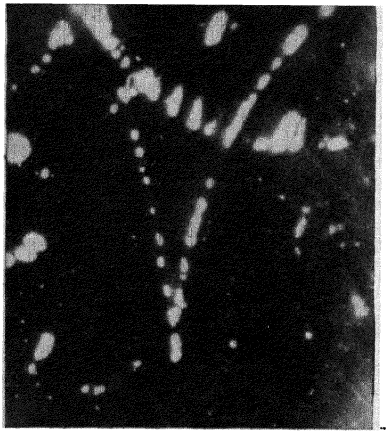


FIG. 22.9. Pair production in the gas of the cloud chamber; gamma ray coming from below. (*Courtesy of F. Joliot.*)

When gamma rays are passing through heavy matter, say, lead, pair production removes quanta from the ray and so is partly responsible for the absorption of gamma rays. Let us now survey the processes that cause absorption of gamma rays in heavy material like lead. The *photoelectric effect* (removal of a K electron, see Sec. 19.2*c*) is most effective for X-ray quanta of an energy just above the limit of the K series which, for lead, is at 89,500 ev (or at a wave length of 0.138×10^{-8} cm). The contribution of this effect to the absorption coefficient *decreases* with increasing energy of the quanta, hence is much smaller for gamma rays of higher energy. The *Compton effect* (Sec. 19.1*j*) attenuates and scatters gamma-ray quanta as well as X-ray quanta, again with *decreasing* effectiveness when the energy of the quanta is increased. Finally, *pair production* begins to be effective for gamma-ray quanta at 1.02 Mev; this is the only effect that is *increasingly probable* for increasing energy of the quantum. As an example, Fig. 22.10 analyzes the absorption coefficient of lead into the various contributions. It shows that the *total* absorption coefficient has a minimum for gamma-ray energies of 3.5 Mev.

The right branch of this curve, which goes up for high energies, is of importance for cosmic-ray research (Chap. 24).

We are used to the idea that energy stored in a particle, *e.g.*, a nucleus, increases its mass according to Einstein's principle (Sec. 20.4). Our present result, however, represents a still more radical violation of the age-old principle of conservation of *matter*. Here we explain certain observations by the *complete annihilation* of two particles creating radiation or, vice versa, the *production of particles* from radiation. All such processes are

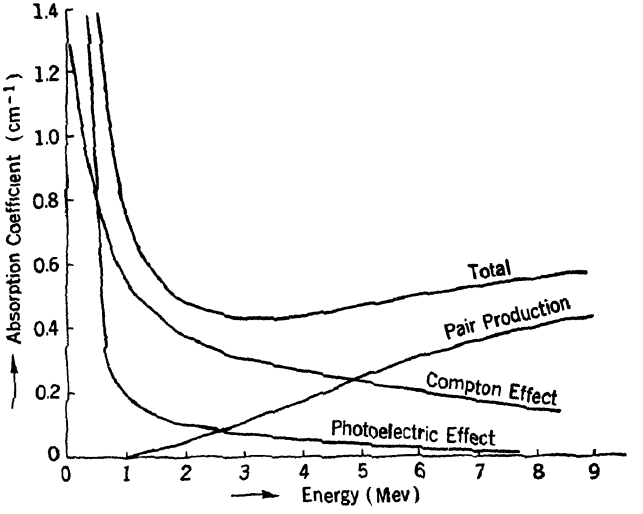


FIG. 22.10. Absorption of gamma rays in lead; comparison of the various processes.

in accord with the principle of conservation of *energy*, provided the change of mass is taken into account according to Einstein's principle.

22.6. Machines for the Production of High-energy Particles. Since 1932, amazing progress in research into artificial radioactivity has been made by the use of artificially produced fast particles. Fast protons and deuterons, which are not emitted in natural radioactivity like alpha particles, have led to numerous new reactions. Moreover, an energy range far exceeding that of natural radioactivity has been made accessible.

a. Production of High Potential Difference. The first artificial transmutation performed with a machine was the breaking up of the lithium nucleus by Cockroft and Walton (1932). They used high voltages generated by a transformer and doubled by an ingenious system of condensers and rectifiers to provide a d-c supply of 700,000 volts.

Another powerful tool, described in elementary textbooks, is the Van de Graaff electrostatic generator which generates up to about 12 Mev. Although it does not give energies so high as those provided by the machines discussed below, it is of importance because it generates relatively

large currents of electrons or ions with sharply defined energies which are used for an accurate determination of threshold energies in nuclear reactions. This technique meets with the outstanding difficulty that the insulating property of the air breaks down at high voltages. However, this difficulty has been partly overcome by the use of higher pressure of air or, preferably, some other gas (Freon, CCl_2F_2) which shows better insulating properties.

But energies of an entirely different order of magnitude are given to ions by machines in which the ions are accelerated *many times in succession* by the same moderate potential difference before they are made to hit the target. As outstanding machines of this kind, we shall describe

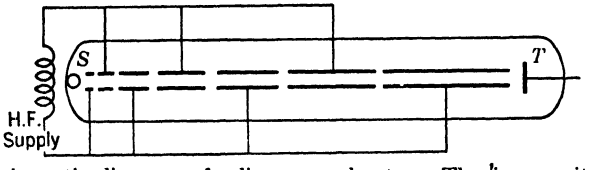


FIG. 22.11. Schematic diagram of a linear accelerator. The ions emitted from the source S are accelerated between the coaxial tubes in steps toward the target T.

four types: the linear accelerator, the cyclotron, the betatron, and the synchrotron. For each machine we shall briefly describe the construction and the operation.

b. Linear Accelerator. In the *linear accelerator* (Fig. 22.11) ions are shot in high vacuum down the axis of a long row of coaxial metal tubes. The tubes are connected alternately with one or the other terminal of a high-frequency generator. Suppose an ion, emerging from an electric discharge (not on the diagram) arrives at the first gap between two tubes at a moment when the potential difference between these two tubes produces maximum acceleration of the ion. After this initial impulse, the ion takes a certain time to travel from the first to the next gap along the axis of the metal tube, *i.e.*, through a field-free region where its speed remains constant. During this time interval the polarity of the alternating current is reversed. Now if the tube's length is chosen properly, the ion will arrive at the second gap simultaneously with a potential difference, which again gives it an acceleration. This proper length, which increases along the path of the ion, is readily determined for a particle of a given specific charge, from a relation between the frequency of the alternating current and the lengths of the tubes. It was with an accelerator of this type that Lawrence and Sloan (1931) succeeded in generating mercury ions of 205,000 volts while applying high-frequency alternating current of only 10,000 volts. Present machines of this type have been vastly improved by the application of the microwave techniques developed for radar since the beginning of the Second World War.

Another linear accelerator, constructed after the war, applies a "wave guide" for accelerating electrons to high energies. In the wave guide, electromagnetic waves, of say 3,000 megacycles, are traveling along a tube with a velocity a little less than that of light. These waves carry a strong *axial* component of the electric field. By the shape of the tube guiding the waves, their phase velocity is adjusted such that it is increasing along the axis. When electrons are injected by an auxiliary device, a few of them are caught and accelerated along the axis by the traveling electric field of the wave. The wave guide is built in such a way that this electric field travels with increasing velocity, just in step with the velocity of these electrons. Hence their acceleration continues along the axis up to velocities approaching that of light.

c. Cyclotron. Lawrence and Livingston (1932) overcame the difficulty inherent in the linear accelerator by the construction of the cyclotron. They describe their method as follows:

> The present experimental method makes use of the same principle of repeated acceleration of the ions by a similar sort of resonance with an oscillating electric field, but has overcome the difficulty of the cumbersomely long accelerating system by causing, with the aid of a magnetic field, the ions to circulate back and forth from the interior of one electrode to the interior of the other.

Consider a closed, round, and very flat pillbox that is cut in half along a diameter. In a cyclotron there are two such halves made of metal and called "dees" because of their resemblance to the letter D. Their diameter in an early cyclotron was about 12 in. but in the largest present cyclotron they are about fourteen times as large. Like the pillbox, the dees are closed all around except at the diameter along which the box has been cut. Insulators support the dees, with a narrow gap between them, in a large high-vacuum chamber (Fig. 22.12 and 22.13). An auxiliary small device (not visible in the figure) inserted at the center of the chamber, generates protons, deuterons, or helium ions. At a certain moment, the high-frequency voltage (say, 50,000 volts) connected to the dees accelerates the ions across the gap. Within the dee, as within a space free of an electric field, the ions would travel in a straight line with uniform velocity. However, the whole vacuum box containing the dees is set in a strong, uniform magnetic field perpendicular to the plane of the dees. This field turns the path of the ions within each dee into a half circle, which brings the ions back to the gap. If the time required to travel one half circle just equals one half period of the alternating current the ions are accelerated again, when passing through the gap. This play continues several hundred times and makes the ions accumulate a high kinetic energy.

In order to select the proper frequency of the alternating current, we compute the time t required to traverse one half circle. We have solved

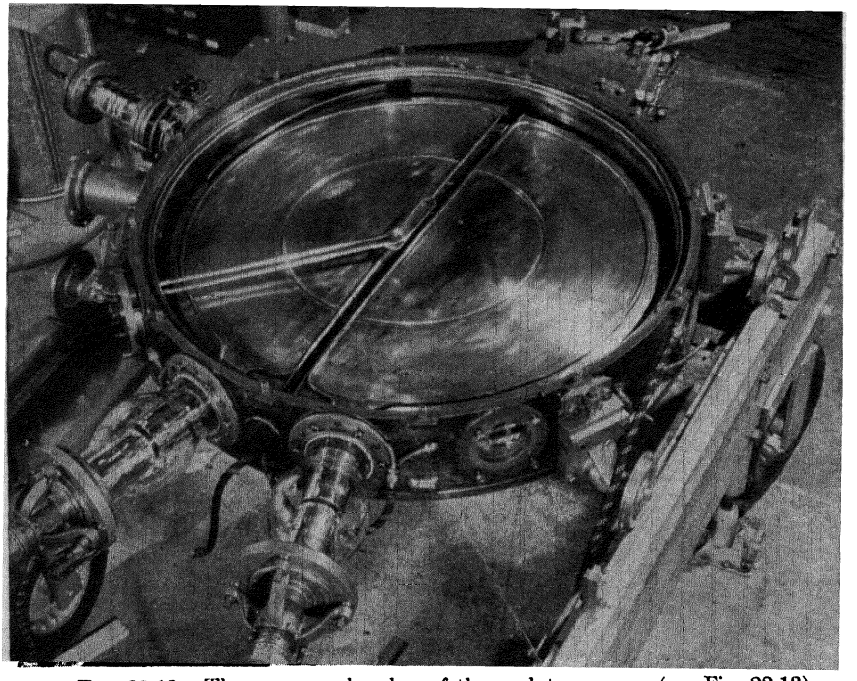


FIG. 22.12. The vacuum chamber of the cyclotron, open (see Fig. 22.13).

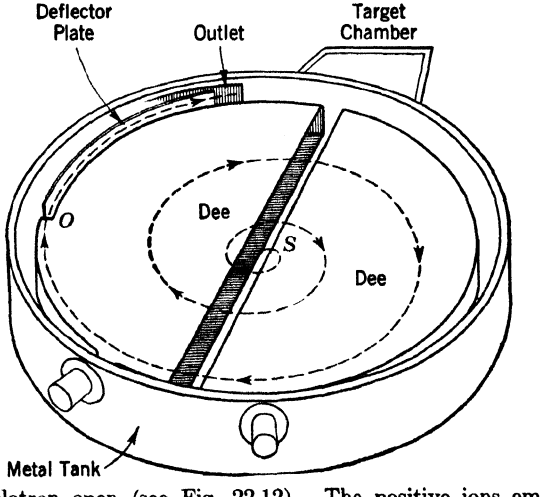


FIG. 22.13. Cyclotron open (see Fig. 22.12). The positive ions emitted from the source S (not shown on diagram) are accelerated in steps between the D-shaped, hollow electrodes, bent on half circles by an axial magnetic field, leave the left dee at the opening O and, finally, are pulled out from their circular path by the negatively charged deflector plate so that they hit the target.

the same problem already in our discussion of the determination of ϵ/μ for electrons by the helical method (Sec. 8.2*c*). Using the same notation, we compute

$$t = \frac{\text{distance}}{\text{velocity}} = \frac{\pi r}{v}$$

Introducing the expression for the velocity $v = H\epsilon r/\mu$ we find

$$t = \frac{\pi\mu}{H\epsilon}$$

It is of outstanding importance for the instrument that r and v drop out of the last equation because, for a larger radius r, the linear velocity v is larger in proportion so that the time t is independent of both. Hence, the *same frequency of alternating current* is as appropriate for the small inner half circles slowly traversed as for the large outer ones traversed with high speed. Thus after passing any half circle, when arriving at the gap, the ion is accelerated again. This is the principle that enabled Lawrence to wind up the path of the ions and so construct the cyclotron with only two electrodes. The last equation gives the condition for tuning. For a given projectile, *e.g.*, deuterons, the time t, identical with one half period of the alternating current, bears a simple relation to the magnetic field H. Hence for a given frequency of alternating current the magnetic field strength must be accurately adjusted. The ion, starting near the center, spirals out in several hundred half circles. When approaching the rim, it escapes through an opening in the cylindrical wall of one of the dees, where it is slightly pulled out of its circular path by a negatively charged "deflector plate" and hits the target.

A considerable group of cyclotrons, designed largely according to the plans of Lawrence, Livingston, and their coworkers, have been built with pole pieces of about 36 in. diameter supplying a deuteron (heavy hydrogen ion) beam of about 8 Mev and 50 microamp (Fig. 22.14. Here the beam is projected through a thin aluminum window into the air). This small value of the current is compensated for by the high energy because the yield of many disintegration processes increases rapidly with the energy of the projectile. Many difficult engineering problems come up in the construction of the cyclotron. For the size just referred to, a power supply of about 10 megacycles and 100 kw is needed. The construction of the magnet, weighing not much less than 100 tons, the vacuum system, the safety devices, all present innumerable problems. The beam produces penetrating radiations, gamma rays, and neutrons, of vicious intensity. The operating crew is protected from neutrons by a 3-ft-thick water tank. Since, during the operation, nobody is allowed near the cyclotron, the control table is placed at a distant corner of the building.

The tendency is toward the construction of much bigger cyclotrons. A

"60-in." has been in operation at Lawrence's radiation laboratory in California for years, largely for medical purposes. A 184-in. cyclotron, built by Lawrence and his coworkers, recently started operations. It produces 195-Mev deuterons or 390-Mev alpha particles. Plans are made for a giant cyclotron in which particles of several billion electron volts will be generated.

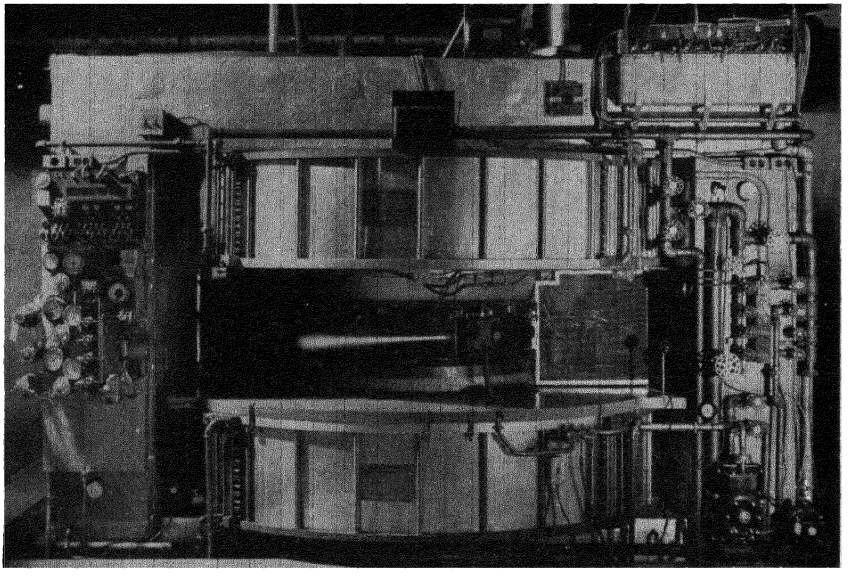


FIG. 22.14. Harvard cyclotron in operation. For demonstration purposes, the target is removed. A thin aluminum window in the rear wall of the target chamber permits the deuteron beam to escape into the atmosphere.

Such enormous energies can be produced only under considerable technical difficulties because already at 15 Mev the deuterons approach the velocity of light so closely that they fail to gain velocity according to the laws of classical mechanics, which are presupposed in the condition for tuning. Here one must apply relativistic mechanics, which predicts that the mass μ of the ion increases with the velocity. How this difficulty is overcome will be described in the section on the synchrotron (Sec. 22.6*e*).

d. Betatron. The *betatron*, constructed by Kerst in 1940, is used for the production of high-energy electrons. These electrons, attaining energies as high as 100 Mev in the largest betatron in operation, are used largely for the production of very hard X rays. The betatron is essentially a transformer whose secondary coil has only one turn and is represented by a ring-shaped high-vacuum tube. The induced emf, which is propor-

tional to the rate of change of the flux (or, if the iron is not saturated, the rate of change of the primary current), is responsible for the acceleration of electrons which emanate from a glowing filament and circle around the ring many times. Hence in the betatron the electrons are accelerated not in many steps as in the cyclotron but continuously as long as the primary current increases. Figure 22.15 shows the evacuated glass chamber built in the shape of a giant doughnut and placed between the pole pieces of a powerful electromagnet, which is designed for alternating current, in contrast to the magnet used in the cyclotron. The two magnetizing coils are placed right above and below the vacuum chamber.

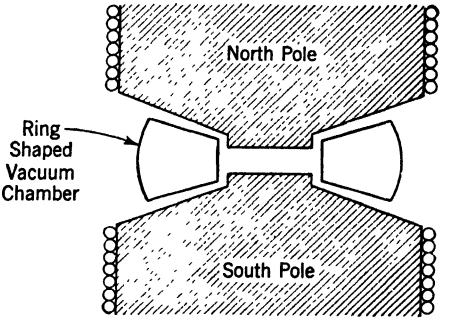


FIG. 22.15. Betatron. Magnet is laminated for use with alternating current. Ring-shaped vacuum chamber serves as a secondary coil of one turn. Electron source and target are omitted.

We shall first write the expression for the emf acting along the circle (keeping in mind that an electromotive force is identical with a potential difference, which here is acting over a circle). The result will enable us to calculate the mechanical *force accelerating the electrons along the circle*. Our second step will be the discussion of the *centripetal force* that prevents the electrons from breaking away from the circle. Third, by correlating the two arguments just given, we shall arrive at the condition for the tuning of the betatron.

We consider electrons starting their journey at the instant when the periodic magnetic flux ϕ goes through zero and its rate of change $\Delta\phi/\Delta t$ has its maximum value. Here the induced emf has its maximum, too, because, according to Faraday's law of induction, emf $= \Delta\phi/\Delta t$ (assuming absolute electromagnetic units). Since by definition the potential difference (or emf) equals electric field $\times$ distance, we compute the electric field E at the periphery of the circle (radius r) as

$$E = \frac{\text{emf}}{2\pi r} = \frac{\Delta\phi}{\Delta t}\frac{1}{2\pi r}$$

Now we express what we are interested in, the mechanical tangential force accelerating an electron emanating from the filament, as

$$\text{Force} = \epsilon E = \frac{\Delta\phi}{\Delta t}\frac{\epsilon}{2\pi r}$$

Because of the circular symmetry this force is everywhere tangential to the circle.

Here this problem differs from that of the secondary coil of a trans-

former. If an electron were subjected only to the tangential force just computed, it would fly off along a tangent. Whereas in the wire of a transformer the motion of the electrons is constrained, in the vacuum chamber nothing prevents them from going off tangentially to the glass wall unless they are forced on a circular path by a centripetal force. This force is automatically supplied by the same magnetic field which represents the flux; but here, to produce the centripetal force, the strength H_p *at the periphery* is effective while the induced emf computed above is determined by the *total flux* $\phi = \pi r^2 H_{av}$ where H_{av} is the average over the whole cross section. (We do not presuppose that the field strength is uniform over the cross section.) The field strength H_p required to provide the centripetal force is given by the same equation that we used in the discussion of cathode rays (Sec. 8.2*a*), namely,

$$\text{Centripetal force} = \frac{\mu v^2}{r} = \epsilon v H_p$$

hence

$$H_p = \frac{\mu v}{\epsilon r}$$

It shows that H_p must be made proportional to the velocity v.

Finally, in order to correlate the two arguments just given, we consider the motion of an electron which emanates from the filament when the flux ϕ goes through zero and which starts its path with zero velocity. At this steepest part of the sine function we may consider the emf $= \Delta\phi/\Delta t$ as nearly constant over a small fraction of the full period. This leads to a constant acceleration and hence to a linear increase of the velocity v with time. This, in turn, requires a magnetic field H_p increasing at the same linear rate to constrain the electron on the circle. Now we see the condition for the tuning of the betatron. The increasing magnetic field must simultaneously fulfill both functions: *speed up* the electrons providing a tangential force and *keep the electrons on a circle* by providing a centripetal force. Mathematically this is expressed by the requirement that the equation for the tangential force and that for the centripetal force apply simultaneously.

We argued that the magnetic field at the periphery H_p must grow at a rate that keeps it *proportional* to the average H_{av}. But must H_p be kept at *the same strength* as H_{av} in order to constrain the revolving electrons on a circle? Suppose that the electromagnet provides an average magnetic field (responsible for the acceleration along the circle) varying at a rate $\Delta H_{av}/\Delta t$. Counting the time as zero when H_{av} goes through zero, then at the time Δt the field strength is ΔH_{av}. In order to find whether the same field strength is suitable for constraining the electrons on a circular path, we first compute the velocity Δv along the periphery acquired after the time Δt and then the required magnetic field H_p acting at the periphery. (We restrict our computation to the low-velocity range governed

by Newtonian mechanics and report only that the final equation applies as well when the velocity of the electrons approaches that of light.) The force ϵE expressed above produces a uniform acceleration along the periphery (introducing the magnetic flux $\phi = \pi r^2 H_{av}$),

$$\text{Acceleration} = \frac{\epsilon}{\mu} \frac{r}{2} \frac{\Delta H_{av}}{\Delta t}$$

This leads to a final velocity after the time Δt,

$$\Delta v = \text{acceleration} \times \Delta t = \frac{\epsilon}{\mu} \frac{r}{2} \Delta H_{av}$$

Hence the magnetic field H_p at the periphery must be

$$H_p = \frac{\mu}{\epsilon} \frac{\Delta v}{r} = \frac{\Delta H_{av}}{2}$$

The conclusion is that, for the operation of the betatron, the magnetic field produced by the large electromagnet must be far from uniform; at the periphery it must be half as large as on the average. This requirement is taken care of by the construction of the pole pieces.

The desired acceleration of the electrons takes place only within less than one-quarter of each period of the alternating current. At the end of the acceleration period, a magnetic field, produced by a sudden condenser discharge through an auxiliary coil, deflects the stream of electrons to a target which then emits X rays.

e. Synchrotron. During the development of large cyclotrons there was a period in which a limit to the accessible kinetic energy of the ions was forecast, based on the fact that the resonance condition gives a value of the a-c frequency without consideration of the theory of relativity. Hence, as soon as the increasing velocity of the ions becomes comparable with that of light, the relativistic increase of the mass does not permit an unlimited gain of the velocity and so causes the ions to fall out of step. The new technique that overcomes this difficulty consists of gradually slowing down the rate at which the dees change their polarity when the velocity of the ions approaches that of light. In other words, frequency modulation is applied to the power supply feeding the dees (Veksler, McMillan 1945). The frequency is changed so slowly, that during any half turn of the particle only a very small decrease occurs. The particle will always arrive at the gap so early that it runs into an *accelerating* field and thus will gain a little energy. It is true that a part of each modulation period is wasted since the mechanism described generates surges of high-frequency particles only during the *decrease* of the radio frequency. But this part of a modulation period is long enough for some particles to perform ten thousands or hundred thousands of circles and so accumulate a high kinetic energy.

It might be expected that this modulation must be carefully adjusted

in order to compensate exactly for the relativistic increase of mass. This requirement, however, is not critical, as will be evident when we consider a special case. We start from the effect of relativity on the condition for tuning $t = \pi\mu/H \times \epsilon$ (see Sec. 22.6*c*). The angular velocity ω follows as the ratio of the angle π to the time t required to cover this angle $\omega = \pi/t = H \times \epsilon/\mu$. This simple equation shows that the angular velocity is independent of the kinetic energy of the particle. In relativistic mechanics, *i.e.*, for linear velocities approaching that of light, the same relation holds with the only modification that the mass μ of the particle (ion or electron) increases with the linear velocity (see Sec. 8.4). (Although the *linear velocity* of the particle is limited, there is no such limit for its *kinetic energy.*) Let us consider a charged particle that has a linear velocity in this high range and, during its revolution, is passing the gap between the dees at the moment of zero potential difference (different from the regular operation of the cyclotron); furthermore, we suppose that the electric field is changing from acceleration to deceleration. In order to investigate the stability of its revolution, let us suppose that the charged particle arrives at the gap too early so that it is accelerated with an increase in mass. Its *angular velocity*, according to the above equation, decreases. Hence the particle is a little late reaching the next gap so that, according to our assumption, it there runs into a decelerating field which has the effect of keeping the particle in step with the frequency of the alternating current. This example illustrates the "phase stability" of the particle (McMillan).

The principle just discussed, called the "synchrotron principle," is based on Einstein's theory of relativity. Therefore, it applies only to high-velocity particles that are initially accelerated by another device. Examples are the large, modern cyclotrons in which, by frequency modulation, *alpha particles* of nearly 400 Mev are generated. Such machines are also called "synchro-cyclotrons." Since the speed of light is much more easily approached by the acceleration of *electrons* than by that of ions, the synchrotron principle is here of great importance. In large synchrotrons under construction, electrons are either injected by an electron gun or are started by the preliminary operation of the machine as a betatron.

22.7. Types of Nuclear Reactions. In a preceding section we first discussed the nuclear reactions caused by *alpha particles*, which led to the discovery of artificial radioactivity, and then those caused by *neutrons*, which produced numerous, new radioactive isotopes all over the periodic table. A wealth of new processes and new radioactive isotopes has been discovered* by the application of projectiles accelerated in the machines

*A complete survey of nuclear reactions has been given by J. Mattauch and S Fluegge, "Nuclear Physics Tables and an Introduction to Nuclear Physics," Interscience Publishers, Inc., New York, 1946.

just described. The first progress in this field was made by Cockroft and Walton (1930) who used a proton beam. Their apparatus is described briefly in Sec. 22.6*a*, their choice of a target being obvious. Since protons cannot easily approach heavy nuclei because of the Coulomb repulsion and since the proton has no effect on other protons or helium nuclei, the authors used lithium, the third element of the periodic table, as a target. As products of the nuclear reaction, they found two alpha particles, recognized by their cloud-chamber tracks. Hence they attributed the effect to the heavy lithium isotope transformed by the proton in the reaction

$$_3\mathrm{Li}^7 + {}_1\mathrm{H}^1 \rightarrow ({}_4\mathrm{Be}^8) \rightarrow {}_2\mathrm{He}^4 + {}_2\mathrm{He}^4$$

We are interested in the energy relation observed in this experiment, considering that in the present book we introduced the equivalence of mass and energy as a *principle*, *i.e.*, as a statement that requires proof by further experiments (Sec. 8.4). The first experimental proof we found for this principle consisted of the mass increase of very fast cathode rays. We have taken the principle for granted when discussing the mass defects of isotopes. Here, finally, the experiments of Cockroft and Walton, in conjunction with Bainbridge's accurate determination of atomic masses, permit another check of the principle. Cockroft and Walton observed that bombardment by protons of 0.3 Mev kinetic energy causes the $_3\mathrm{Li}^7$ nucleus to disintegrate into two helium nuclei of 8.4-cm range. This range indicates a kinetic energy of 8.6 Mev for each particle. The total kinetic energy so observed (17.2 Mev) is so much larger than the share supplied by the impinging proton (0.3 Mev) that most of the total (as much as 16.9 Mev) is supplied by energy stored in the nuclei. On the other hand, knowing all nuclear masses (see Appendix 5), we predict the contribution of the nuclear energy on the basis of Einstein's principle as 17.2 Mev (see Prob. 22.5). The agreement with the experimental value of 16.9 is well within the limit of the experimental error.

With *deuteron* bombardment Cockroft and Walton again found a pair of alpha particles and correspondingly explained the effect as due to the light lithium isotope

$$_3\mathrm{Li}^6 + {}_1\mathrm{H}^2 \rightarrow ({}_4\mathrm{Be}^8) \rightarrow {}_2\mathrm{He}^4 + {}_2\mathrm{He}^4$$

Having discussed in detail the kind of argument used in the pioneer work of Cockroft and Walton and in the interpretation of alpha and neutron reactions (Sec. 22.4), we now refrain from giving more detail on individual investigations and only summarize the results obtained, principally with the cyclotron. The projectiles inducing nuclear reactions are protons, deuterons, alpha particles, neutrons, or gamma rays, abbreviated as p, d, α, n, and γ respectively. Nuclei of higher charge are less effective because of the Coulomb repulsion. The principal types of nuclear reactions

including those we have already discussed are arranged according to the projectile as follows:

p, d	d, p	α, p	n, p	γ, n
p, α	d, α	α, n	n, α	$\gamma, 2n$
p, n	d, n		n, γ	
p, γ			$n, 2n$	

Important examples of nuclear reactions are summarized in Table 22.1, which, however, is far from complete. Many product nuclei are stable, many others unstable, generally emitting electrons or positrons after a characteristic half-life; only heavy nuclei may emit alpha particles (ex-

Table 22.1. *Important Examples of Nuclear Reactions*

Transmutation of elements	${}_7N^{14}$ (α, p) ${}_8O^{17}$	Stable isotopes produced
Artificial radioactivity	${}_{13}Al^{27}$ (α, n) ${}_{15}P^{30}$	${}_{15}P^{30} \rightarrow {}_{14}Si^{30} + {}_{+1}e^{0}$
Neutrons	${}_4Be^{9}$ (α, n) ${}_6C^{12}$	The fast neutron produced may transfer its kinetic energy to protons (paraffin) or cause transmutation of nuclei
Proton reactions	${}_3Li^{7}$ (p, α) ${}_2He^{4}$ ${}_3Li^{7}$ (p, γ) ${}_4Be^{8}$	2 fast α particles observed γ ray of 17.2 Mev observed.
Deuteron reactions	${}_3Li^{6}$ (d, α) ${}_2He^{4}$ ${}_{11}Na^{23}$ (d, p) ${}_{11}Na^{24}$	2 fast α particles observed ${}_{11}Na^{24} \rightarrow {}_{12}Mg^{24} + {}_{-1}e^{0}$
Photodissociation of nucleus by γ rays	${}_1H^{2}$ (γ, n) ${}_1H^{1}$	Binding energy of deuterium and mass of neutron
Slow neutron capture	${}_{13}Al^{27}$ (n, γ) ${}_{13}Al^{28}$	${}_{13}Al^{28} \rightarrow {}_{14}Si^{28} + {}_{-1}e^{0}$
Fast neutron reactions	${}_{13}Al^{27}$ (n, α) ${}_{11}Na^{24}$	${}_{11}Na^{24} \rightarrow {}_{12}Mg^{24} + {}_{-1}e^{0}$
Fission by slow neutrons	${}_{92}U^{235}$ $(n \rightarrow$ various fragments)	Uranium fission; energy released is about 200 Mev

cepting a few light nuclei that may split into alpha particles). This contrasts with natural radioactivity in which only electrons or alpha particles are emitted.

Although neutrons are not repelled by the target nucleus, all charged projectiles are. This partly explains the fact that the yields of all nuclear reactions induced by charged projectiles increase rapidly with the energy of the projectiles. The cloud-chamber photographs of alpha rays (Figs. 21.5, 21.6, and 22.2) show that nuclear collisions are exceedingly rare as compared with ordinary ionization processes evident by cloud formation.

Hence the projectiles are most likely to lose energy before making a nuclear hit. If they do not have an ample excess energy to start with, they have a very poor chance for an effective nuclear collision.

The *d-d* reaction requires the lowest energy of all nuclear reactions induced by charged particles because the Coulomb repulsion has the smallest value; here an effect is observed with an energy as low as 0.02 Mev. Of interest are the product nuclei of the *d-d* reaction. The reaction ${}_1H^2\ (d, p)\ {}_1H^3$ leads to a heavy hydrogen isotope of mass 3 which is an electron emitter with a half-life of 31 years. An alternative is ${}_1H^2\ (d, n)\ {}_2He^3$ which gives a light helium isotope known as a stable isotope occurring in nature with an exceedingly low abundance.

There are a few cases in which two different nuclear reactions generate the same radioactive isotope *with two different values of half-life.* For example ${}_{35}Br^{80}$ has two such values, 18 min and 4.2 hr. Here it must be assumed that the nucleus ${}_{35}Br^{80}$ can exist in two states with different energy contents. Gamma-ray spectra give evidence that all heavy nuclei have sets of energy levels. Here, however, we must introduce the additional assumption that one of the excited levels has a long half-life and, in this respect, resembles a metastable level known in electronic systems (Sec. 16.1*d*). This long half-life gives the excited nuclear level a chance to exhibit its own disintegration. These two states of ${}_{35}Br^{80}$ are called "nuclear isomers." (Isomers are known in chemistry as compounds that are built of the same constituents but differ in properties because of different arrangements of the constituents.) A few cases of nuclear isomers show up in natural radioactivity. For example, ${}_{83}RaC'^{214}$, although principally a beta emitter, shows a few alpha emissions (4 out of 10,000).

The detailed investigation of all possible nuclear reactions has involved an enormous effort since each reaction presents its individual problems to be solved with a special technique. The result is a system of radioactive isotopes which is additional to the well-known system of stable isotopes. At present about 450 radioactive and 275 stable isotopes are known.

In many cases, the same new isotope is being produced by various types of nuclear reaction. For example, the radioactive aluminum isotope ${}_{13}Al^{28}$, characterized by its half-life of 2.3 min and the penetrating power of the electrons it emits, is generated in the following five reactions:

$$ {}_{13}Al^{27}\ (n, \gamma)\ {}_{13}Al^{28};\quad {}_{15}P^{31}\ (n, \alpha)\ {}_{13}Al^{28};\quad {}_{13}Al^{27}\ (d, p)\ {}_{13}Al^{28};\quad {}_{14}Si^{28}\ (n, p)\ {}_{13}Al^{28};\quad {}_{12}Mg^{25}\ (\alpha, p)\ {}_{13}Al^{28} $$

These various reactions leading to the same, well-identified product present an important cross check for the validity of our argument.

Such cross checks are particularly valuable with regard to the effects of neutrons because the evidence of neutrons is based on an argument ever so much more indirect than that for charged particles. Here let us pause and look back over the long chain of experiments and their theo-

retical interpretations leading to the present picture of the neutron and "neutron chemistry." We begin with Chadwick's discovery of the neutron and keep in mind that his argument, in turn, presupposes a great deal of information, experimental and theoretical, regarding various rays and their absorption by matter, in particular regarding atomic collisions and the Compton effect. Next come the discovery of deuterium and the precise determination of its atomic weight, after this the photodissociation of the deuteron, explained by its splitting into a proton and a neutron, and then the determination of the frequency threshold of this process. This figure, interpreted on the basis of the equivalence of mass and energy, leads to the atomic weight of the neutron for which an accuracy of six significant figures is claimed. Finally, we come to neutron chemistry, an elaborate field by itself. We *observe* that radium, beryllium, and aluminum, when brought close together for a while, affect the aluminum by giving it the power to discharge an electroscope. We *hypothesize* that alpha particles emerging from radium eject neutrons from the beryllium nuclei and that these neutrons, in turn, cause a certain reaction in the aluminum. The results of such lengthy arguments are cross-checked with the results of so many other nuclear reactions caused by protons, deuterons, alpha particles, and gamma rays, that we cannot doubt the validity of the whole elaborate picture. In conclusion, the explosion of the atomic bomb may be cited as a fact that gives convincing evidence of neutrons.

The new 184-in. cyclotron that recently started operation in California generates deuterons of nearly 200 Mev. It has led already to new results by disintegrating target nuclei into more complex fragments and by providing an unexpectedly well-collimated beam of high-energy neutrons. It is assumed that such a neutron is generated when a proton (belonging to an impinging deuteron) strikes the edge of a target nucleus and is stripped off while the neutron continues its way. The same machine produces alpha particles of nearly 400 Mev, *i.e.*, of an energy nearly forty times that of the fastest alpha rays occurring in nature. Recently this new technique led to a discovery that is of importance for our knowledge of elementary particles and nuclear structure (1948). The impacts of high-energy alpha particles on various target nuclei generate *mesons*, *i.e.*, new types of elementary particles, which may carry positive or negative charges or be neutral while their masses vary between 100 and 300 times the electronic mass. Mesons had been known before as constituents of cosmic rays (see Chap. 24).

The modern alchemist who attempts to make gold may survey the possible nuclear reactions in order to select the proper target element to be bombarded with the proper projectile. Thus he has a choice, keeping in mind that it may be worth while first to produce the next lighter or heavier element which by electron or positron emission will change into gold.

22.8. Uranium Fission. The discovery of the most widely known nuclear reaction, uranium fission, originated from a systematic attempt to extend the periodic table of elements. We have studied *slow neutron capture* which, by subsequent electron emission, transforms, *e.g.*, ${}_{13}Al^{27}$ into ${}_{14}Si^{28}$, and in general transforms an element into its neighbor of the *next higher atomic number*. Fermi and his collaborators, in their first extensive work on neutron reactions (1934), used this process in order to transform the last element of the periodic table occurring in nature, uranium, into elements hitherto unknown, the "transuranic elements." Presumably these are radioactive, because otherwise they would occur in nature. Uranium is known to have two stable isotopes: ${}_{92}U^{238}$ (abundance, 99.3 per cent) and ${}_{92}U^{235}$ (abundance, 0.7 per cent).

The bombardment of uranium with neutrons leads to a great variety of products that are difficult to analyze because some of them are unknown to the chemist. At present there is no doubt that the process predicted takes place, even with high probability, namely,

$$ {}_{92}U^{238}\ (n,\ \gamma)\ {}_{92}U^{239} $$

As expected, ${}_{92}U^{239}$ is an electron emitter (Sec. 22.4) and so produces the new element, called "neptunium," Np, with the atomic number 93.

$$ {}_{92}U^{239} \longrightarrow {}_{93}Np^{239} + {}_{-1}e^{0} $$

Neptunium being an electron emitter, too, then leads to the element with atomic number 94, called "plutonium," Pu.

$$ {}_{93}Np^{239} \longrightarrow {}_{94}Pu^{239} + {}_{-1}e^{0} $$

Plutonium, finally, is an alpha emitter and so goes back to uranium, forming the rare stable isotope:

$$ {}_{94}Pu^{239} \longrightarrow {}_{92}U^{235} + \alpha $$

(For many years, Uranus was considered to be the most distant planet, as was uranium the last element of the periodic table. More recently, the small planets Neptune and Pluto were discovered at still greater distances.) The two processes of electron emission occur rather rapidly so that the atoms U^{239} and Np^{239} (half-lives 23 min and 2.3 days, respectively) do not accumulate. But Pu^{239} has a half-life of about 30,000 years, long enough for any accumulation during our lives, but not long enough to make the element occur in nature in noticeable quantities; only recently have traces of plutonium been found in uranium minerals.

Two elements of still higher atomic number were produced in the cyclotron in 1944 by Seaborg and his collaborators. The reaction U^{238} (α, n) Pu^{241} generates a plutonium isotope which is a beta emitter and leads to the element called "americium," ${}_{95}Am^{241}$; this, in turn, is an alpha emitter. On the other hand, Pu^{239}, the plutonium isotope of major importance,

leads to the new element "curium," $_{96}Cm^{242}$, by the reaction Pu^{239} (α, n) Cm^{242}; this is an alpha emitter, too.

The products of the neutron bombardment of uranium give evidence of various other half-lives, which have been identified by chemical separation. In 1939 Hahn and Strassmann discovered an entirely unexpected product, *radioactive barium* of a half-life 85 min. Comparing this half-life with those of the known radioactive barium isotopes reveals the product as being $_{56}Ba^{139}$. This result contradicts all previous experience which shows that only light particles, not heavier than alpha particles, are products of artificial or natural disintegration. Here, however, the heavy nucleus goes to pieces entirely. It is of great importance that in the same process several fast neutrons are liberated. The discoverers called this new process "uranium fission." Soon afterward, Lise Meitner, who had collaborated in many preliminary experiments, and Frisch called attention to the vast amount of energy made available by uranium fission. It produces bursts in an ionization chamber ever so much stronger than those due to any other known projectile, and correspondingly heavy tracks are observed in the cloud chamber. Thus the energy liberated by the fission of 1 uranium atom is estimated as 200 Mev. This is 50 million times as much energy as 1 carbon atom generates by its chemical combination with oxygen. The high energy made available by fission is not given to the uranium nucleus by the slow neutron starting the process. This is evident from a comparison of the energies involved. The capture of a neutron by a heavy nucleus makes an energy of about 5 Mev available, only a very small fraction of the total energy that is actually liberated. Hence the neutron acts largely as the trigger releasing the large amount of energy stored in the uranium nucleus. Its high value agrees with the fact that in Aston's curve of packing fractions (Fig. 20.5) the heaviest elements, by their location high above the bottom of the curve, show larger energies stored than the elements in the middle of the periodic table. (A quantitative statement can be derived from the curve only when all fragments of the fission process are known. This is illustrated by Prob. 22.6.)

To determine which of the two uranium isotopes is responsible, Nier separated these isotopes in a mass spectrograph and found the rare isotope $_{92}U^{235}$, which is present in an abundance of only 0.7 per cent, to be susceptible to fission. Here slow neutrons are most effective, *i.e.*, neutrons that, by passing through water, have lost most of their kinetic energy. $_{92}U^{238}$ is very much less susceptible.

Not every fission process produces $_{56}Ba^{139}$; many other elements of medium atomic weight have also been found. If, however, this barium isotope is produced in the fission process itself, the difference of the nuclear charges suggests that krypton, $_{36}Kr$, is associated with it. The heaviest stable krypton isotope $_{36}Kr^{86}$, together with $_{56}Ba^{139}$, leads to the *atomic*

number of the initial combination ${}_{92}U^{235} + {}_0n^1$, but to a *mass* number smaller by eleven. These figures indicate that the initial combination is endowed with excess neutrons, in agreement with the observations that neutrons are liberated in the same process. But we do not claim that we can predict their number since the first fragments of fission may well contain excess neutrons and hence be stabilized only gradually by electron emission like other unstable atoms loaded with excess neutrons (Sec. 22.4). Even the barium which Hahn and Strassmann found by chemical analysis may have been the product of a secondary process. It is observed that by each fission of an ${}_{92}U^{235}$ atom between *one and three neutrons* are emitted. Hence a considerable number of neutrons stick to the fission fragments and make them strongly radioactive.

Which other elements are subject to fission? Only a few heavy elements, the lightest being tantalum, ${}_{73}Ta^{181}$, show fission. Pu^{239}, produced from U^{238}, is susceptible to fission by slow neutrons as U^{235} is. But in lighter nuclei, different from U^{235} and Pu^{239}, fission is produced only by very high-energy projectiles, in tantalum, for example, by 400-Mev alpha particles.

Finally we consider the *probabilities* of the various reactions discussed. The outstanding (not the only) processes produced by neutrons in uranium are "fission capture" by U^{235} and "nonfission capture" by U^{238}. (The latter leads to U^{239} and, after two electron emissions, to Pu^{239}.) U^{235} has a much higher probability of undergoing fission than the other atoms mentioned, in particular U^{238}. Here thermal neutrons (Sec. 22.4) are more effective than fast neutrons. Nonfission capture by U^{238} takes place with a distinct preference for neutrons within a narrow energy range around 25 ev, which is considerably higher than the thermal range. This is called "resonance capture." Fission is induced by *thermal* neutrons only in two atoms: in ${}_{92}U^{235}$, which is found in nature, and in ${}_{94}Pu^{239}$, one of the "transuranic elements" manufactured from ${}_{92}U^{238}$ as reported above.

We summarize the four unique features of fission:

1. Fission is a new type of nuclear reaction.

2. The energy liberated far exceeds that due to any other reaction although it may be started by very low-energy "thermal" neutrons.

3. The reaction is not spontaneous, as radioactive disintegration is, but can be started at will by neutrons shot into uranium.

4. Since the reaction itself *reproduces* the same particle, the neutron, that *starts the reaction*, we may expect that in a large body of ${}_{92}U^{235}$ the reaction will perpetuate itself because the first nucleus going into fission will cause one or several others to do the same, etc. Hence, in the ideal case, 1 neutron may burst the whole block of uranium. In chemistry this is called a "chain reaction."

We realize, however, that this picture is idealized by the imagination of an optimist who forgets that neutrons may easily fail to continue the

chain because they may escape from the block of uranium or be caught by nuclei other than U^{235}. How these difficulties are overcome will be discussed in the next chapter.

22.9. Report on the Theory of the Nucleus. In the chapter on natural radioactivity (Chap. 21), we reported on a mechanical model of the nucleus which, in conjunction with a result of wave mechanics, gives a picture of the emission of an alpha particle (Sec. 21.5). In the present section we shall present another model of the nucleus which serves a different purpose: The fission of a heavy nucleus is represented by a picture that can easily be visualized without the mathematical treatment. We shall first study this theory, which is of particular interest for the *heavy* nuclei. Next, we shall discuss the more general problem of nuclear stability in order to judge which nuclei, *light or heavy*, offer the better prospect for our gaining access to their energies.

What is known about the mutual *distances* between the various constituents of atoms? The distances between the external electrons and the nucleus are so large that the *whole atom* is similar to the *planetary system*. This greatly simplifies the theory of the electronic structure. On the other hand, within the nucleus the constituent particles are so closely packed together that the *nucleus* may well be compared to a *drop of a liquid* (Gamow, 1930). In a drop, the molecules are kept together by forces of mutual attraction. The molecules in the *interior* feel *no average force* because on all sides they are surrounded by neighbors. The *surface* molecules, however, have neighbors only on one side and hence are pulled *toward the body* of the droplet. The forces so explained exert the same effect on the droplet as if it were wrapped in an elastic envelope, an effect mathematically described as "surface tension." This tension determines the most stable shape of the drop as a *sphere*, which is the body with the smallest surface for a given volume.

In ordinary liquids these forces are attributed to the electronic structure of the molecules. What are the corresponding forces in the nucleus keeping the particles together? (See Sec. 21.5.) The positively charged particles, presumably as protons, exert a *strong mutual repulsion* and so tend to explode the nucleus. Hence, in order to explain the stable existence of nuclei, we must assume additional *forces of attraction* which, over small distances, overwhelm the Coulomb repulsion yet are negligible over longer distances. These two types of force act together and keep the particles in the nucleus assembled like the molecules in a drop of a liquid.

This picture of a drop serves for visualizing some details of a nuclear reaction. In ordinary liquids the surface tension is not strong enough to prevent completely any part of the drop from flying off. Parts may be lost by either one of two events: (1) Molecules, which by the random thermal motion are given a sufficient energy, may *evaporate* from the sur-

face. (2) The drop as a whole may vibrate about its stable, spherical configuration and thus occasionally *split* into two parts of more or less equal size. In particular large drops are subject to this splitting. This is why raindrops never exceed a certain size.

The forces effective in the two cases considered are of entirely different nature, intermolecular forces in the liquid and nuclear forces, whatever they are, in the nucleus. These forces have in common the property that they provide "cohesion."

Aston's curve of packing fractions (Sec. 20.4) gives information on the energies liberated or consumed when nuclei, light or heavy, are broken up or assembled. As an example, we computed the energy liberated when 4 hydrogen atoms *combine* to form 1 helium atom (Prob. 9.10). We can compute the enormous energy that would be liberated if ${}_{92}U^{235}$ were *broken up* into ${}_{56}Ba^{139}$, ${}_{36}Kr^{86}$, and 10 neutrons (see Prob. 22.6). This process does not really occur. Even if we do not know exactly what the resulting nuclei are, we derive from Aston's curve the general conclusion that the nuclei with large excess energy, *i.e.*, those of the right and left wings of the curve, are able to *liberate* energy, the light atoms by combination, the heavy atoms by fission (see Sec. 20.4). On the other hand, the atoms at the minimum of the curve, near atomic number 60, are stable.

Why do not these processes, the combination of light atoms and the fission of the heavy ones, occur spontaneously in nature, following the frequently mentioned general tendency toward the most stable configuration? This question is answered by the analogy with certain chemical reactions. For example, the mixture of hydrogen and oxygen is an explosive; nevertheless, at room temperature, the mixture seems completely stable, as if there were a barrier separating any hydrogen molecule from any oxygen molecule. It takes a high temperature to overcome this obstacle. Such a system as this mixture is called "metastable" like certain excited states of atoms (Sec. 16.1*d*) which contain stored-up energy but are mysteriously prevented from going down to their stable states. Carbon and oxygen represent another familiar example. In chemistry this barrier or obstacle is described as an "energy of activation." At high temperature the mixture of hydrogen and oxygen explodes. Here thermal motion *supplies* the energy of activation and so *liberates* the larger energy of the reaction. A mechanical picture is that of a rock located in a groove high on the slope of a mountain, *i.e.*, in a metastable position. A small amount of energy, the energy of activation, must be *supplied* in order to make the rock roll down the slope and so *liberate* its larger potential energy.

Aston's curve of packing fractions gives only the *energies liberated*, not the *energies of activation* by which nuclear reactions may be retarded or even prevented. The energies of activation were explored by Bohr and Wheeler (1939) on the basis of Gamow's picture representing the nucleus

as a droplet. When a particle, *e.g.*, a neutron, is caught by a nucleus, its energy of condensation (estimated to be about 5 Mev for a neutron, see Sec. 22.2c) becomes available and produces a violent commotion within the nucleus, which may be described as heating. (The hypothetical "temperature" of the particles constituting a heavy nucleus bears no relation to the temperature of the whole body measured with a thermometer.) This energy, exchanged at random among the particles of the nucleus, may, after an immeasurably short time interval, give so much energy to one particle that it is able to leave like a molecule evaporating from a drop of an ordinary liquid. This is the picture of a reaction in which one particle is caught and another ejected. Alternatively, the excess energy may be emitted from the nucleus as a gamma ray. One or the other of these events stabilizes the nucleus. In this theory the "compound nucleus," introduced above in Sec. 22.1 for the convenience of the computation, is an essential part of the reaction although of so short a life that it cannot be observed.

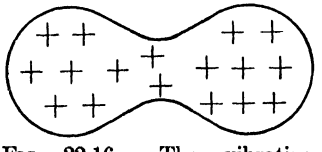


FIG. 22.16. The vibrating droplet as a model of nuclear fission.

A very different process, fission of the heaviest nuclei, is well represented by the same idea. Instead of the evaporation of one particle, a vibration within the whole drop about the spherical shape as equilibrium may be induced by a collision or neutron capture. It is true that, by the effect of the surface tension, a spherical drop is stable for a small deformation. However, if the impact or capture causes a violent vibration, the drop may be elongated to the shape of a dumbbell to such an extent that fission occurs (Fig. 22.16). This picture illustrates the limited stability of the nucleus with respect to vibration. A well-defined energy of activation must be *supplied* to initiate fission; this energy, however, is much smaller than that *liberated* by fission.

In the case of fission, the energy of activation is supplied by the incoming neutron, partly by its kinetic energy, partly by its energy of capture, estimated to be of the order 5 Mev. Thermal neutrons are of outstanding importance because their capture has a much higher probability than that of fast neutrons. This limits the fission by thermal neutrons to those elements which can be excited beyond the limit of stability by the energy of capture of the neutron, about 5 Mev. This is true for U^{235} and Pu^{239}, but for no lighter nucleus. From the point of view of the mechanical picture, it is satisfactory that the largest nuclei, like the largest drops, are most unstable. Fast neutrons have a somewhat wider choice of heavy nuclei in which they may cause fission.

On the other hand, as derived above from the packing-fraction curve, *light* nuclei may deliver large energies by *combining*. Here again an activation energy exists—otherwise all light nuclei would have changed to the

most stable configuration. In this case the activation energy is explained by a more obvious picture. Such an energy exists for all *charged* projectiles because charged particles are prevented by the Coulomb repulsion from approaching each other so closely that the nuclear forces of cohesion, whatever they are, can come into effect. Only neutrons prove to be highly effective for nuclear reactions even at thermal energy (about 1/30 ev).

The energy of activation is measured separately in the experiment of Cockroft and Walton (Sec. 22.7). In the reaction ${}_1H^1 + {}_3Li^7 \rightarrow {}_2He^4 + {}_2He^4$, the energy liberated is as large as 17.2 Mev. But in spite of the large energy liberated, the reaction does not occur when a slow proton approaches the lithium atom because the Coulomb repulsion prevents a sufficiently close approach. It has been observed that the reaction occurs only when protons are shooting into the lithium target with an energy of at least 0.125 Mev. This value represents the energy of activation. (Strictly speaking this energy is not wholly available because the laws of conservation of energy and momentum require that a part of this energy be preserved as kinetic energy; this correction is computed in Prob. 22.7.) The lightest nuclei offer the best chance for overcoming the Coulomb barrier because they carry the smallest electric charges.

We summarize the outstanding result. The curve of packing fractions gives evidence of the fact that the *light* nuclei may liberate large amounts of energy by *combination;* the *heavy* nuclei by *fission*. This argument refers only to the energies of the reaction but not to the barriers protecting the nuclei from the reactions. These barriers, *i.e.*, the activation energies, have been estimated by Bohr and Wheeler. For *heavy* nuclei the energy of activation is identical with the minimum energy of vibration that must be given the nuclear droplet to cause fission; this energy is lowest for the largest nuclei. On the other hand, for *light* nuclei the Coulomb repulsion provides a similar barrier, which is lowest for the lightest nuclei. According to this theory, it is not a mere coincidence that the heaviest atom occurring in nature, uranium (Sec. 23.1), and the lightest atom, hydrogen (Sec. 23.3), play outstanding parts in the liberation of nuclear energy. These are the atoms whose energies are fenced in by the lowest barriers.

At this point it seems appropriate to survey the various energy relations encountered in nuclear reactions, relations similar to those familiar to chemists. Energy may be given off by *combination* as in the formation of the ${}_2He^4$ nucleus from two ${}_1H^1$ and two ${}_0n^1$. The initial particles have a larger total mass than the product. This compares to the chemical combination, *e.g.*, of two H atoms forming an H_2 molecule (see Prob. 9.9). Energy may also be given off by *disintegration* as in the emission of an alpha particle from a radium nucleus; here the explosive character of the radium nucleus is recognized by the fact that it has a larger mass than the fragments produced.

The energy relations involved, in case a collision is required to produce the reaction, are somewhat complex. We distinguish two different situations: (1) The reactant nuclei do not contain the energy required for the reaction unless the kinetic energy of a collision

supplies it; an example is the disintegration of a $_7N^{14}$ nucleus by a fast $_2He^4$ into $_8O^{17}$ and $_1H^1$, studied by Rutherford. Here the initial particles (disregarding the kinetic energy) have a smaller total mass than the products. (2) The initial particles contain more energy than the products, *i.e.*, they form an unstable system. Their total mass is larger than that of the products. Nevertheless an explosion is prevented by a barrier similar to the barrier known in chemistry which, at low temperature, prevents the explosion of the hydrogen-oxygen mixture. In this case the collision brings the reactants over the barrier, *i.e.*, supplies the energy of activation. We discussed the following outstanding examples of this case. The energy of activation is supplied by *kinetic energy* in the process $_1H^1 + {}_3Li^7 \rightarrow {}_2He^4 + {}_2He^4$; it is supplied by the *energy of capture* of a neutron in uranium fission; *both types of energy combined* act as a trigger for the fission of certain other heavy nuclei which is induced by bombardment with fast neutrons.

SUMMARY OF CHAPTER 22

1. Artificial transmutation was discovered by Rutherford who observed that nitrogen when bombarded with alpha particles gives off protons, first recognized by their long range, later identified by their cloud-chamber tracks.

2. Beryllium, when bombarded by alpha particles, gives off an exceedingly penetrating radiation which knocks protons out of paraffin or water. Chadwick identified this radiation as consisting of neutrons $_0n^1$. All nuclei are supposed to consist of a combination of protons and neutrons, the number of protons defining the atomic number, the number of both particles together defining the mass number. The atomic weight of the neutron is accurately determined by the atomic weights of the proton and the deuteron and the energy required for the splitting of the deuteron into its constituents. This energy is measured by photodissociation of the deuteron.

3. The positron has been discovered on a cloud-chamber photograph as a secondary particle ejected by a cosmic ray. The positron has the same absolute charge and mass as the electron but carries a charge of the opposite sign.

4. Bombardment of various light elements with *alpha rays* causes nuclear reactions that lead to new, radioactive isotopes. An example is the reaction $_{13}Al^{27}$ (α, n) $_{15}P^{30}$. The resulting $_{15}P^{30}$ is a positron emitter with a half-life 2.5 min. A great variety of nuclear reactions, many of them leading to radioactive isotopes, are caused by *neutron* bombardment. In particular, neutron capture leads to stable isotopes or electron emitters. In most cases of artificial radioactivity, the particle ejected is a positron or an electron; in any case the particle emitted has such a sign that the nucleus reverts to a stable configuration.

5. The life of a positron ends by its combination with an electron leading to the emission of two gamma-ray quanta of 0.51 Mev each (annihilation of a pair). One gamma-ray quantum of an energy above 1.02 Mev in-

cident on matter may generate a positron-electron pair (pair production).

6. The outstanding machines for the production of high-energy particles are the voltage doubler of Cockroft and Walton, the Van de Graaff generator, the linear accelerator, the cyclotron, the betatron, and the synchrotron.

7. The projectiles that may cause nuclear reactions are, written in the conventional way, p, d, α, n, and γ. Ionizing particles (p, d, and α) produce nuclear reactions with a yield rapidly increasing with their energy, as contrasted with neutron capture which is most efficient for slow neutrons. In many cases the same radioactive nucleus can be produced by various reactions starting from various elements. This gives important cross checks for the interpretations of the individual reactions. Some important nuclear reactions are summarized in Table 22.1.

8. ${}_{92}U^{235}$, when bombarded with slow neutrons, splits into two fragments of nearly equal atomic weight and several neutrons with a liberation of an energy of about 200 Mev (fission). We can start this reaction at will (in contrast to natural disintegration). Neutrons that serve to start the reaction are also generated by the reaction, which thus perpetuates itself like a chemical "chain reaction."

9. The nucleus may be compared with a drop of a liquid. The particles constituting the drop are kept together by surface tension, which here is due to nuclear forces of attraction. Large nuclei compare with large drops by their lack of stability that may cause fission. The packing-fraction curve gives evidence of energies liberated in certain reactions, but not of the barriers, called "activation energies," which retard the reactions. Heavy nuclei liberate energy by fission, light nuclei by combination. The activation energies are computed for heavy nuclei as the limiting energies of the vibrations leading to fission; for light nuclei they are the energies required by charged projectiles to overcome the Coulomb repulsion. The very heaviest and lightest nuclei liberate energy with the smallest activation energy and, therefore, offer the best chance for the utilization of nuclear energy.

PROBLEMS

22.1. *Beryllium radiation interpreted as gamma radiation.* Irène Curie Joliot and F. Joliot discovered that the mysterious radiation from a radium beryllium source knocks protons out of paraffin with a kinetic energy of 5.7 Mev. The authors tentatively supposed that this energy is given to the proton by very hard gamma rays originating in the radium beryllium source and producing a Compton effect when hitting protons. Compute the energy that this gamma-ray quantum must have in order to eject a proton in a forward direction with an energy of 5.7 Mev. Disregard the relativity correction. Chadwick applied the same theory in order to compute the energy of the gamma-ray quantum which gives a forward motion with the observed energy 1.2 Mev to a nitrogen nucleus. Compute the energy of this quantum.

HINT: (*a*) State the fundamental equations of the Compton effect simplified for the case of the forward ejection (Sec. 19.1*j* for the head-on collision, $\phi = 180$ deg). (*b*) Since the scattered quantum $h\nu'$ is not observed, eliminate $h\nu'$. (*c*) Express $h\nu$ in terms of μ and v. (*d*) Introduce the numerical values for both cases.

COMMENT: In order to understand why we assume that the scattered quantum $h\nu'$ travels *backward* ($\phi = 180$ deg), try the alternative assumption that it travels *forward* ($\phi = 0$ deg). Now the equations lead to the result that no Compton effect can occur.

22.2 *Discovery of the neutron.* In this problem the reader is asked to go through an essential part of Chadwick's argument leading to the discovery of the neutron. Chadwick wanted to identify the particles which, by elastic impacts, produce "recoil protons" and "recoil nitrogens" of measured energies. A particle of the unknown mass m_1 and velocity u_1 when hitting a proton (mass m_H) head on, transfers to it the velocity $v_H = 3.3 \times 10^9$ cm/sec, inferred from the range of the cloud-chamber track. When hitting a nitrogen nucleus (mass m_N), it transfers the velocity $v_N = 4.7 \times 10^8$ cm/sec. Compute m_1 and u_1. Use the results and the notation of Prob. 14.1, "elastic collisions."

HINT: In the problem "elastic collisions," the velocity given to the target particle is expressed in terms of the velocity of the projectile. Write this equation once for the proton as representing the target and once for the nitrogen. From these two equations compute m_1 and u_1 as the unknowns.

22.3. *Nuclear photoelectric effect.* In the disintegration of ${}_1H^2$ by gamma rays (energy of quantum = 2.65 Mev) protons are observed of 0.25 Mev. The other particles so produced, supposedly neutrons, are not observed in the cloud chamber. As they have the mass number 1, they pick up the same kinetic energy as the protons. (*a*) Compute the energy required to disintegrate a ${}_1H^2$ nucleus into ${}_1H^1 + {}_0n^1$. (*b*) Compute the atomic weight of ${}_0n^1$ on the basis of the atomic weights of ${}_1H^2$ and ${}_1H^1$ (see Appendix 5) and the energy of disintegration derived in (*a*).

22.4. *Lack of stability of the neutron.* Since we may imagine that a neutron giving off an electron changes into a proton, it is of interest to compute the energy relation between these particles. How large is the energy E by which neutron and electron are bound together? Use the same idea as applied in the text to the deuteron.

COMMENT: The negative sign shows that energy is *gained* by taking apart the neutron into a proton and an electron. Hence the neutron is *unstable*. This does not necessarily lead to the conclusion that the neutron spontaneously disintegrates because its two constituents may be kept together by a high, possibly unsurmountable barrier (see Secs. 22.4 and 22.9). On the other hand, in order to take apart the deuteron (Sec. 22.2*c*), energy must be *spent*. Hence the deuteron cannot spontaneously disintegrate into a proton and a neutron.

22.5. *Disintegration of lithium by proton impact.* From the atomic weights, compute the energy liberated in the process: ${}_3Li^7 + {}_1H^1 \rightarrow {}_2He^4 + {}_2He^4$, disregarding the kinetic energy of the impinging proton (see Sec. 22.7). Although we are interested in a relation between the *nuclear* masses, we can apply the conventional atomic weights since the number of external electrons is the same before and after the reaction.

22.6. *Energy of uranium fission.* Suppose that in uranium fission ${}_{92}U^{235} + {}_0n^1$ split into ${}_{56}Ba^{139}$, ${}_{36}Kr^{86}$, and 11 neutrons. Compute the total energy made available by this fission process; given the atomic weights: U^{235} 235.12; Ba^{139} 138.92; Kr^{86} 85.94; ${}_0n^1$ 1.009.

Actually only between 1 and 3 neutrons are liberated at once, and many others remain bound to the heavy fragment nuclei. Some of these neutrons come off within about 1 min as delayed neutrons; others remain bound to heavy nuclei which, after certain lifetimes, emit electrons.

22.7. *Nuclear activation energy (difficult problem).* In the text the statement is made that the energy required to produce a certain proton reaction is measured by the mini-

mum kinetic energy of the impinging proton (0.125 Mev) which is needed to produce the reaction. This statement requires a correction. When a proton impinges on a lithium nucleus, the law of conservation of momentum predicts that the *common center of gravity* will continue its path with unchanged velocity. This law is independent of any detail of the collision process (elastic or inelastic, nucleus or bullet of a gun). Hence in the inelastic collision here considered, we are bound to assume that the compound nucleus ${}_4Be^8$ just formed takes up a part of the kinetic energy which, before the collision, is all concentrated in the fast proton. Compute this kinetic energy given to the compound nucleus. For its excitation only the balance is available. This balance, strictly speaking, is the energy of activation. (This problem is related to Prob. 17.4, "inelastic collisions.")

HINT: (*a*) Compute the velocity v_c of the center of gravity when the proton (mass m, velocity v_p) approaches the lithium nucleus (mass M) which is at rest before the collision. (*b*) Compute the *kinetic* energy given to the compound nucleus. (*c*) Compute the balance available as *excitation* energy of the compound nucleus in terms of m, M, and v_p. This is the activation energy. (*d*) Introduce numerical values.

22.8. *Binding energy of the neutron.* (*a*) Calculate the energy *required* to separate 1 neutron from ${}_8O^{17}$ and so produce a free neutron and ${}_8O^{16}$. (*b*) Answer the same question for the separation of ${}_8O^{18}$ into ${}_0n^1 + {}_8O^{17}$.

COMMENT: The same energies are *liberated* by neutron capture. In each case of capture in which no particle is ejected, the energy liberated is emitted as one or several gamma-ray quanta. Hence this is called a (n, γ) reaction.

22.9. *Tuning of the cyclotron.* In the cyclotron (magnetic field H = 12,000 oersteds) we want to bombard the target (*a*) by protons, (*b*) by deuterons, and (*c*) by alpha particles. Which other quantity is determined by these data? Compute this quantity for the three cases mentioned.

22.10. *Nuclear reactions.* Write the complete schemes of the following nuclear reactions as in Sec. 22.2, including the compound nucleus and the product nucleus. In all reactions given here the product nuclei are either stable or emitters of electrons or positrons. (These particles are indicated as ${}_{-1}e^0$ and ${}_{+1}e^0$, respectively.) In each case state which is true (see Sec. 22.4) and, if the nucleus is active, state what the final *stable* nucleus is (see Fig. 22.4 and Appendix 5. You may extend the figure on the basis of the Appendix). (*a*) ${}_5B^{10}(\alpha, p)$; (*b*) ${}_4Be^9(\alpha, n)$; (*c*) ${}_7N^{14}(\alpha, n)$; (*d*) ${}_{11}Na^{23}(p, \alpha)$; (*e*) ${}_3Li^7(p, n)$; (*f*) ${}_3Li^6(d, p)$; (*g*) ${}_6C^{12}(d, n)$; (*h*) ${}_1H^2(\gamma, n)$; (*i*) ${}_5B^{10}(n, \alpha)$; (*j*) ${}_{11}Na^{23}(n, \alpha)$; (*k*) ${}_7N^{14}(n, p)$; (*l*) ${}_{13}Al^{27}(n, \gamma)$; (*m*) ${}_{15}P^{31}(n, 2n)$.

CHAPTER 23

APPLICATIONS

23.1. Uranium Bomb. The fact that energy may be produced by nuclear processes has been well known for decades. Radium *spontaneously* generates energy by alpha particle emission; but we have to wait 1,590 years until the energy of half our radium supply has gradually been liberated. Rutherford's discovery of artificial transmutation and the discovery by Cockroft and Walton of lithium disintegration led to the *controlled* liberation of energy in many nuclear reactions; but this is true only for a few lucky nuclear hits that are associated with many energy-consuming misses. It was recognized early by Fermi and his collaborators that uranium fission might have the unique quality of perpetuating itself like a chemical chain reaction since each fission process which *consumes one neutron* should *generate several new neutrons.* Hence uranium fission might lend itself to economical energy production; it might even lead to an explosion.

We shall summarize the nuclear reactions of uranium that are of outstanding practical importance. Slow neutrons or, less effectively, fast neutrons cause fission of the rare isotope U^{235} into two heavy fragments of nearly equal mass and, in addition, several fast neutrons. Neutrons, preferably of about 25 ev, *i.e.*, with energies above the thermal range, transform the abundant isotope U^{238} into U^{239} by neutron capture; U^{239} spontaneously and rapidly disintegrates by the emission of two successive electrons and so forms plutonium ${}_{94}Pu^{239}$. Plutonium, in turn, which has a very long life, is susceptible to fission by neutrons, slow or fast, like the rare uranium isotope U^{235}. In this summary we disregard the pitfalls that threaten the survival of the neutrons before they do their useful work. They may react with impurities or may escape from the uranium. The whole picture is so complex and the probabilities of the individual reactions, desired or undesired, vary over so wide a range depending on the speed of the neutrons, that the prediction of the outcome is very complicated.

Everybody has heard of the development that culminated in the explosion of the atomic bomb. Following the official report by H. D. Smyth* we shall discuss how the nuclear reactions have been utilized. The Smyth Report is highly recommended for everybody who wants to study the

*SMYTH, H. D., "A General Account of the Development of Methods of Using Atomic Energy for Military Purposes," Superintendent of Documents, U.S. Government Printing office, Washington, D.C. 1945.

method of research interlinked with large-scale technical development. In the early days of the Second World War, the ultimate aim was the explosion of the *uranium bomb*. It is hoped that of greater significance for the future of humanity will be energy production by fission in the *uranium pile*. We shall first discuss the bomb, which is of a simpler construction than the pile.

The atomic bomb must be constructed in such a way as to produce as much fission as possible within the shortest possible time. For this purpose the rare isotope U^{235} is separated from U^{238} which is much less "fissionable." (In Sec. 20.6 we mentioned the difficulties of isotope separation.) We may imagine that mass spectrographs, specially constructed for the handling of large quantities perform the separation. Instead diffusion of gaseous uranium compounds is successfully used. In the bomb the uranium must be very pure since most impurities would consume neutrons. Since the great majority of the neutrons would escape from a *small* bomb, the explosion occurs only if the bomb is larger than a "critical size." The explosion must be as sudden as possible because a slow explosion would, at its beginning, split the bomb into fragments, each one of them below the critical size and, therefore, lost for the effect. No experimenting with small-scale explosions is possible.

U^{235} is susceptible to slow more than to fast neutrons. Although the neutrons due to fission have a great excess of energy beyond the most favorable value, no provision is made to slow them down by elastic collisions (as it is done in the pile, see Sec. 23.2) for two reasons: (1) Extra material added for this purpose would make the bomb too heavy; (2) the slowing down of the neutrons would take so much time (counted in microseconds) that the explosion would lose its extreme suddenness. Hence the explosion relies upon *fission of U^{235} by fast neutrons*. Here it is evident that U^{238} must be carefully eliminated because it would remove too many neutrons by "nonfission capture."

The bomb is *detonated* by bringing together several *subcritical* masses of U^{235} to form a *supercritical* mass or by removing a neutron absorber. Stray neutrons available anywhere start the chain. The very sudden assembly of a more than critical mass presents a difficult problem. Possibly it is done by shooting one part of the bomb against another part as a target. In order to reflect as many neutrons as possible from the surface back into the uranium, the bomb is surrounded by an envelope called the "tamper" which reduces its critical size. Furthermore, the inertia of the envelope delays the expansion of the reacting uranium. The bomb is detonated at a certain height above ground to give the maximum blasting and heating effect. The radioactive products are carried upward by the heated air and distributed over so wide an area that they are made harmless.

The *uranium bomb* requires the thorough separation of the rare uranium

isotope, which presents an exceedingly difficult problem because of the small relative mass difference between the two isotopes. It was mentioned in Sec. 22.8 that the only other element as susceptible to fission as U^{235} is Pu^{239}, which originates from U^{238}. Plutonium is produced in quantities in the uranium pile (see Sec. 23.2). Here, however, no *isotope separation* is needed but, instead, a *chemical separation* which, although difficult, lends itself to mass production much better than isotope separation. The plutonium so produced is assembled into a bomb according to the same principles that underlie the construction of the uranium bomb.

23.2. Uranium Pile. *a. Construction and Operation.* The uranium pile was built before the uranium bomb because the slower processes in the pile permit experimentation. However, its principles are more involved. During the war, the purpose of the pile was to transform U^{238} into plutonium to be used in the bomb. Since plutonium is much more fissionable than U^{238}, this complicated procedure had the effect of gaining access to the large store of nuclear energy of U^{238} (abundance 99.3 per cent) and making it indirectly available for the bomb.

The pile requires a construction widely different from that of the bomb. The *bomb* is built for the single purpose of producing as much fission as possible within the shortest possible time. On the other hand, the designer of the *pile* balances two processes: fission capture of neutrons by U^{235}, which keeps the chain going, and nonfission capture by U^{238}, which produces plutonium. In any case capture by impurities and escape must be reduced to a minimum. The pile consists of natural uranium, *i.e.*, uranium containing both isotopes in the natural proportion. Since the neutrons emitted by fission are too fast (several Mev), for efficient nuclear reactions they are first slowed down by elastic collisions with the nuclei of a medium that does not capture them. This medium, which occupies the major part of the space, is called the "moderator." Hydrogen, having nuclei of the same mass as neutrons, is most effective in slowing them down; but unfortunately it swallows them occasionally forming deuterons (Sec. 22.7) and hence cannot be used. Deuterium has all qualities desired but it is too rare. Actually pure graphite is used which, although somewhat heavier than desirable, shows almost no reaction with neutrons. It is estimated that fast neutrons must diffuse through 40 cm of graphite in order to slow down to thermal speed.

In accordance with this consideration, a pile is constructed as follows: A large block of graphite accommodates numerous rods of natural uranium, each in an airtight aluminum container, which prevents the diffusion of the fission products. This is called a "rod lattice." In order just to keep the chain reaction going, it is necessary that a neutron originating from one fission process in turn cause another fission process. The excess neutrons are consumed by competing processes, partly desirable

(capture by U^{238}), partly undesirable (capture by impurities, escape). In order to reduce the number of escaping neutrons, the pile must be large. A small-sized pile does not operate at all. Hence in the first successful construction of a pile the guiding point of view was to build it big enough to keep the chain reaction going, but not so big that the reaction would get out of control. Cadmium strips serve as neutron traps and allow the delicate control of the chain reaction. It will be remembered that cadmium is an outstanding consumer of slow neutrons (Sec. 22.7); its presence, therefore, has the same effect as an adjustable escape for neutrons.

During the Second World War the pile served for the production of plutonium to be used in the atomic bomb. This necessitates an exceedingly heavy load on the pile since we are not at liberty to devote neutrons to the production of Pu^{239} at the expense of the neutrons continuing the chain. It has been estimated that the production of 1 kg of plutonium per day requires the dissipation of an energy of the order 10^6 kw (see Prob. 23.1) and, for cooling, the water supply of a fair-sized city. In the Smyth Report, this estimate is combined with the statement that a single bomb will require the order of 1 to 100 kg of plutonium. After the first experiments in Chicago, a pile of intermediate size was built at Clinton, Tenn., operating on a power level of 1,000 kw. The main production plant was erected in a more isolated location, at Hanford, Wash. Here in the early summer of 1945 several piles were in operation "producing plutonium and heating the Columbia River." The radioactivity built up in a pile is estimated to be the equivalent of about a million tons of radium.

To start the chain reaction it is not necessary to introduce neutrons into the pile since a few stray neutrons are available everywhere, possibly due to cosmic rays, possibly to rare spontaneous reactions in the pile. The operation of the pile will become clear when we consider the life history of a group of neutrons just emitted by fission. By collisions, largely with the nuclei of the moderator, they slow down, many of them to room temperature where they cause more fission of U^{235}. Other neutrons, before completely slowing down, are captured by U^{238} and so start its transformation into Pu^{239}. A very few only, when they are still fast, cause fission of U^{238} and so help continuing the chain reaction. On the other hand, neutrons are lost by escape or by absorption in various materials.

The first pile built in Chicago was gradually assembled. From step to step the *neutron density* was measured and its increase, as the critical size was approached, was watched. The cadmium strips provided safety by destroying neutrons. We quote the report of Fermi:

> On the morning of December 2, 1942, the indications were that the critical dimensions had been slightly exceeded and that the system did not chain react

only because of the absorption by the cadmium strips. . . . Actually, when about seven feet (of cadmium strip) were removed the (neutron) intensity rose to a very high value but still stabilized after a few minutes at a finite level. It was with some trepidation that the order was given to remove one more foot and a half of the strip. This operation would bring us over the top. When the foot and a half was pulled out, the intensity started rising slowly, but at an increasing rate, and kept on increasing until it was evident that it would actually *diverge*. Then the cadmium strips were again inserted into the structure and the intensity rapidly dropped to an insignificant level.

This experiment marks the beginning of a new epoch in the history of the energy production by human beings. It was the first time that a self-maintaining nuclear chain reaction had been initiated.

Considering the sudden explosion of the atomic bomb, it seems strange that the Chicago physicists, starting the operation of the pile, dared to watch the automatic rise of the neutron intensity by their instruments and, before the pile exploded, had time to stop it. This delay of the threatening explosion is explained by the action of "delayed neutrons." Not all the neutrons liberated by the fission process go off instantaneously; about 1 per cent of them are delayed by periods up to 1 min. Near the critical stage of the pile this delay of a small group retards the development of the chain sufficiently to permit the control by cadmium strips. On the other hand, in the explosion of the atomic bomb these delayed neutrons cause only an insignificant energy loss.

From time to time the rods of natural uranium, forming the lattice in the graphite of the pile, are taken out in order to remove the plutonium produced during operation. Plutonium has a long half-life (3×10^4 years). Its removal is complicated by the unavoidable presence of all the fission products, *i.e.*, the fragments into which U^{235} splits. We mentioned barium and krypton only as examples. Actually there are a great number of different elements of medium atomic weights produced, most of them viciously radioactive. The problem of chemical separation is especially difficult as, for the atomic bomb, plutonium of very high purity is required. Because of the very strong radioactivity all chemical operations must be performed by remote control.

It is evident here how rapid the technical progress has been. Before the Second World War, the quantities of most elements produced by artificial transmutation were unweighable. In cyclotron work it was a great success that gold was transformed into mercury in a quantity sufficient for a spectroscopic analysis, presumably of the order of a milligram. A few years later the new element plutonium has been manufactured in a quantity that may be gauged from its power to destroy part of a city.

In our discussion of the pile and the bomb we considered only the few processes desired and how to produce them. This by no means gives an

adequate picture of the difficulties that had to be overcome. The problems of chemistry were as big as those of physics. It is easy to postulate that "pure uranium" be used or plutonium be separated from uranium. As a matter of fact the concentration of some impurities in the uranium and the graphite, used in the pile, had to be reduced to a value as low as a few parts in a million. This requirement compares with the fact that, up to 1940, only a few grams of not very pure uranium metal had been produced. Furthermore, the separation of plutonium from uranium is obviously not described in any handbook of chemistry; all properties and reactions of plutonium must be worked out.

The Hanford pile consists of natural uranium which contains only 0.7 per cent of the fissionable isotope U^{235}. A more efficient operation is expected when the pile is enriched by the addition of fissionable material, U^{235} or Pu^{239}. Although the *uranium pile* serves two purposes: the production of plutonium and the generation of power, a *plutonium pile* seems to offer the best chance of a relatively small atomic power plant. Since plutonium is sufficiently susceptible to fast neutrons, a plutonium pile, called a "fast reactor," may be built without the moderator that forms the great bulk of the uranium pile. Hence a plutonium pile resembles a plutonium bomb except for the fact that it must be below the critical size. Both the pile and the bomb are surrounded by a tamper (see above) which reflects the escaping neutrons as efficiently as possible back into the pile.

b. Prospect for Future Use. We discussed uranium fission as a tool of destruction. Therefore, we considered the uranium pile as a device to convert U^{238} into Pu^{239} which, in turn, is to be used in the bomb. In this operation nobody minds the waste of the energy liberated which goes down the Columbia River as heat. It is hoped that the energy of the pile, now wasted, will be used for the benefit of humanity. Then the plutonium generated will be left in the pile and contribute to the energy production. The energy may serve for boiling water and thus driving steam turbines which, in turn, generate electrical energy as shown schematically on Fig. 23.1.

Can we expect to utilize the energy of other heavy nuclei, predecessors of thorium and uranium, in the periodic table? Aston's curve of packing fractions (Fig. 20.5) gives evidence of large energies stored in all heavy nuclei. We do not know, however, whether these energies are fenced in by obstacles, called "activation energies," so high that they prevent chain reactions (Sec. 22.9). Fission has been observed for a few lighter elements, the lightest being tantalum $_{73}Ta^{181}$ (1947). But here projectiles of a very high energy (400 Mev alpha particles generated in the cyclotron) are responsible for the fission process. Therefore, we cannot expect chain reactions, which are needed for the large-scale spontaneous liberation of nuclear energies, to occur. Hence our great success in the exploitation of the

nuclear energy of uranium has not opened the door to the energies of many other nuclei. The energy stored in hydrogen nuclei will be discussed in the next section. For the time being we do not see a way of making available the nuclear energies of any but the heaviest elements.

How great is the *economic importance* of power production from uranium compared with that from other fuels such as coal, oil, and natural gas? (At present water supplies only about 10 per cent of the power consumed

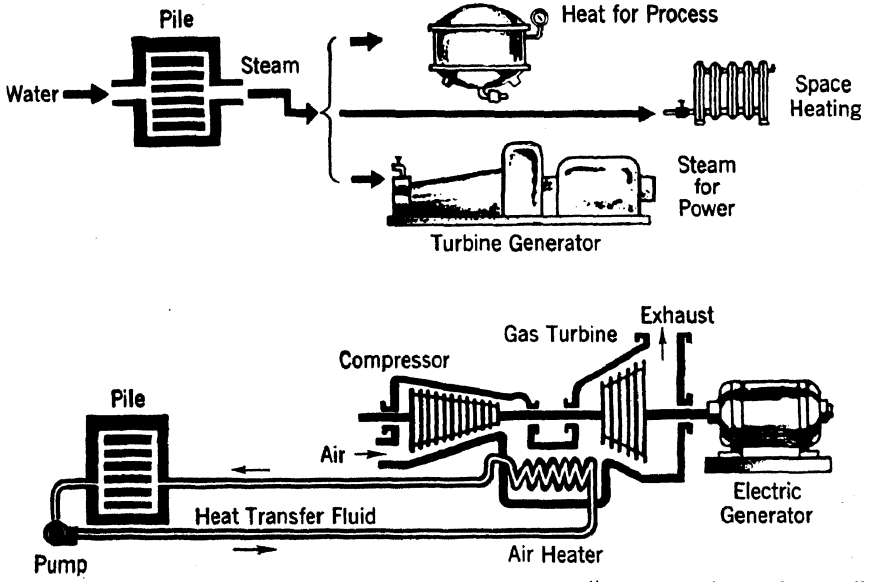


FIG. 23.1. Applications of the pile. (*Reprinted from "Man vs. Atom—Year 1," copyright 1946, McGraw-Hill Book Company, Inc.*)

in the United States.) All known deposits of uranium may represent a total amount of energy of the same order of magnitude as the energy available from the combustion of fuel. In this estimate the energy of U^{238} is included. Hence the energy famine threatening the human race within a few thousand years may be postponed but will not be averted by uranium fission.

Is there any prospect of an ample supply of energy from another source? Unless abundant energy is gained from other nuclei, light or heavy, the power of *solar radiation* far surpasses any other supply available for our rapidly increasing needs. This follows from the "solar constant," which gives the power arriving per square centimeter at the position of the earth (1.96 cal min^{-1} cm^{-2}). Assuming that only half of this power penetrates through the atmosphere, we compute the power of solar radiation incident on 1 sq mile, placed perpendicular to the rays, as 1.7×10^6 kw. This is comparable to the capacity of a large hydroelectric power plant. It has

been stated that the total power of the solar radiation incident on the roof of a factory if efficiently harnessed would drive all its machinery which now receives energy ultimately from combustion of coal or water power. "Enough energy falls on about 200 square miles of an arid region like the Mohave Desert to supply the United States" (quoted from C. C. Furnas, 1941). It is true that the utilization of solar energy meets great technical difficulties since it is *too dilute*, arriving in quanta of a few electron volts, distributed over the surface of half the earth. This difficulty is in contrast to that encountered in the exploitation of nuclear energy which, coming in quanta of 200 Mev, is *too concentrated* for easy utilization. Such technical difficulties, however, do not seem insurmountable. Future research in nuclear physics may change the picture completely.

It may be anticipated that the release of nuclear energy will profoundly affect the course of human civilization. This development will depend not so much upon the total amount of nuclear energy available as upon the ease with with this energy can be utilized; in other words, upon the cost of nuclear energy as compared with that of chemical energy. As a starting point for the new development, we may expect that in industrialized countries where the coal deposits are depleted uranium power plants will prove efficient in the near future. Apart from the *quantity* of the energy available we are sure that here energy of an entirely new *concentration* has been found. The control of this energy should lead to the solution of problems that have seemed beyond our grasp. Now that one such problem, the construction of the atomic bomb, has been solved, one may hope that human as well as physical energy will be expended upon problems of a different nature. One forecast, however, is reliable. The neutron intensity in a pile exceeds by a huge factor that which could be reached with the cyclotron. These neutrons are available for the abundant production of artificially radioactive isotopes all over the periodic table. In one of the next sections we shall discuss the use of these isotopes in a new method of attack upon problems of physics and chemistry as well as biology and medicine.

Any rational plan for the future beneficial use of nuclear energy is in contrast to the events of recent years. In 1939, the basic facts of nuclear fission were discovered as the outcome of research that was not directed to practical purposes. During the Second World War, the arduous development from the observation of fission to the atomic bomb was accomplished by an unheard of concentration of physicists, chemists, mathematicians, engineers, and many other experts. The production of plutonium involved the waste of an enormous amount of energy, equivalent to the output of a big hydroelectric power plant. The production of pure U^{235} may not have been more economical. This gigantic effort was successfully directed toward the instantaneous and most efficient destruction of cities.

The decisive success of the atomic bomb has aroused a universal consciousness of the waste and danger inherent in the present situation.

23.3. Energy Production in Stars. *a. Carbon Cycle.* In order to make clear the importance within the cosmos of the processes to be discussed in the present section, we start from a review of the thermal and chemical history of the earth. When a mixture of reactive gases, like hydrogen and oxygen, is slowly cooled starting from very high temperature, it ends up in the most stable configuration, *i.e.*, water (with a possible excess of one of the reactants). This is what we may expect for the earth gradually cooling down after its separation from the body of the sun. So we understand that almost no free hydrogen is available on the earth because most of it is bound with oxygen as water. We should expect the same to be true for carbon and oxygen, hence as much CO_2 as possible to be formed and not both the isolated elements, carbon and oxygen, to be available. As Gamow puts it, nobody would expect a natural deposit of dynamite. If this expectation were realized, no chemical energy would be available at the surface of the earth and no organic life could exist.

Everybody knows that actually the situation is entirely different. Carbon and oxygen do not all occur as CO_2, but the separate elements are available as well. The carbon is not evenly dispersed but highly concentrated and easily accessible in plants and as a mineral. We have discussed this before and found that all animal life depends on the availability of food energy supplied by plants (Chap. 12 and Sec. 17.9). *What is the source of our chemical energy?* It all comes from solar radiation absorbed by the chlorophyll in the green leaves which, in photosynthesis, assimilates the carbon present in the air as CO_2. The energy of light breaks up the structure of this most stable carbon-oxygen compound. This same process in which carbon compounds are formed in the plant liberates oxygen into the atmosphere. For millions of years this process has been going on.

This answer confronts us with the next question: *Where does the solar energy come from?* This we shall try to answer in the present section. The most trivial guess is that the sun is a hot body in which, according to its heat capacity, energy is stored and radiated from its surface. On this basis one computes (Prob. 23.2) that even within a few years the cooling of the sun's surface would be noticeable; it would be very appreciable during the known period of human history. Hence this guess is obviously wrong. The estimate is not much improved when we assume a chemical reaction, like the combustion of carbon, to be responsible for the heat production of the sun. With this estimate we compare the facts of biology. It is known that the evolution of living beings on the surface of the earth is an exceedingly slow process. It has been estimated that the present state of animal life is the result of an evolution reaching over 500 million years during which the surface of the earth must have been at a temperature

sufficiently uniform for organic life. Since this temperature depends directly on the solar radiation, we must assume that the sun has had a rather uniform temperature through this vast period. Although we are unable to judge the accuracy of this figure, there is no doubt that, in the sun, we must assume a source uniformly producing energy far exceeding any possible supply of chemical energy.

Next it was suggested that the sun is heated by nuclear transmutations; more specifically, that the combination of 4 hydrogen atoms forming a helium atom (or 2 protons and 2 neutrons forming a helium nucleus) would supply the solar energy (see Probs. 9.10 and 9.11). This assumption, however, has the obvious drawback that the process seems to require a simultaneous collision of four particles, which is a highly improbable event.

This great and old problem of the energy production in the interior of the sun has recently been solved by Bethe (1938) who went into the detail of all nuclear reactions involved. The same cycle of reactions was simultaneously suggested by von Weizsäcker. A sequence of nuclear reactions is assumed, each one of them requiring only the collision of two particles. The individual steps involved have not been invented for this purpose but have been really performed in experiments with the cyclotron; so their probabilities have been estimated. Bethe accepts the calculation, made by astronomers, of a temperature in the interior of the sun of 20 million degrees K. Although at this temperature the average energy of translation of any particle is only about 2,000 ev, hence much too small for any nuclear reaction, there are always a few nuclei present which, owing to the Maxwell distribution (Sec. 7.1), possess a much higher energy. In selecting plausible reactions, preference is given to light nuclei since the smaller Coulomb repulsion gives better chances of close approaches. Hydrogen is outstanding partly because of its small nuclear charge, partly because of its overwhelming abundance in the sun. What are the possible reactions of a proton? It does not react with another proton or a helium nucleus; but it does react with the next heavier nuclei, Li, Be, and B, so readily that they presumably have disappeared at an early stage of the history of the sun and similar stars.* Thus the next element ${}_6C^{12}$ turns out to be the plausible partner for a nuclear reaction with fast protons. The products of the reaction are in turn susceptible to proton collisions and so lead to a cycle of reactions as shown in the accompanying table. On the left side we list the particles consumed, in the middle the particles produced. The lifetime of each reactant consumed, ${}_6C^{12}$, etc., is estimated on the basis of observations made with the cyclotron. Except for the spontaneous decompositions (2) and (5) the lifetimes depend upon the concentration

*We do not enter into the closely related speculations concerned with the early history of stars. A highly recommended discussion is given by G. Gamow, "Atomic Energy in Cosmic and Human Life," The Macmillan Company, New York, 1946.

Consumed	*Produced*	*Lifetime*	
${}_6C^{12} + {}_1H^1$	${}_7N^{13} + \gamma$	2.5×10^6 years	(1)
${}_7N^{13}$	${}_{+1}e^0 + {}_6C^{13}$	10 min	(2)
${}_6C^{13} + {}_1H^1$	${}_7N^{14} + \gamma$	50,000 years	(3)
${}_7N^{14} + {}_1H^1$	${}_8O^{15} + \gamma$	4×10^6 years	(4)
${}_8O^{15}$	${}_{+1}e^0 + {}_7N^{15}$	2 min	(5)
${}_7N^{15} + {}_1H^1$	${}_2He^4 + {}_6C^{12}$	20 years	(6)

of protons and the temperature; hence they are uncertain by about the factor 10 either way.

This sequence of processes is easily remembered when its significance is understood. The carbon nucleus ${}_6C^{12}$, which presumably is built of *three* alpha particles, successively assembles four protons. Whenever an unstable nucleus is formed, it soon loses its excess positive charge by the emission of a positron and so changes into a stable nucleus. This, in turn, waits until it swallows the next sufficiently fast proton. Thus gradually the charges and masses are collected for the building up of the "compound nucleus" ${}_8O^{16}$ which, if stable, would be built of *four* alpha particles. However, because of the energy of the last collision, it is unstable and immediately goes to pieces into ${}_2He^4 + {}_6C^{12}$. Hence the over-all effect is the *consumption of four protons* and the *creation of one helium nucleus and two positrons.*

The carbon nucleus entering into the reaction emerges unchanged although it plays an essential part. This function of the carbon, instigating a reaction without ultimately being consumed, is typical for a "catalyst" in a chemical reaction. Therefore, all we have to assume is that in the interior of the sun carbon nuclei and protons are present at very high temperature. Instead of carbon, any other nucleus occurring in the scheme, *e.g.*, ordinary nitrogen, ${}_7N^{14}$, would serve the same purpose. In the computation of the energy output, the creation of three gamma-ray quanta must be taken into account.

The carbon cycle is a very slow process. This follows from the average lifetimes of the principal reactants given above. The low probabilities of the reactions (1) and (4) are responsible for the conclusion that the completion of one cycle, beginning and ending with an individual ${}_6C^{12}$ nucleus, may take about 6 million years. On the basis of reasonable assumptions regarding the abundances of hydrogen and carbon, Bethe was able to estimate the total energy production which satisfactorily agrees with the total energy loss by radiation from the sun.

What is the importance of the carbon cycle for organic life on the earth? Its importance is twofold. Solar radiation, ultimately fed by the carbon cycle, is *heating* the earth to a nearly constant temperature and is providing the *chemical energy* needed for organic life. Astronomers assume that the

sun has gradually reached a *stationary temperature* determined by equal values of *energy loss* from the surface and *energy production* in the interior. This balance has kept the solar temperature appreciably constant through hundreds of millions of years. The earth, if alone in space, would rapidly cool down. Actually, however, solar radiation keeps the temperature of its surface at a certain level. Thus the small earth, in turn, has reached a temperature as stationary as that of the sun but much lower. It appears as a mere coincidence that this stationary temperature of the earth is within that narrow range required for the evolution of organic life. This then is the rare combination upon which organic life depends, the *constancy of the temperature and its value.*

Now we come back to our original question: Where does the *chemical energy* that feeds organic life come from? What agent separates carbon and oxygen at the surface of the earth? This is the other contribution made by solar radiation during the vast period of nearly stationary temperature. Solar radiation (within a narrow wave-length range in the red) continually provides the energy for photosynthesis and so separates the stable CO_2 into carbon and oxygen. Thus solar radiation has stored large energy treasures of plants and coal on one hand and, on the other hand, gaseous oxygen. This energy is indispensable for life as well as for industrial activity. Thus these three agents cooperate to create and maintain life: the carbon cycle generating energy in the sun, the solar radiation keeping the temperature of the earth on a favorable level, and the photochemical processes transforming a small part of the solar radiation into chemical energy available to organisms.

When we realize the vast periods of time during which solar energy has been stored, separating carbon and oxygen, we are appalled by the fact that our present activity in industry and war consumes this treasure at a rate far exceeding the rate of replacement. Our wastefulness places before the physicist the problem of how to utilize the vast reservoir of nuclear energy available at the surface of the earth. How can we liberate energy at will by the combination of four hydrogens forming helium? Actually we are doing it when we duplicate the carbon cycle in the laboratory, *i.e.*, when we are running four cyclotrons bombarding ${}_6C^{12}$, ${}_6C^{13}$, ${}_7N^{14}$, and ${}_7N^{15}$, respectively, with protons. (For the energy gain it is immaterial whether we go through the cycle with identically the same nuclei.) However, it is unfortunate that the running of the cyclotrons consumes a great deal more energy than that gained by the nuclear reactions. Is this inefficiency of the cyclotron to be blamed on its poor construction or is the energy waste inherent in the process? Every cloud-chamber photograph of alpha or proton tracks gives the answer (Fig. 21.5). The desired collisions with nuclei are rare events as compared with the innumerable ionization processes, each one of them contributing one droplet to the cloud. This is a

waste of energy that we cannot avoid since we are shooting our projectiles at random into the target material without aiming them at the nuclei.

Consequently, although with great effort and expense we can go through the reactions forming the carbon cycle, at present there is no economical way of utilizing the resulting energy. Moreover, there is at present no theoretical suggestion how to attain this goal. We can only compute the tremendous energy that would be available if we should be able to transform all the hydrogen of the ocean into helium. We do not know whether men will gain access to nuclear energy other than that due to fission of the few heaviest nuclei.

b. Abundance of Isotopes and Elements. Bethe's theory of the carbon cycle, introduced in order to explain the stationary temperature of the sun, at the same time suggests the answer to another great problem. What determines the relative abundances of the various isotopes measured in the mass spectrograph? They are so well defined that, for a long time, the chemical atomic weights, depending upon these abundances, were considered to be fundamental constants of nature. Now we find that, in the interior of the sun, the relative abundance of C^{12} and C^{13} is determined by the *relative probabilities of the various nuclear transmutations* induced by proton bombardment. This follows from the lifetimes given in the survey of the carbon cycle. C^{13} is rare because it is highly receptive to proton bombardment; C^{12} is abundant because it is about fifty times as reluctant to change its status. When turbulence within the body of the sun brings matter from the hot interior to cooler regions near the surface, the nuclear reactions suddenly stop altogether; hence, the relative abundance determined in the hot interior persists as a "frozen equilibrium." The same applies to the nitrogen isotopes. Also the relative concentrations of carbon and nitrogen, both partners in the same cycle, should be determined by similar considerations. Our argument by no means *completely* explains the relative abundances but, as an outstanding factor, it indicates the probabilities of the transitions occurring in the oven where the elements are cooked.

23.4. Applications to Physics, Chemistry, and Biology. Applications of artificial radioactivity enter into so many fields that, instead of a systematic survey, only examples can be given.*

The application of radioactive atoms as *tracers*, started by Hevesy and Paneth (1913) using natural radioactivity, has developed into a wide field by the production of artificially radioactive atoms of all elements. Typical is the investigation of self-diffusion. Two lead cylinders of equal size are prepared, one of ordinary lead, the other of lead with a small addition of radium D (half-life, 22 years) which is an isotope of lead. These two cyl-

*A full discussion is given in E. Pollard and W. L. Davidson, "Applied Nuclear Physics," John Wiley & Sons, Inc., New York, 1942.

inders, just fitting face to face into a glass tube, are melted and kept in the liquid phase for several days. After cooling, the ordinary lead is cut in slices; the radioactivity of each individual slice indicates the amount of lead that has diffused into it from the active part. So the coefficient of diffusion of lead atoms in lead is measured. This is a problem that can be solved only with the help of a tracer which may be either a radioactive atom as here described or, in similar problems, a rare isotope as discussed in the chapter on Isotopes (Sec. 20.8). By the same method the surprising result has been obtained that atoms are diffusing, although only very slowly, *in the solid state*, too. The method has been applied to metals. For example, zinc atoms diffuse through zinc single crystals at 410°C (9°C below the melting point) at a slow rate which shifts a noticeable concentration of the activated atoms within a few hours over distances of a few thousandths of an inch.

An application of artificial radioactivity to spectroscopy has occasionally been mentioned before (Sec. 23.2*a*). By the reaction ${}_{79}Au^{197} + {}_{0}n^{1} \rightarrow {}_{79}Au^{198}$ and the subsequent spontaneous electron emission, the stable mercury isotope ${}_{80}Hg^{198}$ is produced which, in natural mercury, occurs mixed with six other isotopes. This single isotope emits very sharp spectral lines that are well suited for primary standards of wave lengths (Wiens and Alvarez, 1940).

The elements with the atomic numbers 43, 61, 85, and 87 which are not found in nature, are manufactured in the cyclotron. They are called technitium, prometheum, astatine, and francium, respectively. In the pile the elements 93 and 94, neptunium and plutonium, are produced (Sec. 23.2). Plutonium, in turn, has a long half-life and serves as the starting element for the production of the next heavier elements 95 and 96, americium and curium.

Of particular importance for biology are the radioactive carbon isotopes, C^{11} and C^{14} (half-lives 20.5 min and 1,000 years, respectively). They have been used, *e.g.*, in the investigation of photosynthesis, to trace the fate of carbon atoms that are assimilated from CO_2 by the chlorophyll. Related investigations have been carried out with the rare isotope C^{13} as a tracer (Sec. 20.8).

The rate at which sodium spreads through the human body is measured by feeding a person a salt solution containing a trace of radioactive sodium (half-life 14.8 hr). The counting rate of a Geiger counter placed in the individual's hand begins to rise after a few minutes. Many biologists consider the tracer method and its wide application as the greatest progress in the technique of biological and medical research since the discovery of the microscope. For therapeutic purposes neutrons may, in special cases, be preferable to X rays. The effect of neutrons as well as that of X rays is due to secondary particles, which produce ionization. But in the case

of X rays the secondary *electrons* cause a dilute ionization, whereas in the case of neutrons the secondary *protons* produce a much more concentrated ionization. This contrast is evident on the cloud-chamber pictures, Figs. 21.10 and 22.3. (It is immaterial whether the secondaries are produced by gamma rays or X rays.) The more condensed effect due to neutrons may, in some cases, give a preference to neutrons. The effects on the human body of the products of the pile are so strong that, in any work near the pile, health protection presents a problem of great difficulty.

A ray of fast protons generated by one of the machines (Sec. 22.6) seems to offer a good prospect for surgical applications. Very fast protons penetrate considerable layers of matter with only small losses of their energy. However, when the protons slow down, they deliver a great deal of energy concentrated within a short distance. (A similar behavior of *electrons* is evident in Fig. 21.10; here the densities of the tracks indicate the energy losses; the fast electron has a less dense track than the slow electrons.) Hence, when a beam of very fast protons is directed toward the human body, it scarcely affects the skin (contrary to X rays) and the surface layers but acts like a knife on deeper layers (R. R. Wilson).

SUMMARY OF CHAPTER 23

Fission of a uranium atom U^{235} consumes 1 neutron and in addition generates several of them, thereby lending itself to a nuclear chain reaction. This is used in the uranium bomb and the uranium pile. The outstanding properties of uranium atoms are as follows: U^{235} is susceptible to fission by slow or, less effectively, fast neutrons; U^{238} readily captures neutrons of rather low speed (about 25 ev) and so forms U^{239} which in two steps rapidly changes to plutonium ${}_{94}Pu^{239}$; this, in turn, is an alpha emitter of a long lifetime which, however, is as susceptible to fission by neutrons as U^{235}.

1. The *bomb* consists of pure U^{235} or Pu^{239}. In a block exceeding a critical size, the fission processes lead to a rapidly growing chain and so to explosion.

2. The *pile* consists of natural uranium (or uranium enriched by addition of U^{235}). The fast neutrons originating from fission are slowed down by collisions with the nuclei of the moderator (graphite). This makes them more effective for producing fission. The critical size is such that the chain reaction is maintained without leading to an explosion. Many neutrons not used for the chain reaction are captured by U^{238} and so transform this indirectly (see above) into Pu^{239}. This process makes the nuclear energy of the isotope U^{238} (abundance, 99.3 per cent) available for the chain reaction. The plutonium may be *chemically* separated from the pile and used in the bomb or, else, it may be left in the pile to contribute to the energy production. The vast amount of heat produced in the pile may serve industrial purposes.

3. The energy radiated from the sun probably originates in the hot interior of the sun from a set of nuclear reactions in which a carbon nucleus, ${}_6C^{12}$, gradually captures 4 protons and so helps in building up a helium nucleus. This sequence of processes liberates two positrons and two gamma-ray quanta and finally restores the ${}_6C^{12}$ nucleus, which, therefore, acts only as a catalyst. Through many millions of years the energy *production* in the sun by this process and the energy *loss* by radiation have been balanced. The uniform solar radiation so produced has provided a uniform temperature of the surface of the earth and so created the conditions favorable for the origin and development of organic life. At the same time, by photosynthesis, solar radiation has stored the chemical energy indispensable for organic life.

4. The most important application of artificial radioactivity is that for "tracer" work. Examples are given from physics, chemistry, and biology. Neutrons are applied, instead of X rays, for therapeutic purposes.

PROBLEMS

23.1. *Power of the pile.* Suppose that in a pile each fission process contributes *one neutron* toward the transformation of U^{238} into Pu^{239} Furthermore, the fission process liberates 200 Mev. How much power (in kw) is released when the pile produces 1 kg of plutonium per day?

23.2. *The energy balance of the sun* (Sec. 23.3*a*). Where does the energy radiated from the sun come from? The first guess is that the sun consists of a material similar to that of the earth and gradually cools down because of the heat loss by radiation. In order to check this guess we suppose that the sun radiates as a black body. Furthermore, we specify that the material is iron and that convection and conduction of heat within the sun are so rapid that the temperature is uniform over the whole sphere although heat is lost only from the surface. Compute the time it takes the sun to cool 1°K.

HINT. (*a*) Write an equation expressing the following idea: the heat radiated during the (unknown) time interval Δt equals the loss of heat content suffered while the sun cools by $\Delta T = 1°K$ starting from its present temperature T. In this equation the heat radiated is stated by the Stefan-Boltzmann law. (*b*) Solve this equation for Δt. Temperature of the sun $T = 6000°K$ (average of the results of several methods); radius of the sun $r = 6.96 \times 10^{10}$ cm. Take the other numerical values needed from a textbook. Make sure that you express all energies in the same unit.

CHAPTER 24

COSMIC RAYS

Cosmic rays are rays, occurring in nature, that have a penetrating power far exceeding that of any other radiation known. Their study is of outstanding interest for two reasons: (1) Since cosmic rays consist largely of particles and quanta endowed with much larger energies than can be produced in the laboratory, they give rise to processes otherwise unknown. The investigation of these particles and processes by the methods of nuclear research represents a field of major importance. (2) The occurrence of cosmic rays gives evidence of processes in the cosmos that still are a mystery and accessible only to speculation.

We shall discuss first results obtained with the simple technique by which cosmic rays were discovered, *i.e.*, by observing the *discharge of an electroscope*. Then we shall report the much more refined results obtained with *Geiger-Müller counters* and *cloud chambers*. In the following sections we shall deal with the evidence obtained by the various methods, regarding the nature of the primary and secondary rays and the conversion of primaries into secondaries.

24.1. Fundamental Observations. It is known that every charged condenser, in spite of the most careful insulation, gradually loses its charge. This was first explained by the presence of traces of radioactive substances emitting rays that cause a weak ionization of the air. However, during balloon flights it was discovered that this loss of charge takes place much more rapidly at high altitude. This cannot be explained by a greater concentration of radioactive gases present because, at high altitude, this concentration is actually much smaller than that at sea level. From such observations, Hess (1910) concluded that the ionization of the air is continually being produced by rays coming from outside, later called "cosmic rays." This radiation has an extraordinary penetrating power which enables it to reach the surface of the earth.

This may not seem unusual since we are used to the penetration of sunlight through the whole atmosphere. However, this complete transparency of the atmosphere for visible light is a specific property of certain gaseous molecules in a limited wave-length range. It is due to the fact that the first absorption lines of the atmospheric gases are located in the ultraviolet.

Cosmic rays penetrate water to such an extent that at any depth yet investigated traces of them are found. They penetrate thick lead plates

that would absorb gamma rays, the most penetrating radiation occurring in natural radioactivity. As far as these experiments go, the situation is similar to that in the field of X rays before the discovery of X-ray diffraction (Sec. 19.1*d* and *f*). We measure the rate of discharge of an electroscope protected by various layers of lead. The resulting curve, representing the rate of discharge versus the thickness of the lead, is not simply an exponential curve. It shows that some parts of the radiation are readily absorbed in about 10 cm of lead while other parts have much greater "hardness."

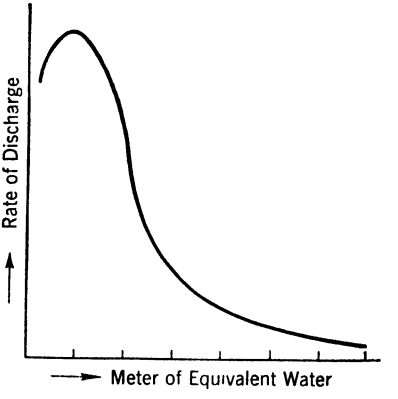


FIG. 24.1. Cosmic-ray ionization at various altitudes (computed for a uniform atmosphere).

The various components, however, are related to each other as is revealed by their absorption in air. For its investigation, Millikan and his collaborators sent an electroscope carried by sounding balloons into the stratosphere. Once every 4 min the electroscope was charged and then its rate of discharge measured. The ionization of the air so measured follows a rather complex law since it is affected by two factors: the intensity of the cosmic rays and the density of the air, decreasing with altitude. In order to correct for the decrease of the density of the air, a curve was derived from the data representing the ionization as it would be if the air had a uniform density all over. For the sake of this computation the sounding balloons carried recording barometers and thermometers in addition to the electroscopes. Thus, in Fig. 24.1 the abscissa represents the total mass per unit area of the atmosphere above any altitude. This is expressed in terms of an equivalent water column. On this scale the highest altitude reached is represented by about 20 cm and sea level by 10.3 m of water. The ordinate represents the rate of discharge (in ions per cm^3 and sec). In this plot the absorption of, say, X rays would yield a simple decay represented by an exponential curve. The actual curve, however, has a maximum at high altitude as shown in the diagram. This is explained as follows: It is assumed that at the highest altitude the cosmic rays consist of particles (or possibly quanta) of exceedingly high energy which are known to dissipate their energy in collisions with molecules only at a low rate (see Sec. 21.2*b*; Fig. 21.10 shows that the straight track due to a fast electron has a smaller density of water droplets than the curved tracks belonging to slower electrons). Gradually these particles generate secondaries so that the few particles of highest energy are gradually replaced by many particles of lower energy that ionize more heavily. This

explains the increase of ionization when, starting from the highest altitude reached (absorbing layer 20 cm water equivalent), we go down to the maximum ionization which occurs at 80 cm water equivalent. The powerful decrease of ionization toward sea level (10.3 m water equivalent) is explained by the gradual dissipation of the energy of the cosmic rays. The low residual ionization at sea level is only 1 per cent of the maximum value in the representation of the diagram. Further investigation of individual rays shows that this residual ionization is due, for the most part, to secondaries.

The study of the ionization as a function of the altitude leads to the total ionization produced by cosmic rays. If tentatively the production of each ion pair is associated with an energy of 30 ev, one can compute the *total energy* incident on the earth by cosmic rays. This is of the same order of magnitude as the total energy incident as starlight.

The results so far discussed have all been obtained with the simplest technique, recording the rate of discharge of an electroscope. The *Geiger-Müller counter* permits a demonstration of cosmic rays in a laboratory experiment. We have already discussed the coincidence counter (Sec. 22.5). This acts like a combination of two Geiger-Müller counters connected in series, which respond only when both are made conducting *simultaneously*. Two such counter tubes are placed in a parallel position (geometrically, not electrically) at a short distance from each other, forming the two opposite sides of a square. First, the two coincidence counter tubes are placed in a *vertical* plane, each tube horizontal, one above the other; next they are placed in a *horizontal* plane. In the vertical plane they register many more counts per minute than in the horizontal plane. (The counts must be corrected for accidental coincidences.) This simple measurement indicates that in the *vertical* direction there exists a radiation penetrating both counters. One should not conclude that *outside the earth*, the cosmic rays show such a preference for the vertical direction, but only that vertical rays have to pass through the minimum layer of air and, therefore, have the best chance of reaching the surface of the earth.

Most instructive observations of individual particles are made with the *cloud chamber*. The atmosphere is not so densely filled with cosmic rays that any random cloud-chamber photograph would show them. In order to avoid waste, the cloud chamber is operated with the help of coincidence counters just described. For this purpose two parallel counter tubes, each horizontal, are placed in a vertical plane, one counter above, the other below the cloud chamber (Fig. 24.2). Hence a cosmic ray shooting through this "counter telescope" is sure to pass through the chamber. Through a relay, the coincidence counters operate the expansion and illumination of the chamber and so restrict its operation to the moments when a ray has just passed through. This elaborate arrangement is called the "counter-controlled cloud chamber."

24.2. Primary Rays. After discussing the experimental methods and some fundamental results, we want to explore the nature of the primary and secondary rays. Are the primaries photons or, possibly, neutrons or charged particles? The answer is found by using the magnetic field of the earth as that of a gigantic mass spectrograph. The intensity of the total incoming cosmic radiation is measured all over the earth with the ionization chamber. In order to obtain comparable data, A. H. Compton (1931) sent the same carefully built chamber with a built-in electroscope over long trips from the Northern to the Southern Hemisphere. The outstanding result, known as the *latitude effect*, is that the intensity of the radiation is lower at the equator than at the poles by about 10 per cent. The latitude effect is much more pronounced on mountain tops where the rays contain a larger percentage of their primary constituents than at sea level.

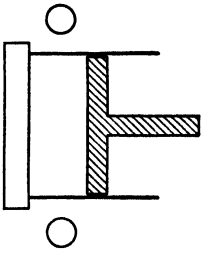


FIG. 24.2. Counter-controlled cloud chamber. The pair of coincidence counters, through a relay, operate the cloud chamber.

In the theory of this effect, the primary cosmic rays are assumed to be charged particles that shoot toward the earth from all directions and are deflected by the magnetic field of the earth. The atmosphere of the earth occupies only a thin layer; 97 per cent of the mass of the atmosphere is contained in a layer of 25 km thickness; this amounts to only 1/250 of the radius of the earth. However, the magnetic field of the earth, considered as a large permanent magnet, reaches much farther out. Hence the primary particles or quanta, when approaching the earth, travel long distances through the magnetic field before they strike the atmosphere.

We consider particles approaching in the direction perpendicular to the surface because they suffer the least absorption. Furthermore, we restrict our discussion to two special cases: to particles approaching either in the direction of the magnetic axis or in the plane of the magnetic equator. Particles shooting *along the magnetic axis* toward one of the magnetic poles are not affected by the magnetic field because here the particles travel in the direction parallel to the field. On the other hand, particles approaching in the plane of the *magnetic equator* are deflected, the angle of deflection depending on their kinetic energy (Fig. 24.3). Particles of low kinetic energy do not reach the earth at all. Only the fastest particles suffer so little deflection that they penetrate the magnetic field to the surface of the earth. It has been computed that an electron approaching in the equatorial plane must shoot toward the earth with an energy of at least 10 billion electron volts (abbreviated Bev) in order to reach sea level (neglecting absorption in the atmosphere.) Such observations, however, do not permit a determination of the masses. We should not expect particles observed at sea level to follow this theory accurately since what we

observe are largely secondaries. However, this comparison is sufficient to explain the fact that the cosmic-ray intensity at the equator is lower than that at the poles; at the equator the charged particles of lower energy are lost altogether. Most important is the conclusion that the primary cosmic rays consist principally of *charged particles.*

The *sign* of their charges is manifest in the east-west effect. Figure 24.3 shows that the primary particles are incident on the magnetic equator under a certain angle whose direction (east or west) depends on the sign of their charges. Johnson investigated these angles using an elaborate apparatus which was essentially a row of parallel counters in a coincidence circuit. This "counter telescope" could be pointed in the various directions. He found a preference for particles coming from the west indicating a preference for *positive charges.* Although this effect is barely noticeable at sea level because of the preponderance of secondaries, it is so pronounced at high altitude that one assumes that the majority of the primaries, possibly even all of them, are positively charged particles, presumably positrons or protons. Since the *proton* is the outstanding positive particle with no negative counterpart while the *positron* may be expected to be associated with negative electrons, the preponderance of positively charged particles is interpreted as indicating *protons* as the primary particles. A more conclusive argument in favor of *protons* is furnished by the very high penetration of the primary rays discussed below. This cannot be attributed to light particles like *positrons*, which are easily deflected when passing near nuclei and so generate gamma rays and further secondaries. These processes would dissipate the energies of positrons and, hence, are not compatible with the high penetration observed.

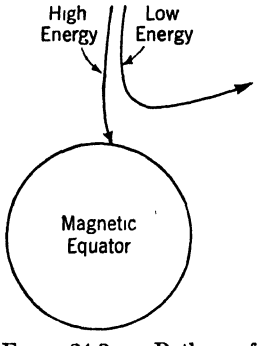


FIG. 24.3. Paths of charged cosmic-ray particles arriving in the magnetic equatorial plane of the earth. The magnetic field is normal to the plane of the figure.

The analysis by the magnetic field of the earth gives evidence of the energies of the primary rays. Protons approaching in the equatorial plane must have at least 9 Bev in order to reach sea level. The higher intensity observed near the poles proves that primaries of lower energy are also incident. An indication of cosmic rays of vastly higher energy has recently been found. Coincidence counters give evidence of large showers of cosmic rays (see below), with each individual ray endowed with high energy. Their simultaneous incidence forces us to assume that they represent numerous secondaries, all generated in the air and originating more or less directly from one primary. The energies and number of the secondaries lead to the estimate of the energy of the primary. The result is as high

as 10^6 or even 10^7 Bev; it vastly surpasses the energy of any particle measured heretofore.

The intensity of the *total* cosmic radiation, on its way through the atmosphere, follows a complex law because the loss of primaries is accompanied by the generation of secondaries. Of particular interest is the absorption of the *primary protons*. One may try to measure their absorption in the atmosphere by measuring the change with altitude of effects that may be attributed to the action of primaries. Such an effect is, for example, a typical nuclear disintegration into many particles which produce tracks in the form of a star (see Sec. 24.4). The frequency of occurrence of such stars as a function of the altitude leads to a decrease of the primary radiation by the factor $1/e$ in about 1.5 m water equivalent.

In the comparison of alpha rays with X rays (Sec. 21.2*a*) we noticed that X rays follow an *exponential decay* while alpha rays are characterized by a *well-defined range*. We explained this difference by the different processes of energy loss. While an X-ray quantum transfers its whole energy to an atom *in one process* which has a characteristic probability, an alpha particle gradually loses its energy by very many ionization processes along its track. Therefore, we are surprised here to find *particles*, the primary protons, which decay according to an *exponential law* like X rays. This observation forces us to assume that these high-energy protons lose their energies by single, rare events rather than by the gradual process of ionization as alpha particles do. Presumably disintegrations producing "stars" (see Figs. 24.7 and 24.8) represent such events. We have no knowledge of processes that would generate particles of this enormous energy range. Not even the annihilation of the heaviest nuclei, if it should ever occur, would provide energies of this order of magnitude.

In recent high altitude flights a cloud chamber and photographic plates were carried to heights of 28 km and gave evidence of heavy nuclei of atomic numbers up to 40 which, presumably, are parts of the primary cosmic radiation.

No clear-cut evidence regarding the origin of the primary cosmic rays is known. The great majority of them do not come from the sun or the stars of the galaxy since the position of the sun or the galaxy fails to show a noticeable effect on their intensity.

24.3. Secondary Rays. Evidence regarding the nature of the *secondary* cosmic rays is much more abundant because they are plentiful at sea level. Cloud-chamber observations, supplemented by the application of magnetic fields, give evidence of all particles and rays known in nuclear physics, electrons, positive and negative, protons, neutrons, alpha particles, recoil nuclei, gamma rays. As a matter of fact, the positron was discovered as a cosmic-ray secondary before it was found as an abundant product of artificial radioactivity (Sec. 22.3, Figs. 22.5 and 22.6).

The systematic exploration of cloud-chamber photographs revealed the existence of other fundamental particles not known heretofore. They were identified by the investigation of the three outstanding characteristics of a cloud track: its *density* (number of drops per centimeter), its *curvature in a magnetic field*, and its *range*. On the basis of arguments, which we omit, these three quantities permit at least an approximate determination of the *charge*, the *mass*, and the *energy* of the particle. We presuppose that charges occur in multiples of the electronic charge. The accuracy of the result does not compare with that obtained by the mass spectrograph. However, electrons and protons differ in their cloud-chamber tracks so vastly that they can easily be distinguished and an intermediate particle can be identified. This is illustrated by one of the first cloud-chamber photographs of such a particle taken by Anderson and Neddermeyer (1936; Fig. 24.4). From the lead plate (0.35 cm, visible as a horizontal strip) a group of particles are ejected, one of them shooting upward, showing a strikingly heavy ionization, much heavier than that due to electrons. Let us tentatively assume this particle to be a proton. For protons the relation between the range and the kinetic energy has been empirically determined and, for the range here observed, leads to an energy of 1.5 Mev (or more, if a part of the track is located within the lead plate). From these data one *predicts* the radius of curvature ρ of the path of the particle in the magnetic field ($H = 7{,}900$ oersteds) to be $\rho = 20$ cm (Prob. 24.1). However, the *observed* radius ρ is only 7 cm. Consequently our guess, interpreting the particle as a proton, is wrong. A more detailed examination leads to a mass about 200 times that of the electron. In such pictures both charges, positive and negative, occur. This new particle is called the "meson" (or mesotron). At sea level mesons are the most abundant secondary particles.

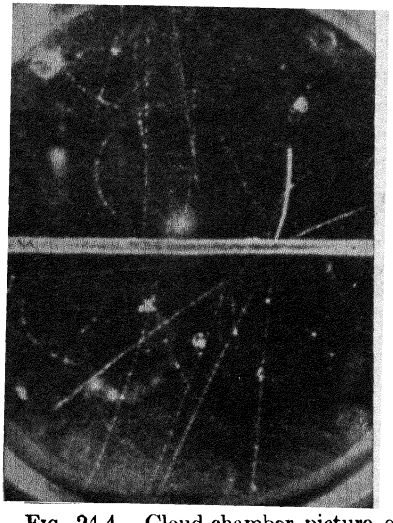


FIG. 24.4. Cloud-chamber picture of a meson and several electrons. (*Courtesy of C. D. Anderson and S. H. Neddermeyer.*)

A spontaneous decay of mesons is indicated by various arguments of which the simplest is as follows: It is observed that the cosmic-ray intensity at sea level decreases slightly with increasing temperature. If *all* secondaries were absorbed solely by air molecules, heating of the air would not affect the cosmic-ray intensity because it would make no difference whether

the same total amount of air is more or less dense. The effect actually observed proves that some of the secondary particles, presumably the mesons, disappear simply because at higher temperature the air extends farther upward so that the particles have a longer time of flight before reaching sea level; in other words, they disintegrate spontaneously. On this basis the half-life of the meson is estimated as of the order 10^{-6} sec.

Great progress has recently been made by a surprisingly simple technique. In photographic plates that are several weeks old, preferably plates with extra-thick emulsions, the microscope reveals tracks, comparable to

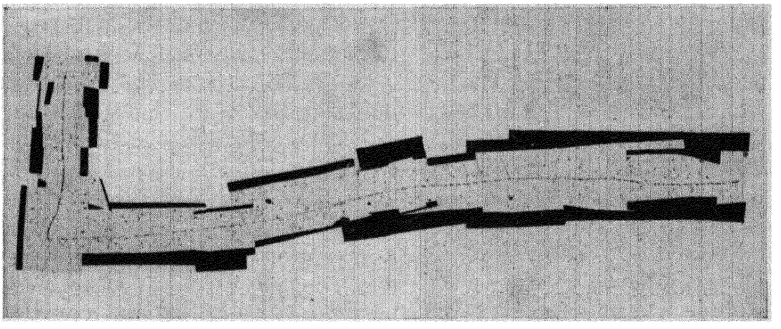


FIG. 24.5. Emulsion picture of the tracks of mesons; primary meson with secondary (lighter) meson. (*Courtesy of C. F. Powell and G. P. S. Occhialini.*)

cloud-chamber tracks but much shorter due to the greater density of the medium. These tracks in emulsions have an advantage over cloud-chamber tracks in that they show the *whole lengths* of the tracks of high-energy particles. Thus important new discoveries have been made. The occurrence of several types of meson has been definitely established. The track of a heavy meson can be followed to the end where it disintegrates into a lighter meson (showing a less dense track) and, presumably, another particle that leaves no track (Fig. 24.5; the figure is a mosaic made of several microphotographs). The artificial production of mesons by 400-Mev alpha particles is discussed in Sec. 22.7.

24.4. Conversion Processes. The conversion of primary into secondary rays, followed by numerous further conversion processes, takes place largely in the atmosphere, although we observe more commonly the conversions occurring in the metal parts of our instruments. Conversion processes are observed on cloud-chamber and emulsion photographs, of which we shall discuss only a few important examples. Outstanding conversion processes are *showers* and *stars*. Figure 24.6 shows a typical "cascade shower." It is evident that several rays originate from one spot at the top of the chamber; the rays multiply by producing more secondaries in a lead plate mounted in the chamber. Cascade showers represent an alternation be-

tween electron pairs and gamma-ray quanta. A fast electron or positron, when suddenly deflected near a highly charged nucleus, generates a gamma-ray quantum which, in turn, soon changes into a positron-electron pair (Sec. 22.5), etc. The large momentum of the initial particle is manifest in the downward components of all constituents of the cascade shower. Gradually less energetic particles and quanta are produced, which are likely to lose their energies by other processes (ionization and Compton effect, respectively) until, finally, all energy of the shower is consumed. In the absence of heavy metals, cascade showers develop in the atmosphere and spread over large volumes. They are observed by coincidence counters placed several meters or even hundreds of meters apart. They give evidence of the vast energies of certain high-energy primaries mentioned above. Other showers consisting of much more penetrating particles do not show the rapid multiplication of cascade showers.

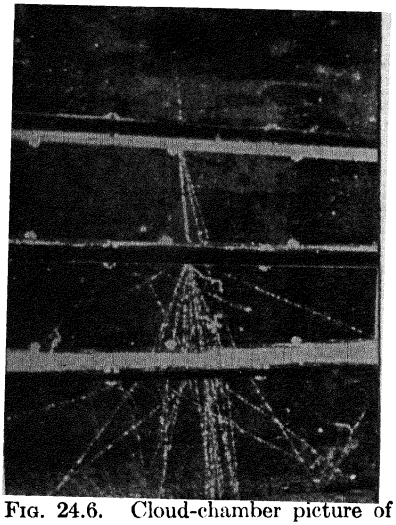


FIG. 24.6. Cloud-chamber picture of a cascade shower (multiplied in lead plates). (*Courtesy of L. Fussell, Jr.*)

Another important conversion process produces numerous tracks in the form of a star (Fig. 24.7). (This and the following picture are taken in the emulsion of a photographic plate.) Here a high-energy particle, possibly one of the primary protons, causes a thorough disruption of a nucleus and so creates many secondaries. Another example of a star is given by Fig. 24.8 which shows a so-called "hammer" track. Here one of the secondaries, a short time after emerging from the star-shaped explosion, disintegrates; presumably it is a $_3Li^8$ nucleus (half-life, 0.9 sec) disintegrating into an electron (not visible) and two alpha particles whose tracks are in a straight line since the Li nucleus has no momentum when disintegration takes place. Long before these cloud-chamber and emulsion pictures were known, the simple technique of the ionization chamber had already shown rare, heavy "bursts" which are superimposed on the usual, more uniform ionization. They are called "Hoffmann bursts" after the discoverer. They represent a more primitive observation of the same showers that are analyzed in much greater detail by cloud-chamber and emulsion pictures.

Our discussion of cosmic rays shows the great significance of the fact that here we are dealing with particles and quanta endowed with energies that far surpass those generated in the laboratory. Only recently have

the modern high-energy generators begun to reach the energy range that is predominant in cosmic rays.

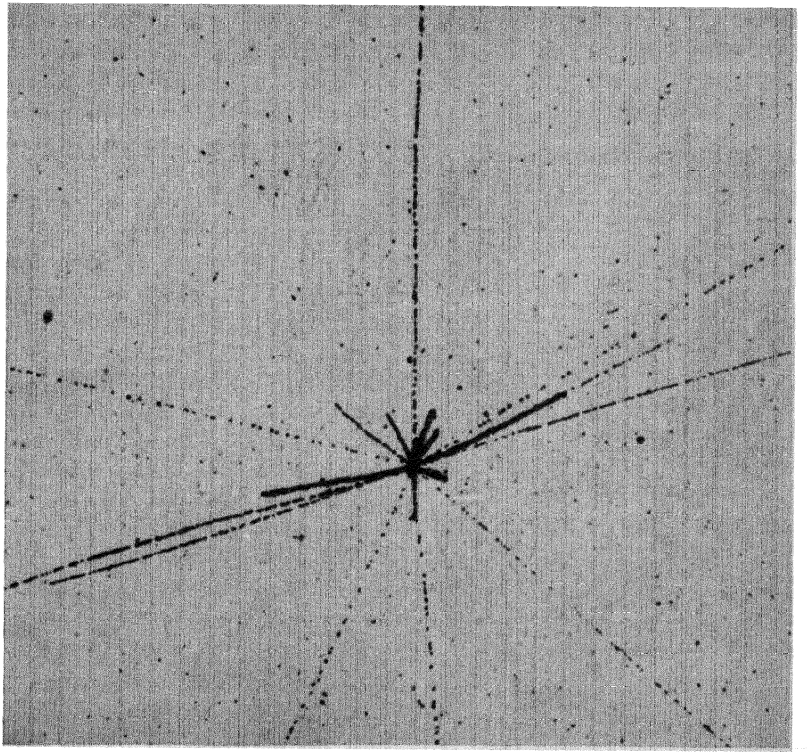


FIG. 24.7. Emulsion picture of star. (*Courtesy of C. F. Powell and G. P. S. Occhialini.*)

SUMMARY OF CHAPTER 24

The unavoidable slow discharge of all electroscopes, which is much more pronounced at high altitude than at sea level, is attributed to the ionization of the air by cosmic rays, *i.e.*, rays coming from the cosmos and able to penetrate the atmosphere, many meters of water, and even heavy lead plates. The ionization plotted against the depth of the atmosphere in terms of the equivalent water column shows a maximum at high altitude. This indicates that in the atmosphere a gradual conversion of the high-energy primaries into secondaries of less energy takes place. Cosmic rays are investigated with ionization chambers, Geiger counters, in particular coincidence counters, cloud chambers, and photographic plates.

The deflection in the magnetic field of the earth is responsible for the "latitude effect," which indicates that the primary cosmic rays are charged

particles of energies of 10 Bev or more. The east-west effect proves that the great majority of the particles are positively charged. Presumably they are protons. The primary rays when passing through the atmosphere are absorbed at such a rate that their intensity decreases by about the factor $1/e$ when they pass through an equivalent of $1\frac{1}{2}$ m of water.

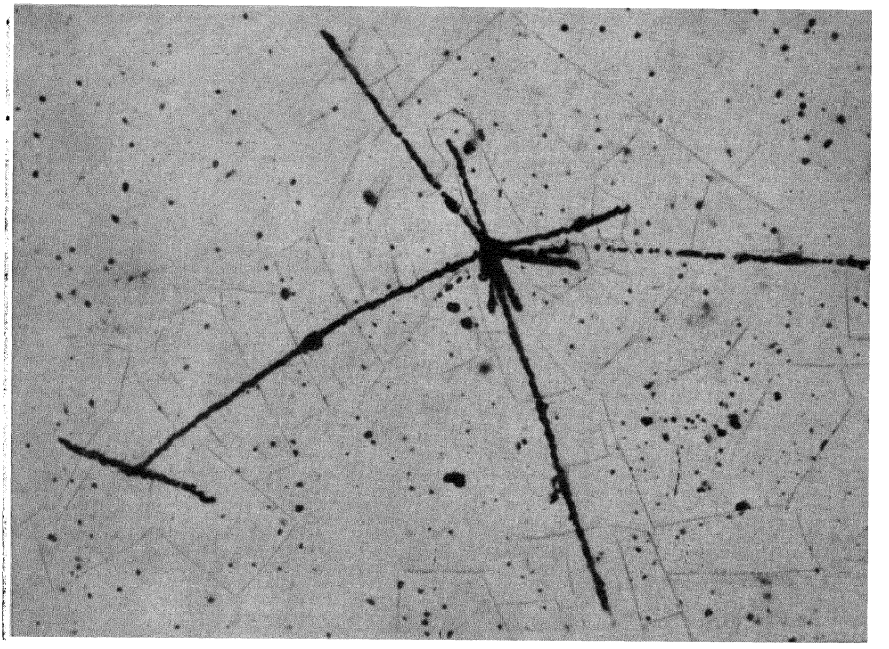


FIG. 24.8. Emulsion picture of star with hammer track. (*Courtesy of C. F. Powell and G. P. S. Occhialini.*)

The secondary rays consist of all particles and quanta known in nuclear physics and a new type of particle, the "meson," which is endowed with the electronic charge, positive or negative, and a mass between those of electrons and protons.

In the conversion of primaries into secondaries there occur outstanding events known as "showers" and "stars." Certain rare cascade showers of unusually high total energy are attributed to primaries of an energy as high as 10^6 or 10^7 Bev.

PROBLEM

24.1. *The meson.* On a cloud-chamber picture taken by Anderson and Neddermeyer a heavy track is tentatively interpreted as due to a proton. On the basis of the empirical range versus energy diagram, its energy is determined as 1.5 Mev. Compute the radius of curvature given to the path of this particle by a magnetic field of 7,900 oersteds. (Your result will deviate slightly from that given in the text due to the fact that the track is not exactly in the plane of the paper, hence not exactly perpendicular to the magnetic field. This is investigated by stereoscopic photographs.)

PART VII

WAVE NATURE OF MATTER

CHAPTER 25

DIFFRACTION OF ELECTRONS

In our discussion of the nature of light we were left with an intolerable discrepancy. For more than a century the old controversy between the corpuscular theory and the wave theory of light seemed to have been decided since the phenomena of *diffraction and interference* gave clear evidence of its *wave nature* (Young, 1801; Fresnel, 1815). Much later, however, the *photoelectric effect* and the *Compton effect* furnished proof of the quantum structure of light and so revived the *corpuscular theory* (Einstein, 1905; Compton, 1923). These two theories appear to be incompatible.

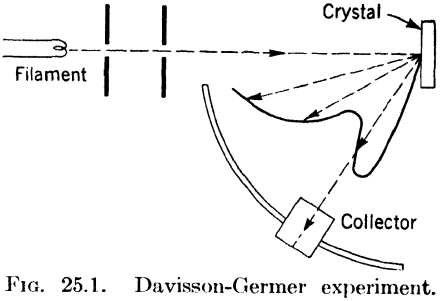


FIG. 25.1. Davisson-Germer experiment. The collector is rotated about the point of incidence on the crystal. The electron currents scattered in the various directions (broken lines) show intensities given by the curved line.

Before, however, we try to reconcile the theories of *light*, we must report an observation which, at first glance, seems to make the situation worse. The discovery of electron diffraction by Davisson and Germer (1923; final results, 1927) introduced a similar discrepancy in the description of *matter* by two opposing theories. We shall first describe the experiments and afterward give a brief outline of wave mechanics, which reconciles the corpuscular nature and the wave nature for matter as well as for light.

In a systematic investigation of "secondary electrons" produced by electron impact on metals, Davisson and Germer explored the scattering of a well-defined beam of electrons impinging on a single crystal of a metal (Fig. 25.1). In high vacuum, a beam of electrons emanating from a glowing filament is accelerated by a potential difference of the order 50 volts. Two diaphragms narrow the beam down to a thin pencil. When this beam is incident on the surface of a single crystal of nickel or another metal, many of the impinging electrons flow into the metal while others bounce back. The observer measures the intensity of the beam of electrons scattered into any direction by collecting them on a small, isolated piece of

metal which can be turned around the point of incidence on the crystal. A retarding field (not indicated on the diagram) keeps away from the collector all electrons that have lost some energy so that the electrons recorded are only those that bounce off the crystal with their full initial energy.

This experiment, simple in principle but difficult in the performance because of secondary effects, gives results that are indicated on the same diagram. The intensity of the electron beam scattered into any direction is represented by the length of the vector drawn in this direction. The

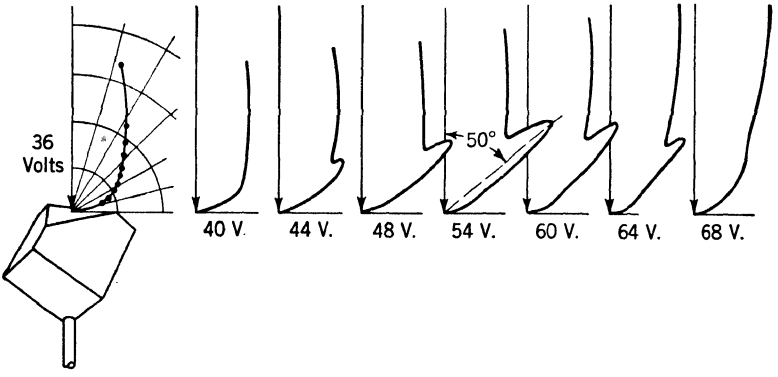


FIG. 25.2. Electron diffraction pattern for different voltages.

ends of the various vectors are connected by a line. The entirely unexpected result is that the scattered electrons do not show simply a diffuse distribution as anybody would expect; instead they show a pattern with a well-defined maximum and minimum resembling a diffraction pattern. When the accelerating potential difference is varied, the maximum mentioned shows up more or less distinctly (Fig. 25.2); it is best defined at a potential difference of 54 volts and at an angle $\phi = 50$ deg from the incident electron beam.

Let us tentatively attribute this maximum to diffraction and defer the more thorough discussion of this explanation to the next chapter. We derive the wave length indicated by the maximum as follows: Diffraction by a crystal grating, as distinct from the ruled grating, is discussed in the chapter on X Rays (Sec. 19.1*f*). There we argued that this *diffraction* is identical with an apparent *reflection* of the X ray on a crystal plane, *i.e.*, a plane rich in atoms. (Since the rays enter into the body of the crystal, this plane is not necessarily identical with the surface plane.) In the experiment described, the angle ($\phi = 50$ deg) between the incident beam, which is normal to the surface, and the diffracted beam indicates that "reflection" takes place (under an angle $\theta = 65$ deg) not from the surface but from an interior plane as shown in Fig. 25.3. From X-ray data the

grating constant of nickel in this plane is known as $d = 0.91 \times 10^{-8}$ cm. Since only one maximum shows up, we assume $n = 1$. Bragg's equation leads to a wave length $\lambda = 1.65 \times 10^{-8}$ cm. For the interpretation of this wave length, a fundamentally new idea introduced in the next chapter will be needed.

Are these patterns that resemble diffraction patterns a specific property of electrons or can they be observed for other particles, too? With great experimental effort traces of such patterns have been found for helium atoms and hydrogen molecules by Stern and his collaborators (1929). Hence, the patterns represent a more general property of very small particles.

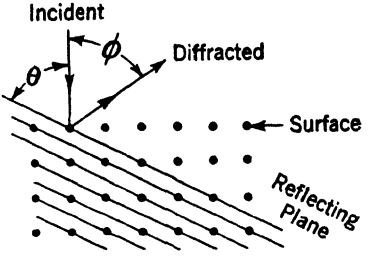


FIG. 25.3. Electron diffraction treated as Bragg reflection on a crystal plane. θ = angle between ray and crystal plane; ϕ = angle of deflection.

Another method for the observation of electron diffraction has been developed by G. P. Thomson (1927). In our discussion of X rays we mentioned the crystal powder method in which two narrow holes (not two slits)

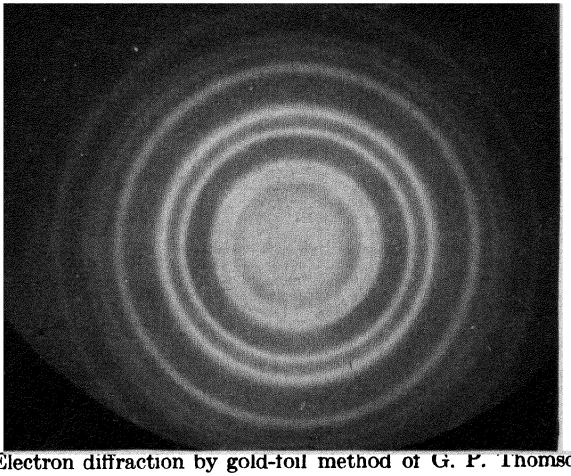


FIG. 25.4. Electron diffraction by gold-foil method of G. P. Thomson (photographic positive). This pattern is to be compared with that of X-ray diffraction by aluminum (Fig. 19.9). Gold and aluminum have the same crystal structure. (*Courtesy of G. P. Thomson.*)

limit a narrow pencil of X rays which are reflected from all the various crystal planes presented by a powder. Accordingly, in Thomson's experiment a narrow pencil of *electrons* is incident on a crystal film which is so thin that they largely pass through. The numerous, very small single crystals of which the film is composed act like the crystal powder and are responsible

for the ring-shaped diffraction pattern observed behind the crystal film. Figure 25.4 shows the diffraction of 60,000-volt electrons by a film of simple cubic crystals (KF). This picture of *electron* diffraction may be compared with that of diffraction of monochromatic *X rays* by a powder of simple cubic crystals (Fig. 19.9). The fact that each ring in one pattern has its counterpart in the other is a striking demonstration of the fact that the wave nature is common to both these rays.

From the sharp pattern observed and the known crystal constant of KF, Thomson was able to derive the wave length which must be attributed to 60,000-volt electrons in order to make the pattern explicable by diffraction. In the next chapter we shall correlate this result with de Broglie's idea of matter waves.

Since electrons are diffracted according to Bragg's law as well as X rays, a beam of electrons can be equally well used as a beam of X rays for the exploration of regular structures like crystals. However, electrons have much less penetrating power than X rays. This distinction makes the diffraction of an electron beam useful for the investigation of the structures of surfaces and complex organic molecules. Such molecules are made to travel as a beam of low density (see Sec. 4.1) which, when traversed from the side by a beam of electrons, causes their diffraction. The diffraction pattern gives evidence of regularities in the molecular structure.

A summary of the present chapter will be found at the end of Chap. 26.

CHAPTER 26

REPORT ON WAVE MECHANICS

Wave mechanics has given the solution of the discrepancy between the wave theory and the corpuscular theory of light. Moreover, it has reconciled the new discovery of electron diffraction, which is described in the preceding chapter, with the older concept of matter. This young branch of theoretical physics, which requires an advanced mathematical treatment, does not readily lend itself to an elementary discussion; nevertheless, we shall try to give an outline of the underlying ideas.

Dealing with the Compton effect, caused by X-ray or gamma-ray quanta colliding with free electrons or atoms (Sec. 19.1*j*), we associated a momentum = $h\nu/c$ with a quantum. Rays of the shortest wave lengths, *i.e.*, hard gamma rays, have the largest momenta. The relation between the wave length λ and the momentum is easily written (replacing ν/c by $1/\lambda$)

$$\text{Momentum} = \frac{h}{\lambda}$$

This relation, which is no longer new for *quanta*, was applied to *corpuscles* in a purely speculative way by L. de Broglie (1922) before Davisson and Germer discovered the pattern of scattered electrons resembling diffraction. De Broglie argued as follows:

> Determination of the stable motion of electrons in the atom introduces integers; and up to this point the only phenomena involving integers in physics were those of interference and of normal modes of vibration. This fact suggested to me the idea that electrons, too, could not be regarded simply as corpuscles, but that periodicity must be assigned to them.

Hence by analogy with the equation correlating the wave length of light and the momentum of a quantum, de Broglie introduced the hypothesis that to any corpuscle of momentum mv a wave length λ is mysteriously attributed

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

In 1922, this definition of the de Broglie wave length λ seemed remote from any direct relation to an experiment.

After the publication of the preliminary experiments of Davisson and Germer, Elsasser (1925) found that the de Broglie wave length of the

electrons incident on the nickel crystal gives a striking explanation of the complicated pattern observed among the scattered electrons (Fig. 25.2). In the preceding chapter, from the diffraction pattern observed we computed the wave length 1.65×10^{-8} cm. On the other hand, for 54-volt electrons the de Broglie wave length is computed to be 1.66×10^{-8} cm in excellent agreement with the experimental value. The simple equation correctly predicts the shift of the diffraction maxima brought about by an increase of the accelerating potential. Furthermore, a good agreement with the de Broglie wave length is reached in G. P. Thomson's diffraction pattern (Fig. 25.4). This is a surprising fruit of what appeared to be a mere mathematical speculation.

The value of de Broglie's hypothesis is evident when we find that it replaces Bohr's quantum condition defining the stationary states of the hydrogen atom. It is argued that stationary states are analogous to stationary waves in a string, which are defined by the well-known condition that a whole number of half wave lengths equals the length of the string. In order to apply this idea to the revolving electron, we first express the linear velocity v of the revolving electron (mass μ). This enables us to define the de Broglie wave length $\lambda = h/(\mu v)$. By analogy with stationary waves, the hypothesis is introduced that the only stationary orbits are those whose circumferences are multiples of the de Broglie wave lengths. The radii of these stationary orbits are computed as follows: We proceed systematically as in Bohr's theory (Sec. 15.4) using the same notation. First, we compute the orbits defined by classical mechanics

$$\frac{\mu v^2}{r} = \frac{Z\epsilon^2}{r^2} \qquad \text{or} \qquad v^2 = \frac{Z\epsilon^2}{\mu r}$$

As far as this step goes the variables v and r cover continuous ranges between 0 and ∞. From the continuous assembly of orbits so defined we select the quantized orbits, but now replacing Bohr's quantum condition by the new condition for stationary orbits

$$2\pi r = n\lambda = \frac{nh}{\mu v}$$

From the last two equations we eliminate the variable v and so express the radius r of the orbit in terms of the quantum number n and the fundamental constants

$$r = \frac{n^2 h^2}{4\pi^2 \mu Z \epsilon^2}$$

This equation describing the quantized orbits is identical with that given by Bohr. We do not need to continue the theory since the computation of the energies and the predicted frequencies of the spectral lines is identical with that given in Bohr's theory. Hence, de Broglie's quantum condition is equivalent to Bohr's quantum condition.

De Broglie's hypothesis of matter waves has been the starting point of *wave mechanics* (Schrödinger, 1926) which replaces Newtonian mechanics in the description of the motion of the lightest particles, hence, in particular, of processes within the atom. An equivalent description of such processes has been given by Heisenberg's "matrix mechanics" (1925). We shall report some results of Schrödinger's wave mechanics as well as it can briefly be done without integrating differential equations. In wave mechanics Schrödinger gives a mathematical form to de Broglie's hypothesis by introducing a "wave equation" and postulating that the stationary states are defined by integrals of this equation meeting certain conditions. Wave mechanics covers a wider ground than the older quantum theory of Bohr and Sommerfeld. This will be clear when we briefly survey the successes of the new theory. First of all, it explains electron diffraction. The spectrum of the hydrogen atom (including the effects of magnetic and electric fields and fine structure) is represented as well as by the older theory of Bohr and Sommerfeld. Wave mechanics surpasses the older theory by giving account of the *intensities* as well as the *frequencies* of the spectral lines. The spectrum of the "two-electron system," *i.e.*, the helium atom, which is not covered by Bohr's theory, is correctly predicted as far as we are able to carry through the mathematical treatment. Many general features of the spectra of more complicated atoms and of molecules are correctly described. An outstanding success of wave mechanics consists of the description of the chemical bond (Heitler and London, 1927). In our brief discussion of polar molecules (Sec. 18.5) we emphasized the fact that the Coulomb attraction between positive and negative ions is only one aspect of the chemical bond because this force fails to describe the molecules of elements like H_2. Wave mechanics, however, predicts the properties of the hydrogen molecule and thus gives the general idea of the "nonpolar bond." In nuclear theory likewise, the successes of wave mechanics are great.

It is no objection to the validity of wave mechanics that our mathematical technique fails in the solution of the more complex problems. The theory of the hydrogen atom has been carried through in great detail. But the helium atom, consisting of a nucleus and 2 electrons, offers mathematical difficulties as great as the "three-body problem" in astronomy which has been solved only for special cases by approximations. Hence, for more complicated atoms and molecules we are unable to integrate the equations. But the successes are so great that there is no doubt of the validity of the general idea.

Wave mechanics explains the great advantage of the electron microscope (Sec. 8.2*c*) over the well-known optical microscope. For both instruments the resolving power is limited by the wave nature of the light and of the electrons to about one-half of the wave length applied. This limit is for

visible light about 2.5×10^{-5} cm and for 60,000-volt electrons used in an electron microscope about 2.5×10^{-10} cm. The limiting resolving power has technically been reached many years ago for the optical microscope while the electron microscope, although surpassing the optical microscope (Fig. 8.7), is, at its present stage of development, far from its theoretical limit.

Our starting point was the discrepancy between the two opposed theories of *light*. By introducing wave mechanics, *i.e.*, by introducing the same discrepancy into the description of *particles*, we have apparently only made the situation worse. What is the significance of *waves* describing the motion of *quanta* or *particles?* The answer has been given by Born (1926). The discrepancy is intolerable when we assume that the quanta and the particles are governed by the laws of ordinary mechanics. This idea must be discarded. It is replaced by the assumption that the light waves guide the motion of quanta and likewise the de Broglie waves the motion of particles. This has the following significance. When electrons (mass μ) of a certain velocity v are incident on a nickel crystal, we predict their motion by computing the propagation of the waves of wave length $\lambda = h/\mu v$, diffracted by the nickel crystal and so forming the characteristic pattern described. The maxima indicate that here plenty of electrons will travel while the minima predict that here no or hardly any electrons will travel. Strictly speaking, the hypothesis is made that *the square of the amplitude, computed for any spot in the diffraction pattern, is proportional to the probability of finding electrons traveling through this spot.* Hence the de Broglie waves are not identical with matter, and they are not uniformly covered with matter or energy. They have only the rather abstract significance of describing a probability. When we assume a very weak electron current, say 1 electron per second, hitting the nickel crystal we may be able to notice the individual electrons (*e.g.*, by scintillations on an ideally sensitive screen) showing up here or there; by observing their distribution through many days we expect to find the same diffraction pattern that would show up all at once if the electron beam were a billion times more intense. This extreme example illustrates that we think of the waves and their diffraction pattern as existing permanently; this pattern is valid even if only once in a while it has a chance to guide an electron. We shall come back to this example when discussing the uncertainty principle.

The same idea applies to light waves guiding quanta and so producing an interference pattern. The light waves are not supposed to be uniformly covered with energy; they only provide the guidance for the quanta in which the energy is concentrated. Again, in the case of an extremely weak light ray, we think of the waves as existing permanently although only once in a while there comes a quantum that needs guidance. The

concepts of *waves*, on the one hand, and *quanta* or *particles*, on the other, are not mutually exclusive but complementary to each other. Our old warning (Sec. 11.3) still holds that the analogy between light waves and matter waves should not lead to the conclusion that light is a special kind of matter. A striking distinction is given by the fact that light in vacuum always travels with the velocity 3×10^{10} cm/sec; matter never does.

We shall better appreciate how this theory resolves the discrepancy when we consider the extreme cases of short and long waves, first light waves and next matter waves.

1. For *very short light waves* the theory predicts a diffraction pattern so narrow that practically rectilinear propagation results. This is observed for gamma rays. The distribution of the energy is far from uniform since the individual quantum carries a very large energy which, for example, may be delivered to an individual nucleus and so show up by an individual cloud-chamber track in nuclear photoelectric effect or by pair production.

2. *Very long light waves* are identical with radio waves. They show pronounced diffraction and so readily go around corners. The distribution of the energy is practically uniform all over the wave front since the individual quantum carries an energy of only, say, $1/10^8$ that of a quantum of visible light. Since no effects of these individual, exceedingly small quanta are to be expected, radio waves are in every respect satisfactorily described by Maxwell's classical theory of electromagnetic radiation.

3. *Very short matter waves* belong to all motion observed in daily life (see Prob. 26.1). The theory predicts rectilinear propagation. This agrees with the facts described by Newton's first law stating that all bodies not subjected to forces travel in straight lines. Here is the connecting link between wave mechanics and Newton's mechanics which is supposed to be only approximately valid.

We mentioned in Sec. 8.4 that Newton's mechanics breaks down for velocities approaching that of light; here we find another limitation coming into effect for the lowest velocities or, rather, the lowest momenta. Between these extremes, there is an immense range in which not the slightest deviation from Newton's mechanics has ever been observed.

Now we understand why the observation of these diffraction patterns is restricted to the lightest particles. They are the only ones that show diffraction that is just observable with X-ray technique. All heavier bodies have de Broglie wave lengths so extremely short that we fail to observe any diffraction.

4. Finally, *very long matter waves* do not occur practically. They would belong to very slow electrons which, however, cannot be handled experimentally. The fact that practically all matter waves are so much shorter

than light waves explains why electron diffraction has been observed only two and a half centuries later than the diffraction of light.

Wave mechanics has introduced a fundamentally new concept into physics by describing the motions of particles only in terms of certain *probabilities*. Here it is important that wave mechanics does not pretend at all to predict the motion of one individual particle. Going back to the example mentioned above, we consider 1 electron traveling from the filament to the nickel crystal. Into what direction will it be diffracted? The theory fails to give the answer since it makes only a statement regarding the statistical distribution of very many electrons.

The theory, however, goes one great step further. Heisenberg, in his *uncertainty principle*, argues that this is not a deficiency of our theory but that it is *fundamentally impossible* to describe the motion of the individual particle in all detail, more specifically, that it makes no sense to give an accurate statement regarding the *position and velocity* of a particle. This will be understood when we consider the problem of measurements from the "operational point of view," emphasized as a general guiding idea by Bridgman. He argues that the definition of a physical quantity makes sense only if the operations required for its measurements are fully described. How is the position of a particle measured by the ideal physicist who commands the most refined apparatus? He observes the position under a microscope. Since its resolving power is limited to about one half wave length of light he has a choice; either he uses visible light and so determines the position with only low accuracy, or he constructs a special microscope for gamma rays and so obtains an accuracy a million times higher, but still limited. But here he runs into a fundamental trouble that he cannot overcome by refinement of his apparatus. The gamma ray, which shows the *position* of the particle, knocks it out of the way by the Compton effect. Hence he loses his chance of observing the *velocity* since this requires two determinations of the positions separated by a certain time interval. So this is his dilemma: If he uses light of long wave length, then the velocity is hardly disturbed but the position is not exactly measured; if he uses light of short wave length, the situation is reversed. In any case he is fundamentally unable to measure both quantities, the position and the velocity, with unlimited accuracy. This is an outstanding example of Heisenberg's uncertainty principle.

The principle deeply affects the fundamentals of thought in physics. It shows a limitation of the principle of causality which seemed to be the foundation of all research in science. This will be evident when we compare wave mechanics with Newton's mechanics. The causal principle has found its mathematical expression in Newton's mechanics. There we learn that, when we know all positions and velocities of an isolated system of masses, we can predict its future. Heisenberg's uncertainty principle takes ex-

ception to this statement. His principle claims that this statement, although not *wrong*, is *void* because we are fundamentally unable to fulfill the condition, *i.e.*, to know accurately both the positions and the velocities; hence we shall never be able to predict the future, *e.g.*, of an individual electron or hydrogen atom, except with a certain lack of accuracy. This applies especially to individual, very light particles while the uncertainty is negligible for heavy bodies.

The physicist doing experimental research with the most refined tools *practically available* need not be worried by the uncertainty principle because the observations practically accessible to our instruments are ever so much cruder than what the theoretical physicist is able to visualize; for the time being, there is no gamma-ray microscope. But it is important to distinguish this *practical* limitation from the *fundamental* limitation that would make the gamma-ray microscope useless for our purpose. Therefore, this practical consideration does not detract from the great importance of the principle. After finding the limitations of so many apparently well-established laws of physics like Newton's mechanics and the conservation of mass, finally we come to a limitation even of the principle of causality.

This then is the outstanding result of wave mechanics. Particles as well as quanta of light do not follow the laws of ordinary mechanics but, instead, are governed by waves, which by their amplitudes predict the probability that a particle or quantum will travel in one or the other direction. For matter this effect of waves is noticeable only for the lightest particles when traveling with low velocities. For light as well as for matter there is no *alternative* between the corpuscular theory and the wave theory; instead both aspects *supplement* each other. It is a strange idea that the observations practically accessible in laboratory experiments can be predicted by a theory that is fundamentally unable to describe the fate of individual quanta or electrons, hence gives up the principle of causality as applying to these individuals and instead describes their fate only by statistical statements.

The student who is not satisfied by our vague outline of wave mechanics should realize that the thorough study of this field presupposes several years of mathematical preparation.

SUMMARY OF CHAPTERS 25 AND 26

When electrons of uniform velocity impinge on a single nickel crystal, the scattered electrons show a striking pattern resembling a diffraction pattern that varies with their velocity (Davisson-Germer experiment). Similar patterns have been discovered for rays of helium atoms and hydrogen molecules scattered by crystal surfaces.

These patterns are quantitatively explained by attributing to each

particle (mass μ, velocity v) the wave length $\lambda = h/\mu v$, called "de Broglie wave length," and applying the theory of X-ray diffraction.

De Broglie's idea of matter waves leads to Bohr's condition for the stationary states of a revolving electron when we postulate that only such orbits are stationary for which the circumferences of the circles are multiples of the de Broglie wave lengths of the electrons.

The idea of waves attributed to particles has been generalized and mathematically expressed in Schrödinger's wave mechanics. This theory covers a much wider range of atomic phenomena than the older theory of Bohr and Sommerfeld.

The dilemma between the corpuscular theory and the wave theory is solved by the hypothesis of Born who assumed that the amplitudes of matter waves indicate the probabilities for particles like electrons to travel in one or the other direction. When the electric current is exceedingly weak, only once in a while is an electron traveling; nevertheless the waves have the permanent significance of guides for electrons although they are not permanently covered with uniformly distributed mass or energy. The analogous statement applies to the relation between light waves and light quanta.

Wave mechanics makes only a statement regarding the statistics of many processes, not regarding the individual process, *e.g.*, the scattering of one individual electron from a nickel crystal. Heisenberg's uncertainty principle claims that this is not a deficiency of wave mechanics but that we are fundamentally unable to predict the fate of individual particles because we cannot measure both their positions and velocities with unlimited accuracy.

PROBLEM

26.1. *Matter waves.* Compute the de Broglie wave lengths of the following bodies: (*a*) 1-volt electron; (*b*) 10-volt electron; (*c*) electron in Bohr's first orbit; (*d*) hydrogen atom at 0°C; (*e*) 100,000-volt proton; (*f*) mass of 1 g moving at a velocity 1 cm/sec; (*g*) automobile (2 tons) at 50 mph.

SURVEY OF HISTORY AND METHOD

The theory of atoms has its origin in antiquity in the speculations of Democritus (400 B.C.) who originated the idea of an indivisible particle and called it an "atom." From Democritus to modern times there has been a great deal of theorizing on atoms without sufficient correlation to observed facts. The great step due to Dalton (1803) consisted of giving a firm basis to the atomic hypothesis by successfully applying it to the interpretation of the fundamental facts of *chemistry*. In chemistry each atom is characterized by its relative weight and its chemical properties. Because of the great importance of this idea, chemistry has developed into an independent realm of science. In the *theory of gases* (Joule, Clausius, Maxwell, initiated in 1848) the chemical properties of atoms and molecules become irrelevant, and one describes each molecule by its mass, size, and speed thus explaining the pressure and viscosity of gases. The next great step was the discovery of the *atomic structure of free electricity* (J. J. Thomson, 1897) where each electron is described by its mass and charge. (We did not elaborate that detail of the structure of spectra where a spin, *i.e.*, an angular momentum and an associated magnetic moment, is attributed to each electron.) For the emission and absorption of light the quantum structure of light (Einstein, 1905), inferred from the photoelectric effect, is equal in importance to the atomic structure of matter. These three outstanding results—the atomic structure of matter, the electronic structure of electricity, and the quantum structure of light—form the foundation on which our knowledge of the structure of individual atoms is built.

The theory of the *structure of individual atoms* is based on Rutherford's observation of the scattering of alpha particles in metal films which led him to the idea of the nuclear atom (1911). Here the nucleus is summarily described as having a certain mass (given by the atomic weight) and charge (given by the atomic number). In *Bohr's theory* (1913) detailed rules are assumed for the computation of the quantized orbits of a revolving electron and the frequencies of the spectral lines that are due to transitions between these orbits. This theory predicts in great detail the spectrum of the hydrogen atom. We described briefly the spectra of the more complicated atoms. Their analysis had started before Bohr's discovery. But this discovery led to a more profound understanding and to new experimental methods for their investigation. Later (1925) the very foundation of atomic physics was rebuilt by the discovery of wave mechanics.

In a way, quantum theory may disappoint the beginning student. In classical physics he derives satisfaction from the understanding of phenomena. For example, when taught the wave nature of light, he feels that the wealth of interference and diffraction experiments well fit into his experience derived from observing water waves. In quantum theory, however, he cannot at all judge, on the basis of his experience, whether or not a hypothesis is plausible. Bohr's hypothesis, concerned with the angular momentum of a revolving electron, bears no relation whatever to his experience. This is unavoidable in a theory that claims that the interior of the atom is not described by classical physics. Here our judgment on the value of the theory is based only on the comparison of the theoretical prediction and the observed fact.

In recent years great progress has been made in the analysis of the *nucleus*. It is typical of the nucleus that the energies involved are about a million times larger than those of chemical reactions. Here the progress in our knowledge is all bound to the development of machines providing energies of millions of electron volts, as Lawrence's cyclotron (1930). This has led to a great development in experimental technique as well as in theoretical knowledge of the nucleus. Now the nucleus can be described as built of so many particles although the forces keeping them together or making them explode are by no means known so well as the forces governing the electronic structure of atoms.

Most striking is the high development of experimental technique, which is indispensable in nuclear research. For example, in the investigation of nuclear reactions the utmost development is involved in high potential apparatus, electron tubes, vacuum chambers, large magnets, chemical analysis, Geiger counters, cloud chambers, mass spectrographs, and other devices. The teamwork of experts familiar with the various experimental methods is as indispensable for fruitful work as is the cooperation of experiment and theory.*

From this historical survey we shall try to derive a critical attitude toward the method of research. First of all we notice the interlocking of experiment and theory. In most cases, the experiment comes first, and next the simplest possible theory is devised such that its principles permit a derivation of the observed facts. In order to make clear how completely our theoretical knowledge is based on experiments, we may, however, have overstated this development by first discussing the experiment and then the theory. Historically, a great share of the progress is due to bold theories, many of them finally proving wrong but their whole assembly

*Students who wish to become acquainted not only with the facts and theories but, beyond that, with the method of research are advised to study such monographs as R. A. Millikan's book referred to in Sec. 9.1 and H. D. Smyth's book mentioned in a footnote to Sec. 23.1.

stimulating experiments. But the experimental result is considered the supreme judge of what is true.

In a way, history should make us *skeptical* by revealing mistakes, but it gives us *greater confidence* when we observe the correction of mistakes. History makes us *skeptical* because it makes manifest how limited our knowledge is. This inevitable limitation was not universally recognized in the late nineteenth century, *i.e.*, in a period in which all our physical knowledge seemed so well rounded that it could be considered to be essentially complete. Typical of this older attitude is Michelson's judgment (1894) "that most of the grand underlying principles have been firmly established . . . that the future truths of Physical Science are to be looked for in the sixth decimal place."

This was just before the great era of atomic physics, inaugurated around 1895 by the discoveries of X rays, radioactivity, and free electrons. Since that time great new discoveries have not only added to the stock of our knowledge but overthrown many of our old fundamental concepts, or, more precisely, manifested their limitations. Let us review such *revolutionary changes*. Einstein's theory of *relativity* (1905), supported by Michelson's famous experiment (1881) showed that even the grand underlying principles of Newton's mechanics are not general but valid only within a limited range. In the field of *light and radiation*, Einstein's theory of the quantum structure of light, apparently contradicting Maxwell's electromagnetic theory, gave a new interpretation to light waves (1905). Furthermore, classical electrodynamics, which, in 1894, was believed to give a full account of electricity and light, was repudiated by Bohr in his theory of the radiation from hydrogen atoms (1913). In *atomic physics* the revolution started with Thomson's discovery that the atom—contrary to the meaning of the word—can be split into parts (1897). More profound is the change in our understanding of matter due to the discovery of the transmutation of the elements, spontaneous (1902) and artificial (1934). Even the law of conservation of matter, although representing the most primitive experience, has been recognized as being only an approximation and merged with the more general law of conservation of energy (1905); annihilation of particles (1932) is now considered to be a well-established process. Our concept of the nature of matter has further been revolutionized by the discovery of the wave nature of matter (1926). This new theory describes the motion of the smallest particles by an argument in which even the principle of causality, although apparently the foundation of all research in science, is questioned (1927).

This consciousness of the limitations of our knowledge prevents us from predicting what will happen outside the range explored by experiments. Machines now under construction greatly expand the energy range of our nuclear projectiles. What fundamentally new results should we expect

from these new experiments? We admit that we cannot answer this question.

Another aspect of the inadequacy of our knowledge and foresight is the historical fact that great discoveries, forming cornerstones within modern atomic physics, have been made where nobody could anticipate them. This is true of the discoveries of X rays by Roentgen and radioactivity by Becquerel. It is just as valid for great theoretical advances like Einstein's theory of the quantum structure of light and is strikingly true for the most unexpected of all discoveries, de Broglie's idea of the wave nature of matter.

Although history makes us *skeptical* by showing the limitations of our knowledge, at the same time the history of the last half century *strengthens our confidence* in our methods. In the Introduction we called attention to the gap between experiment and theory, which in atomic physics is wider than in any other branch of physics. We mentioned the critical attitude of a distinguished chemist who as late as 1904, after a century of triumphs of the atomic hypothesis applied to chemistry, questioned the very existence of atoms stating that "the atomic hypothesis has the special advantage that it cannot be disproved because it is not accessible to an experimental test." This chemist gave up his criticism only after the discovery of positive-ray analysis which, by entirely independent experiments, confirms the atomic hypothesis and quantitatively leads to the same set of atomic weights as determined by chemical methods (Secs. 2.2 and 8.3).

This is the type of confirmation which strengthens our confidence in our theory although we must admit that, to an outsider, our elaborate structure of theories may seem more fragile than ever before. The nonscientist may be shocked by the fact that, instead of single theories like the existence of atoms, we are now building long chains of theories, each theory linked to a preceding one, the first link being the existence of atoms, the last link, say, the structure of the nucleus. We used "neutron chemistry" as an example of a long chain of experiments interlinked with theoretical interpretations (Sec. 22.7). They are all needed for explaining what happens when we place a radium sample, a piece of beryllium, and a piece of aluminum close together, in other words, when fast neutrons are causing a transmutation of aluminum nuclei.

How sure are we that these chains of theories will hold together? Our firm confidence is based on the fact that, beyond the experimental test for the individual theory, we find numerous cross checks for the entire system. For example, Planck's constant h appears in the theories of five independent experiments: (1) black-body radiation, (2) the photoelectric effect, (3) the spectrum of the hydrogen atom, (4) the continuous X-ray spectrum, (5) the excitation potential of atoms determined spectroscopi-

cally and by electron impact. All five methods lead to the identical numerical value of Planck's constant although the experiments proper, when we disregard the theory, seem unrelated. However well these chains of ideas are checked, their complication gives us a warning. We must not be surprised if theories are *modified* as was the case when Bohr's theory was gradually developed into wave mechanics. A theory may well represent a great step toward the truth, it may be useful by leading to new discoveries, yet it must not be considered to be infallible.

When surveying the vast realm of observations from the viewpoint of our theoretical knowledge, like surveying a country from the summit of a mountain, we are impressed by the fact that the perspective is thoroughly changed. The physicist who would reject the theory and simply list observed facts would be unable to organize and remember the wealth of material. Seen from the high viewpoint of the theory, however, the observations look much simpler, connecting links otherwise hidden become evident, the access to new branches hitherto unknown is discovered, the judgment of what is unimportant or important is thoroughly changed.

APPENDIX 1

UNITS

The difficulties with units experienced by the beginning student vanish when he consistently applies one system of units, *e.g.*, metric absolute units, specifically in electricity absolute electromagnetic units. He must keep in mind that some equations of physics contain constant factors that depend on the choice of the system. For example, Coulomb's law (for vacuum) when expressed in electromagnetic units contains the factor c^2, where c is the velocity of light; but when expressed in electrostatic units, it does not. Therefore, strictly speaking, with each equation (definition or law) the system of units should be specified although this is not done usually because ambiguities, like the above, are rare.

In many problems the situation is confusing because the units are given as they are read on technical instruments, or easily derived from such readings, as, for example, miles per hour, foot-candles, calories, electron volts, or kilowatt-hours. Then a safe method consists of converting all units to those of the absolute system mentioned above. The accompanying table, Electromagnetic Units, will help in doing so. It lists the electric and magnetic quantities in the order in which they are defined in the absolute electromagnetic system.

Another less comprehensive system is formed by the practical units: ampere, coulomb, volt, ohm, farad, henry. They are defined, in combination with the units joule and watt, so that a group of important equations, namely, the equations for electric circuits, can be used with these practical

Electromagnetic and Practical Units

Quantity	1 emu Equals
Magnetic pole	No practical unit
Magnetic field	No practical unit*
Electric current	10 amp
Electric charge	10 coulombs
Electromotive force	10^{-8} volt
Electric field	10^{-8} volt/cm
Resistance	10^{-9} ohm
Capacitance	10^{9} farads
Inductance	10^{-9} henry
Energy	10^{-7} joule
Power	10^{-7} watt

*"Oersted" does not belong in the practical system but is another name for emu of magnetic field.

units as well as with absolute electromagnetic units. But this limits their usefulness. One cannot apply them, for example, to the computation of a magnetic field H near a wire carrying a current I unless the equation is specifically adapted by a numerical factor. This equation, therefore, requires a statement of the units applied. The same applies to Faraday's law of induction.

The absolute system mentioned above is *convenient* in scientific papers. It is *not the only correct system* prescribed by a law of nature, because it is based on arbitrary definitions. The *mks system* is based on the meter, kilogram, and second as fundamental units and gives dimensions to the dielectric constant and permeability. It has the advantage that the practical electrical units mentioned above (ampere, coulomb, volt, ohm, farad, henry, joule, watt) are members of the system. In this system the electric field is measured in volts per meter (1 emu = 10^{-6} volt/m) and the magnetic field in ampere-turns per meter (1 emu = 10^{3} amp-turns/m).

In any case the choice of the system (with the corresponding factors adapting the equations) is arbitrary. In most problems one system or another is recommended for the sake of convenience. The student, however, should realize that the difficulty in the choice of units is not inherent in nature but is arbitrarily introduced into physics. This is evident from the fact that one can cover the whole field of physics while applying only one system of units.

In the present book we give preference to the absolute electromagnetic system. Only in Bohr's theory, following the majority of books, do we apply the electrostatic system. This means only that, in the discussion of Bohr's theory we write Coulomb's law without the factor c^2. As we are dealing only with measurements in vacuum or near vacuum, we assume throughout that the dielectric constant and the permeability are unity.

APPENDIX 2

DEMONSTRATION AND LABORATORY EXPERIMENTS

REFERENCES

HOAG, J. D. and S. A. KORFF, "Electron and Nuclear Physics," 3d ed., D. Van Nostrand Co., Inc., 1947.

HARNWELL, G. P., and J. J. LIVINGOOD, "Experimental Atomic Physics," McGraw-Hill Book Company, Inc., New York, 1933.

SUTTON, R. M., "Demonstration Experiments in Physics," McGraw-Hill Book Company, Inc., New York, 1938.

Most of the experiments listed here have been performed at the Jefferson Physical Laboratory of Harvard University; additional experiments are described in the references. This list includes only those experiments which are on the same level as the rest of the text and which require only equipment available in most laboratories.

A. LECTURE-ROOM DEMONSTRATIONS

3.1. *A force as produced by a bombardment.* The experiment is described in the text. An inexpensive two-pan balance is good enough. The motion of the pan that carries the steel plate is damped by a horizontal disk mounted under the pan, dipping into oil. The pointer of the pan is mounted upward and the force is measured by the deflection of this pointer. A shadow of the whole apparatus can well be projected by an arc lamp.

3.2. *Model of a gas.* After R. W. Pohl.

4.1. *Microprojection of Brownian motion.* After R. W. Pohl. The last two experiments are described by N. H. Black, *J. Chem. Education*, **5**, 868 (1928).

5.1. *Long free path of atoms at low pressure.* A silver bead S is fixed on a tungsten helix and evaporated in high vacuum (Fig. App. 2). The silver transmitted through a cross-shaped diaphragm D is deposited on the glass wall W and there forms a cross. The apparatus is connected with a diffusion pump.

8.1. *Low-pressure electric discharge.* This shows a cathode ray and a positive ray (Central Scientific Company, experiment of Knipp and Kunz).

8.2. *Measurement of* ϵ/μ. K. T. Bainbridge, *Am. Phys. Teacher*, **6**, 35, (1938).

8.3. *The cathode-ray oscilloscope.* Electric deflection, magnetic deflection; both deflections compensating one another.

9.1. *Stokes' law.* Fall of small steel spheres through glycerin, to be projected.

10.1. *Space-charge current and saturation current.* Hoag and Korff, pp. 103, 116.

11.1. *Photoelectric effect.* Sutton, p. 488.

14.1. *Penetrating power of alpha and/or beta particles.* Discharge of an electroscope by rays from a radium sample, Sutton, 502. For a radium D sample, see Hoag and Korff, p. 295.

15.1. *Balmer series.* A powerful discharge (0.4 amp) through a water-cooled low-pressure discharge tube is needed to project the two or three first lines of the Balmer series on the screen.

17.1. *Excitation of neon by controlled electron impact.* G. Hertz, *Z. Physik*, **22**, 18 (1924). A difficult experiment.

17.2. *Ionization of mercury vapor by controlled electron impact.* Sutton, p. 474.

17.3. *Potential drop near cathode of low-pressure discharge.* A-c discharge of Fig. 17.4, 2 in. wide, 10 in. long, pressure of air so low that the dark space in front of the cathode is 3 or 4 cm long; electrostatic voltmeter to be connected with electrodes or cathode and probe at a distance from the cathode of about 3 or 4 cm at the edge of the dark space. The probe consists of a thin metal wire sealed through the cylindrical glass wall.

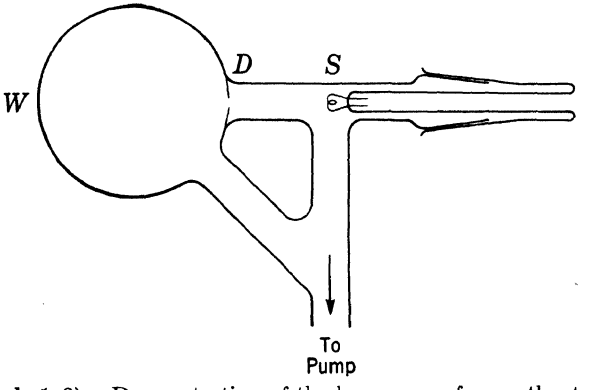


FIG. APP. 2 (scale 1:3). Demonstration of the long mean free path at low pressure. Silver atoms evaporating from the bead S form a deposit with the shape of the diaphragm D on the wall W.

17.4. *Absorption spectrum of sodium vapor.* Sutton, p. 476.

17.5. *Absorption spectrum of chlorophyll.* Sutton, p. 415.

17.6. *Fluorescence radiation of iodine vapor.* A few iodine crystals are distilled into a highly evacuated glass bulb (diameter 8 in.); the bulb is sealed off. The light from a carbon arc concentrated by a condenser lens produces intense fluorescence radiation.

17.7. *Fluorescence radiation of sodium.* R. W. Wood, *Phys. Rev.*, **56**, 1172 (1939). (W. M. Welch Co., Chicago, Ill.)

17.8. *Fluorescence radiation of kerosene.* Excited by ultraviolet light (Stokes' law). Sutton, p. 417.

17.9. *Phosphorescence.* Illumination of certain powders excites phosphorescence radiation.

17.10. *Fluorescence radiation of iodine vapor, quenched by air* (impacts of the second kind). Another bulb is prepared like the one just described; before the sealing off, 1 atm of air, made dustfree by filtering through glass wool, is admitted. This bulb shows absorption of light but no fluorescence radiation.

X rays. Sutton, p. 495. P. Kirkpatrick, *Am. J. Phys.*, **9**, 14 (1941) and **10**, 233 (1942).

19.1. *The turning-crystal spectrometer.* In the spectrometer described by Harnwell and Livingood (p. 351) the line K_α of molybdenum can be demonstrated with the help of a well-shielded Geiger counter.

21.1. *Geiger counter.* See A. L. Hughes, *Am. Phys. Teacher*, **7**, 271–292 (1939). Alpha and beta rays can be distinguished by a counter with mica window and various absorbers. The counter can be made sensitive for alpha rays only by applying a sub-

normal voltage. Beta and gamma rays can be distinguished by their widely different penetrating power.

21.2. *Range of alpha particles.* Sutton, p. 502.

21.3. *Wilson cloud chamber* for projection. Sutton, p. 504; R. Hilsch, *Physik. Z.*, **40,** 594 (1939). A weak radium D sample shows tracks of the alpha rays from polonium. For the preparation of the sample, see Hoag and Korff, p. 295.

Neutron demonstrations. Described by R. Döpel, *Physik. Z.*, **38,** 980 (1937) and C. Gerthsen, *Verhandl. deut. physik. Ges.*, 3. Reihe, 19. Jahrgang. No. 1, p. 18 (1938). A strong neutron source permits very impressive demonstrations of artificial radioactivity and uranium fission by slow or fast neutrons (J. R. Dunning).

The processes occurring in the atomic bomb and the pile are visualized in the film "Atomic Energy" (Encyclopaedia Britannica Instructional Film, No. 370).

25.1. *Electron diffraction.* Hoag and Korff, p. 63.

B. LABORATORY EXPERIMENTS

4.1. *Distinction between monatomic, diatomic, and polyatomic gases.* Determination of c_p/c_v, method of Clément and Desormes; method of Kundt's tube.

6.1. *Masses and sizes of molecules.* The student measures the density of air, gaseous and liquefied, and the viscosity of air. The density of commercial liquid air is likely to be higher than that of liquid air of the same composition as the atmosphere (density = 0.92 g/cm^3) since the commercial product contains an excess of oxygen. Viscosity of air, see F. H. Newman and V. H. L. Searle, "The General Properties of Matter," 2d ed., p. 211, The Macmillan Company, New York.

8.1. *The specific charge of ions* (Faraday constant). Measured with the copper voltameter.

8.2. *The specific charge of the electron.* K. T. Bainbridge, *Am. Phys. Teacher,* **6,** 35 (1938).

9.1. *The charge on the electron.* Millikan's oil-drop experiment. Hoag, p. 14; Millikan (see reference in Sec. 9.1).

11.1. *Photoelectric effect.* Planck's constant can be derived with an error of about 10 per cent. A. J. O'Leary, *Am. J. Phys.*, **14,** 245 (1946).

11.2. *Black-body radiation.* J. G. McCue and O. Oldenberg, *Am. Phys. Teacher,* **5,** 173 (1937).

15.1. *The Balmer series of hydrogen.* Determination of the Rydberg constant R and $h^3/\mu\epsilon^4$.

15.2. *Comparison of the spectra of light and heavy hydrogen.* A spectrograph that resolves lines 2A apart is needed.

16.1. *Sodium spectrum in emission.* In the spectrum of the carbon arc amply supplied with Na_2CO_3 the distinction between the sharp and the diffuse series is evident. Self-reversal of the yellow line is noticeable.

17.1. *Excitation potential of mercury vapor.* Method of Franck and Hertz. W. Rudy, *Am. J. Phys.*, **16,** 188 (1948). A tube built for this purpose (the grid close to the plate) may be preferable.

17.2. *Electric discharge through a low-pressure gas.* The probe method (see Sec. 17.2*a*). The discharge tube is connected with a pump; a rotary mechanical pump, if in good condition, is sufficient. The dark space should be 3 or 4 cm long.

17.3. *Sodium spectrum in absorption.* D. C. Stockbarger, *J. Optical Soc. Am.*, **30,** 362 (1940). A quartz spectrograph is needed. With a medium-size Hilger quartz spectrograph 28 members of the principal series can be photographed. The positive

crater of an arc between pure carbon electrodes supplies the continuous spectrum that serves as the background.

17.4. *Mercury spectrum in absorption.* A glass tube, 10 or 20 in. long, with quartz windows contains air and a few droplets of liquid mercury. No heating is needed. Other details the same as in the preceding experiment. For the determination of Planck's constant, see Sec. 17.4*a*.

17.5. *Raman effect.* The mercury line 4358 is scattered by CCl_4. A high-intensity (low-dispersion) glass spectrograph is needed.

For X-ray laboratory experiments see P. Kirkpatrick, *Am. Phys. Teacher*, **9**, 14 (1941) and **10**, 233 (1942).

21.1. *Range of alpha particles.* Hoag and Korff. With a polonium source and d-c amplification (*e.g.*, by the *F–P* 54) the Bragg curve (Hoag and Korff, p. 283) is measured.

21.2. *Decay of thorium emanation.* Hoag and Korff, p. 267. A simple gold-leaf electroscope may be used.

22.1. *Annihilation of a positron-electron pair* (Sec. 22.5). Coincidence counter tubes and a positron source are required.

24.1. *Cosmic rays* (Sec. 24.1). The experiment requires coincidence counter tubes.

APPENDIX 3

FUNDAMENTAL CONSTANTS*

(The last digit of any figure here given is uncertain.)

Velocity of light in vacuum c	2.99776×10^{10} cm/sec
Gas constant R	8.3144×10^{7} erg/(degree mole)
Avogadro's number N	6.023×10^{23} mole^{-1}
Boltzmann constant $k = R/N$	1.3805×10^{-16} erg/degree
Faraday constant F	96,488 coulomb/gram atom
Electronic charge ϵ	1.6020×10^{-20} emu
Specific electronic charge ϵ/μ	1.7592×10^{7} emu/g
Mass of electron μ	9.107×10^{-28} g
Mass of H^1-atom	1.6734×10^{-24} g
Mass of H^1-atom/mass of electron	1837.5
Energy of 1 ev	1.6020×10^{-12} erg
Energy equivalent of mass of unit atomic weight	931.4 Mev
Planck's constant h	6.624×10^{-27} erg sec

*Birge, R. T., *Rev. Modern Phys.*, **13,** 233 (1941). Quantities that involve the mole are listed on the chemical scale of atomic weights (O = 16.0000 for the natural mixture of isotopes). Du Mond, J. W. M. and E. R. Cohen, *Rev. Modern Phys.*, **20,** 82 (1948).

APPENDIX 4

*Periodic Table of Elements**

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
I	1 H 1.0080										2 He 4.003
II	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.01	7 N 14.008	8 O 16.000	9 F 19.00				10 Ne 20.183
III	11 Na 22.994	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457				18 A 39.944
IV	19K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916				36 Kr 83.7
V	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	
	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92				54 Xe 131.3
VI	55 Cs 132.91	56 Ba 137.36	57 to 71 Rare earths†	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	
	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210	85 At				86 Rn 222
VII	87 Fa	88 Ra 226.05	89 Ac 227.05	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np	94 Pu	95 Am	96 Cm	

*Atomic weights based on 0 = 16.000.

†Rare earths:

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
138.92	140.13	140.92	144.27		150.43	152.0	156.9	159.2	162.46	164.94	167.2	169.4	173.04	174.99

APPENDIX 5

STABLE ISOTOPES OF LIGHT ELEMENTS

Isotope	Atomic weight*	Per cent abundance
${}_0n^1$	1.00894	100
${}_1H^1$	1.00813	99.98
${}_1H^2$	2.01473	0.02
${}_2He^3$	3.01711	10^{-5}
${}_2He^4$	4.00389	100
${}_3Li^6$	6.01684	7.9
${}_3Li^7$	7.01818	92.1
${}_4Be^9$	9.01494	100
${}_5B^{10}$	10.01633	18.4
${}_5B^{11}$	11.01295	81.6
${}_6C^{12}$	12.00386	98.9
${}_6C^{13}$	13.00766	1.1
${}_7N^{14}$	14.00756	99.62
${}_7N^{15}$	15.00495	0.38
${}_8O^{16}$	16.00000	99.76
${}_8O^{17}$	17.00449	0.04
${}_8O^{18}$	18.00469	0.20
${}_9F^{19}$	19.00452	100
${}_{10}Ne^{20}$	19.99896	90.0
${}_{10}Ne^{21}$	20.99968	0.27
${}_{10}Ne^{22}$	21.99864	9.73
${}_{11}Na^{23}$	22.9968	100
${}_{12}Mg^{24}$	23.99189	77.4
${}_{12}Mg^{25}$	24.99277	11.5
${}_{12}Mg^{26}$	25.99062	11.1
${}_{13}Al^{27}$	26.9916	100
${}_{14}Si^{28}$	27.9866	89.6
${}_{14}Si^{29}$	28.9864	6.2
${}_{14}Si^{30}$	29.9832	4.2
${}_{15}P^{31}$	30.9843	100

* Based on $O^{16} = 16.00000$.

APPENDIX 6

MEASUREMENT OF NUCLEAR CHARGES BY SCATTERING OF ALPHA PARTICLES

We shall first discuss the deflection of one alpha particle passing near a highly charged, heavy nucleus and then the probabilities of the various deflections of many particles incident on a film of some heavy element.

An alpha particle, if undeflected, would pass a nucleus at the smallest distance p (Fig. App. 6). The nucleus is supposed to be so heavy that no appreciable kinetic energy is transferred to it. The computation of the deflection is a problem of mechanics, well known to the astronomer because it is the same as the computation of the deflection of a comet passing near the sun. The angle of deflection θ is determined on the basis of the same fundamental equations that describe planetary motion. The result is

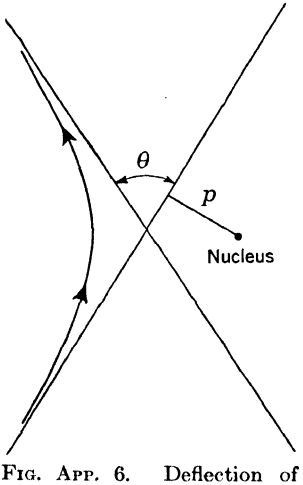


FIG. APP. 6. Deflection of alpha particle by a heavy nucleus.

$$\tan\frac{\theta}{2} = \frac{2Z\epsilon^2}{\mu v^2 p} \qquad (14.1)$$

where θ = angle between incoming and outgoing directions

2ϵ, μ, v = charge, mass, and velocity of alpha particle

$Z\epsilon$ = charge of nucleus

p = shortest distance between nucleus and incoming direction

Next we want to find out how probable the various approaches (measured by the distances p) are. Since most particles are observed as undeflected, we infer that deflections by two or more nuclei may be disregarded. If the film presents n atoms per square centimeter to the incoming alpha ray, we may attribute to each nucleus an area of $1/n$. In order to apply the above equation, we must find out how many particles are passing at a certain distance. As no two particles are passing at exactly the same distance, we must allow a small margin and ask how many particles are passing at distances between p and $p + dp$; in other words, how many

are hitting a ring of the area $2\pi p\,dp$ described about the nucleus. Assuming N alpha particles per square centimeter per second, we compute as follows:

Area attributed to each nucleus	$1/n$
Number per second incident on area	N/n
Number per second incident on ring $2\pi p\,dp$	$2\pi p\,dp\,N$
Fraction of all particles incident on ring $=$	$\begin{cases} 2\pi p\,dp\,N/(N/n) \\ 2\pi p\,dp\,n \end{cases}$

This fraction computed for one nucleus is identical with the fraction of all particles passing at distances between p and $p + dp$ from any nucleus.

In order to introduce observable quantities, we want to compute the fraction F of all particles deflected by angles between θ and $\theta + d\theta$. For this purpose, applying Eq. (14.1), we introduce θ instead of p into the last equation and $d\theta$ instead of dp. Here we need the derivative

$$\frac{dp}{d\theta} = -\frac{Z\epsilon^2}{2\mu v^2}\frac{1}{\sin^2(\theta/2)}$$

We are not interested in the negative sign since the observer does not differentiate between positive or negative values of $d\theta$. The final result is

$$F = \frac{4\pi n Z^2\epsilon^4}{(\mu v^2)^2 \tan(\theta/2)\sin^2(\theta/2)}d\theta$$

This equation indicates to the experimenter what he must measure. For various angles θ (with an arbitrarily selected small margin $d\theta$) the number of deflected particles is counted and divided by the total number of particles constituting the alpha ray. This ratio represents the fraction F. The number n of metal atoms per square centimeter of the foil is computed from the thickness, the density of the metal, and the mass of each atom. The properties of the alpha particle, *i.e.*, 2ϵ, μ, and v, are known (see Sec. 14.1). Thus, as the only unknown in the last equation, the nuclear charge $Z\epsilon$ is computed.

APPENDIX 7

EQUIVALENCE OF MASS AND ENERGY

Because of its great importance, we want to give a derivation of Einstein's law of the equivalence of mass and energy. We largely follow the book of M. Born, "Einstein's Theory of Relativity," E. P. Dutton & Co., New York. We start from a simple problem of mechanics, the *firing and stopping of a bullet.* Presupposing that light consists of quanta (Chap. 11) and that each quantum is endowed with a momentum, we shall apply essentially the same argument to the *emission and absorption of a quantum.*

A railroad car is standing still, able to move without friction. At its front wall a gun (mass M) is rigidly mounted and aimed toward the rear wall where, at the distance L, the bullet is intercepted by a target of the same mass M, rigidly mounted in the car, too. It is convenient to assume that the mass of the car proper is negligible as compared with the mass $2M$ of the gun and target. When the gun shoots the bullet (mass m, velocity v), by the reaction the whole car is given a velocity V, easily computed from the conservation of momentum $2MV = mv$. As soon as the bullet hits the rear wall, it transfers its momentum mv to the car. The momentum so given to the car is just equal and opposite its momentum $2MV$; hence the car stops again. By what distance is the car shifted? It has moved with the velocity $V = mv/2M$ during the time of flight of the bullet (L/v); hence the shift of the car equals $LV/v = Lm/2M$. (In the expression for the time of flight we disregard the fact that the bullet does not quite cover the full length of the car since, during the same time, the car itself is moving in the opposite direction.)

What has happened to the center of gravity of the car? Before the shot, because of the symmetrical distribution of the masses, the center was right in the middle between the gun and the target. After the shot, the car has been shifted by the distance d, furthermore the gun has lost and the target gained the mass m. The student is asked to compute the new position of the center of gravity as seen from an outside observer. The result is that the center has remained unchanged. We could have predicted this simple result because a general theorem of mechanics (simplified for our special case) states: The center of gravity (or mass center) of a system that is at rest to begin with will remain at rest as long as no external forces are acting on the system.

Now we apply the same argument to the flight of a quantum of light

(energy $E = h\nu$; momentum $= h\nu/c = E/c$). Here we *presuppose* the theorem of mechanics just confirmed by our computation; as the unknown we compute the mass which the energy E transfers from the emitter to the absorber. In a closed container (Fig. App. 7) of negligible mass, which is at rest with respect to the observer, two *equal* bodies, A and B, (each of mass M) are rigidly mounted at the mutual distance L, both able to emit and absorb light. When A emits a quantum of energy E in the direction toward B, the whole rigid body suffers a reaction since the quantum carries the momentum E/c. Thus the container is given a veloc-

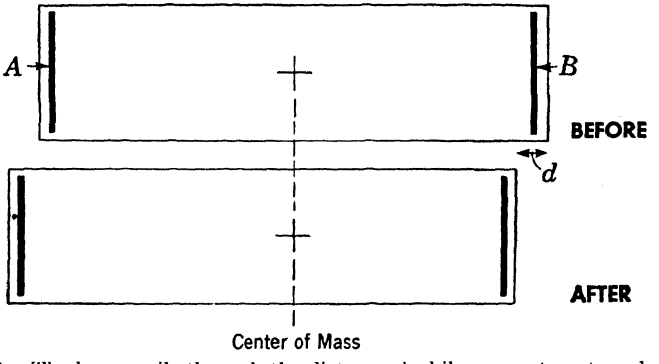


FIG. APP. 7. The box recoils through the distance d while a quantum travels along the box.

ity V, computed from the law of conservation of momentum $2MV = E/c$. During the time of flight L/c of the quantum, the container moves with the velocity V. When the quantum is absorbed by the body B it gives just the opposite momentum to the container; hence, now it stops. During the time of flight it has been shifted by the distance d = time of flight of bullet $\times$ velocity of container $= LE/2c^2M$. All this is seen by the observer who is at rest, outside the container.

The theorem of mechanics referred to above states that the center of gravity of the system has not been shifted by the emission and absorption of the quantum. To start with, this center was exactly midway between the bodies A and B because these are assumed to have equal masses at the beginning. Although the center of gravity remains unchanged, finally both bodies are shifted by the distance d. Hence we are forced to assume that the transfer of the quantum of energy E has taken away mass from the body A and has given it to the body B. Thus we conclude that the addition of energy contributes to the mass of a body.

We compute the mass equivalent μ of the energy E of the quantum on the basis of the same theorem of mechanics; μ must be such that the center of gravity of the system remains unchanged with respect to the

observer; hence it is shifted by the distance d with respect to the bodies A and B. We express this shift by the equation:

$$(M - \mu)\left(\frac{L}{2} + d\right) = (M + \mu)\left(\frac{L}{2} - d\right)$$

As everything else is known, we compute the only unknown μ:

$$\mu = \frac{2Md}{L}$$

and, introducing the above value of d,

$$\mu = \frac{E}{c^2}$$

This is the amount by which the mass of any body increases when it absorbs the energy E.

This computation is special in that it attributes a mass to energy of *light*. We generalize it by considering that in the body A or B a ready exchange takes place between light and other forms of energy. For example, in the body A, before the emission, the energy E possibly consisted of kinetic energy of two atoms which, in an inelastic collision, was changed to energy of excitation of one of the atoms. Such a change would not affect the position of the body A. Hence, our argument is not specific for light but applies to any form of energy.

Einstein's theory of relativity enters only into the last step of the present argument. When saying that the quantum travels with the velocity of light c, we failed to specify the frame of reference with respect to which the velocity is measured. Since Huygens (1678) up to the time of Einstein (1905) it was assumed that light, being a wave motion, must be carried by a medium invented for this purpose and called "ether." Since the container was assumed to travel through the ether with a certain velocity, before Einstein one would have taken into account the velocity of the box with respect to the ether, called the "ether wind," and so would have obtained a more complicated final equation. Einstein established as a principle that the velocity of light is independent of the relative velocity of the observer and the source of light. Therefore, it is basically impossible to measure the velocity of light with respect to the hypothetical ether; in other words, there exists no effect that would be affected by the motion of the apparatus with respect to the ether. Hence the equation mass $= E/c^2$ does not depend upon the motion of our box with respect to the ether and represents the general law.

*

ANSWERS

1.1. (*a*) N_2 and NO; (*b*) 1 volume nitrogen + 2 volumes oxygen = 1 volume nitrogen tetroxide.

2.1. NaCl.

2.2. Analysis by weight leads to CH_2 or C_2H_4 etc. The density leads to the molecular weight 28, hence the formula C_2H_4.

3.1. 0.655 atm.

3.2. 23.6 per cent oxygen, 76.4 per cent nitrogen.

3.3. 1.082 metric ton.

3.4. $F = 2mn\sqrt{2gh}$; $h = 48.0$ cm.

3.5. $F = nmc$.

4.1. 420 cm/sec.

4.2. $R = 8.32 \times 10^7$ erg/(mole degree); $c_v = 2.98$ cal/(mole degree).

5.1. $\eta = 1.82 \times 10^{-4}$ g cm^{-1} sec^{-1}.

6.1. $c = 4.13 \times 10^4$ cm/sec; $L = 8.55 \times 10^{-6}$ cm; 4.8×10^9 collisions per sec; $n = 0.874 \times 10^{19}$ cm^{-3}; $2r = 6.54 \times 10^{-8}$ cm; $\mu = 2.04 \times 10^{-22}$ g; $N = 1.96 \times 10^{23}$ mole^{-1}.

6.2. $n = 9.2 \times 10^8$; $L = 6.9 \times 10^4$ cm; $t = 1.38$ sec.

6.3. (*a*) $\Delta n = -n\ \Delta h\ gm/RT$; (*c*) $\log_e n = -hgm/RT + \log_e C$; (*d*) $\log_e C = \log_e n_0$; $n = n_0 \exp(-hgm/RT)$.

8.1. 3.02 g.

8.2. 28.7 min; ½ liter.

8.3. (*a*) $v \times \Delta t$; (*b*) $nv\ \Delta t$; (*c*) $i = \epsilon nv$; (*d*) force on length $L = \epsilon nv \times L \times H$; (*e*) ϵvH.

8.4. $\epsilon/\mu = 1.759 \times 10^7$ emu/g.

8.5. $v = 5.93 \times 10^8$ cm/sec; $R = 11.3$ cm.

8.6. 18.35 oersteds.

8.7. 419 emu/g.

8.8. (*a*) $y = \epsilon Vl^2/2d\mu v^2$; (*b*) $x = \epsilon Hl^2/2\mu v$; (*c*) $x^2 = y \times \epsilon l^2 dH^2/2\mu V$; (*d*) the fast electrons suffer smaller deflections than the slow ones; (*e*) $\epsilon/\mu = 419$ emu/g; presumably singly charged sodium ions.

8.9. 1.335×10^{20} g/year = 1.335×10^{14} metric tons/year.

9.1. 3.18×10^{-20} emu.

9.2. $v = 3.02 \times 10^{-6}$ cm/sec.

9.3. $t = 1.85 \times 10^{-9}$ sec; $v = 6.50 \times 10^8$ cm/sec; kinetic energy = 192.2×10^{-12} erg.

9.4. (*a*) 62.2×10^7 cm/sec; 1.762×10^{-10} erg; 110 ev; (*b*) 1.45×10^7 cm/sec; same energy; (*c*) 0.304×10^7 cm/sec; same energy; (*d*) 0.325×10^7; 3.524×10^{-10} erg; 220 ev.

9.5. 1.835×10^5 cm/sec, from Eq. (3.4); 5.63×10^{-14} erg = 0.0352 ev.

9.6. 1 kcal/mole = 0.0434 ev/molecule = 0.695×10^{-16} erg/molecule.

9.7. Force = 1.745×10^{-8} dyne.

9.8. 0.264×10^{-8} per cent

9.9. 2.3×10^{-7} per cent; in the atomic weight of hydrogen (Appendix 5) the last digit represents 10^{-3} per cent.

9.10. 26.6 Mev.

9.11. 1.770×10^{20} ergs $= 4.95 \times 10^{6}$ kwhr; \$99,000.

11.1. (*a*) 6.62×10^{-27} erg sec; (*b*) 1.74 ev; (*c*) 7110A.

11.2. 2.13×10^{18} quanta.

11.3. 2.43×10^{12} quanta per cm^2 and sec.

11.4. 1,710 quanta per sec.

14.1 (*a*) $1/2\ m_1u_1^2 = 1/2\ m_1v_1^2 + 1/2\ m_2v_2^2$; (*b*) $m_1u_1 = m_1v_1 + m_2v_2$; (*c*) $v_1 = u_1 \times (m_1 - m_2)/(m_1 + m_2)$; $v_2 = u_1 \times 2m_1/(m_1 + m_2)$; (*d*) (1) $v_1 = 0$, $v_2 = u_1$; (2) $v_1 = -u_1$ v_2 negligible; (3) $v_1 = u_1$; $v_2 = 2u_1$.

14.2. Kinetic energy of alpha particle = potential energy ($2Ze^2/r$) of the alpha particle with respect to the nucleus; $r = 3.0 \times 10^{-12}$ cm.

15.1. (*a*) $\Delta W_p = mg(h_2 - h_1)$ where g = gravitational acceleration. (*b*) The potential energy but not the kinetic energy can be negative. (*c*) $g = GM/r_e^2$. (*d*) $W_p = (-GmM/r + GmM/r_e)$; GmR/r_e. (*e*) $W_p = -GmM/r$.

15.2. $v = 1.118 \times 10^{6}$ cm/sec; velocity of H atoms $= 0.258 \times 10^{6}$ cm/sec.

15.3. (*a*) $\Delta W = GmM\ \Delta r/r^2$; (*d*) $W = GmM\int_{r_1}^{r_2} \frac{dr}{r^2} = GmM\left[-\frac{1}{r}\right]_{r_1}^{r_2}$

$= GmM\left(-\frac{1}{r_2} + \frac{1}{r_1}\right)$.

15.4. (*a*) (I) $\mu r\omega^2 = Ze^2/(r + R)^2$

(II) $MR\omega^2 = Ze^2/(r + R)^2$

(III) $\mu r^2\omega + MR^2\omega = nh/2\pi$

(*b*) $\mu r^3\omega^2(1 + \mu/M)^2 = Ze^2$

$\mu r^2\omega(1 + \mu/M) = nh/2\pi$

(*c*) $r = n^2h^2/4\pi^2\mu Ze^2$; (*d*) $v = 2\pi Ze^2/nh(1 + \mu/M)$; (*e*) $W = W_k + W_p = \frac{1}{2}\mu v^2 + \frac{1}{2}MV^2 - Ze^2/(r + R)$; (*f*) Introducing $R = r\mu/M$ and $V = vR/r = v\mu/M$, $W = \frac{1}{2}\mu v^2(1 + \mu/M) - Ze^2/r(1 + \mu/M)$; (*g*) $\nu_{\text{th}} = \frac{2\pi^2\mu MZ^2e^4}{h^3(\mu + M)} \Big/ \left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$; (*h*) $R_{\text{H}}/R_{\text{He}} = \left(1 + \frac{\mu}{M_{\text{He}}}\right) \Big/ \left(1 + \frac{\mu}{M_{\text{H}}}\right)$.

Theoretical ratio $= 1 - 0.000407$; observed ratio $= 1 - 0.000408$.

15.5. 1,640; 1,215; 1,085; 1,025 for He^+; 1,215; 1,025 for H.

15.6. Gravitational force $= 1.007 \times 10^{-58}/r^2$; Coulomb force $= 23.1 = 10^{-20}/r^2$.

15.7. 10.16, 12.06, 12.76, 13.08 ev.

15.8. 21.65×10^{-12} erg $= 13.58$ ev.

15.9. 2.38A.

15.10 79,000°K; because of the velocity distribution.

17.1. 4.32 ev.

17.2. 746 and 1,076A.

17.3. 12,390 ev $\times$ A.

17.4. (*a*) $u^2 = v^2 + V^2 + 2W/M$; $u = v + V$; (*b*) $Mu^2/2 > 2W$.

17.5. (*a*) $\Delta I = -\alpha\ \Delta l\ I$; (*c*) $\sum_{I_0}^{I_1} \frac{\Delta I}{I} = -\sum_{0}^{l_1} \alpha\ \Delta l$; (*d*) $\log_e (I_1/I_0) = -\alpha l_1$;

(*e*) $I_1 = I_0e^{-\alpha l_1}$.

19.1. (*b*) $\frac{h^2}{\lambda^2} + \frac{h^2}{\lambda'^2} - \frac{2h^2}{\lambda\lambda'}\cos\phi = m^2v^2$;

(*c*) $\frac{2h^2}{\lambda\lambda'}(1 - \cos\phi) = m^2v^2\left(1 - \frac{v^2}{2c^2}\right)$;

(*d*) Eq. (IV) is conveniently rewritten as $hc\frac{\lambda' - \lambda}{\lambda\lambda'} = \frac{mv^2}{2}$ and divided into the last equation (neglecting $v^2/2c^2$). Result: $\frac{h(1 - \cos\phi)}{c(\lambda - \lambda')} = \mu$; $\lambda - \lambda' = \frac{h}{\mu c}(1 - \cos\phi)$.

19.2. (*a*) (1) $2h\nu/c = Mc$; (2) $nA2h\nu/c = nAMC$; (3) Consider that nAC = acceleration; hence, $nAMC$ = force. (*b*) (1) $nA\tau h\nu$; (2) volume (cross section × distance traveled during τ) = $Ac\tau$; density = energy/volume = $nh\nu/c$. (*c*) Force = 6.77×10^{-7} dyne = 6.90×10^{-10} g-weight.

19.3. (*a*) 0.0113; (*b*) 1.44×10^{-6}; (*c*) density of Hg = 20.06×10^{-3} g/cm³; $I/I^0 = 0.718$; (*d*) density of Hg = 3.88×10^{-3} g/cm³; $I/I_0 = 0.682$.

19.4. 9.15 sec.

19.5. $\sin\beta = 1 - \delta$; $\sin\theta = \cos\beta = \sqrt{1 - \sin^2\beta} = \sqrt[4]{2\delta} = 0.00181$ radian.

19.6. 93.3; 87.3; 77.8; 1.54; 2.38×10^{-2}; 5.6×10^{-6} per cent; 12.3 cm aluminum.

19.7. $\lambda = 1.541$A; $\theta_2 = 33°10'$.

19.8. 0.1650A; 1°40′.

19.9. λ': 0.707, 0.714, 0.731, 0.748; θ': 6°42′, 6°46′, 6°56′, 7°6′ in agreement with Fig. 19.12.

20.1. 2,964; 2,540; 456; 434 volts.

20.2. $\epsilon/\mu = 4.19 \times 10^2$ emu/g; atomic weight = 23; Na^+.

20.3. Li isotopes separated by 0.82 cm, resolved; Hg isotopes by 0.025 cm, not resolved.

20.4. (*a*) 7.27; (*b*) 14.48; (*c*) 7.21 Mev.

20.5. 931 Mev.

20.6. 25.0×10^9 kwhr.

20.7. 16.0044.

20.8. ΔW = torque × $\Delta\alpha = mlH \sin\alpha\, \Delta\alpha$; $W = mlH\int_0^{2\pi} \sin\alpha\, d\alpha =$

$$mlH\Big[1 - \cos\alpha\Big]_0^{2\pi} = 2mlH\Big[\sin^2\alpha/2\Big]_0^{2\pi} = 2mlH.$$

21.1. 6.13×10^{23} atoms/gram atom.

21.2. $T' = (\log_e 2)/\lambda$; $T'' = (\log_e 1.111)/\lambda$.

21.3. $\Delta N = -\lambda N\, \Delta t$; $N_1 = N_0 e^{-\lambda t_1}$.

21.4. 6.5×10^8 years.

21.5. (*a*) 1.383×10^{-9} per cent; (*b*) 3.69×10^7 atoms per sec; (*c*) 12.2 per cent.

21.6. (*a*) $v_1 = 3u_1/5$; $v_2 = 8u_1/5$; (*b*) $v_1 = 0$; $v_2 = u_1$; (*c*) $v_1 = -3u_1/5$; $v_2 = 2u_1/8$.

21.7. 6.47×10^{-6} g.

21.8. $\lambda = 1.30 \times 10^{-5}$ sec^{-1}; $N = 2.84 \times 10^{10}$; mass = 1.13×10^{-12} g.

21.9. 7 alpha and 4 beta particles.

21.10. Average energy 187,000 ev; $\lambda = 6.63 \times 10^{-10}$ cm.

22.1. (*a*) $h\nu = h\nu' + \mu v^2/2$; $h\nu/c = -h\nu'/c + \mu v$; (*b*) $2h\nu/c = \mu(v + v^2/2c)$; (*c*) $h\nu = (\mu c/2) \times (v + v^2/2c)$; (*d*) $h\nu = 55$ Mev for hydrogen and 89 Mev for nitrogen.

22.2. $m_1 = 1.16 \times$ mass of proton; $u_1 = 3.1 \times 10^9$ cm/sec.

22.3. (*a*) 2.15 Mev; (*b*) 1.00891.

22.4. $E = -5.8$ Mev.

22.5. 17.2 Mev.

22.6. 158 Mev.

22.7. (*a*) $v_c = v_p m/(m + M)$; (*c*) $1/2\ mv_p^2\ M/(m + M)$; (*d*) 0.109 Mev.

22.8. (*a*) 4.13 Mev; (*b*) 9.05 Mev.

22.9. (*a*) 2.73×10^{-8} sec; (*b*) 5.46×10^{-8} sec; (*c*) 5.43×10^{-8} sec.

22.10. (*a*) ${}_6C^{13}$ stable; (*b*) ${}_6C^{12}$ stable; (*c*) ${}_9F^{17} \rightarrow {}_{+1}e^0 + {}_8O^{17}$; (*d*) ${}_{10}Ne^{20}$ stable; (*e*) ${}_4Be^7$

$\rightarrow {}_{+1}e^0 + {}_3Li^7$; (*f*) ${}_3Li^7$ stable; (*g*) ${}_7N^{13} \rightarrow {}_{+1}e^0 + {}_6C^{13}$; (*h*) ${}_1H^1$ stable; (*i*) ${}_3Li^7$ stable; (*j*) ${}_9F^{20} \rightarrow {}_{-1}e^0 + {}_{10}Ne^{20}$; (*k*) ${}_6C^{14} \rightarrow {}_{-1}e^0 + {}_7N^{14}$; (*l*) ${}_{13}Al^{28} \rightarrow {}_{-1}e^0 + {}_{14}Si^{28}$; (*m*) ${}_{15}P^{30} \rightarrow {}_{+1}e^0 + {}_{14}Si^{30}$.

23.1. 9.3×10^5 kw.

23.2. (*a*) $4\pi r^2 \sigma T^4 \, \Delta t = \frac{4}{3}\pi r^3 \delta s \, \Delta T$ (σ = Stefan-Boltzmann constant, δ = density; s = specific heat); (*b*) $\Delta t = 1.06 \times 10^7$ sec = 0.34 year.

24.1. 22.3 cm.

26.1. (*a*) 12.25×10^{-8} cm; (*b*) 3.86×10^{-8} cm; (*c*) 3.32×10^{-8} cm; (*d*) 2.15×10^{-8} cm; (*e*) 9.05×10^{-12} cm; (*f*) 6.62×10^{-27} cm; (*g*) 1.5×10^{-36} cm.

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