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THE STRUCTURE AND PROPERTIES OF MATTER

BY

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Professor of Chemistry, Indiana University

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PREFACE

The day when chemistry dealt with atoms and molecules as the ultimate divisions of matter is past. The chemist of today must look beyond these forms to consider the nature and even the structures of the electrons, protons, neutrons, positrons, etc., which compose them. In whatever field of chemistry one is engaged, or is most interested, knowledge of the structure of matter is becoming more and more essential for an understanding of the work that is done and the books that are written in the chosen field. This knowledge has been revealed very rapidly during the last twenty years. The physical and mathematical concepts of electrons, atoms, and matter in general attending this growth of knowledge have risen from many sources. They have followed one another in rapid succession and some of them have been associated with radically different points of view; for these reasons, therefore, many of the more recent theories appear formidable, indeed, to those of us who are unacquainted with the facts and developments upon which they are based.

Although science has been enriched enormously, during these early years of the twentieth century, in the physics and chemistry of matter, many chemists in industry and many students of chemistry in the universities and colleges do not find all this newly acquired information in an available form. It must be admitted that, until recently, the usual courses of instruction for students of chemistry did not provide for the introduction of much of this new material. In the universities, there are courses for students who specialize in certain phases of physical chemistry, which deal with many of the physical and mathematical theories of matter and energy. Specialists in this field, however, constitute but a small fraction of the vast number of students pursuing the study of chemistry. Recently, many schools have added courses to their programs in chemistry for the purpose of aiding the great majority of their students in interpreting this material and in applying the most important principles to

chemical problems. This book is written for use in such courses and for the use of the individual student, or the chemist in industry, who desires an interpretation of physical and mathematical concepts of matter written from the point of view of his own subject.

It is not the author's purpose, therefore, to produce a treatise for the physical chemist who is well versed in mathematical and physical theory nor to compile a critical review of the work which has been done. Nor is it his purpose to write a "popular" book on the subject for the person without a knowledge even of general chemistry and elementary physics. Instead, he has attempted to interpret from the chemist's point of view some of the facts and opinions concerning matter as they have been discovered or suggested from the time of Aristotle to the time of Bohr and Schrödinger.

A discussion of this kind must necessarily include many theories long since discarded or at least considerably revised. The inclusion of such material, however, is fully justified. Few, if any, of the ideas which have developed during the history of the physical sciences have proved permanent in their entirety, yet most of them have contained certain elements of truth. It is not sufficient to possess an acquaintance with the theories of the present. One must remember that an accepted theory of today may be an obsolete theory of tomorrow. The fact that a certain idea is accepted at present does not argue for its consideration at the expense of ideas which, perhaps, it has supplanted. For this reason, an acquaintance with one theory may be no more important than acquaintance with another in preparing oneself for an understanding of the work and the theories that will be produced in the future.

Because of the elementary character and brevity of the treatment presented in this book, many topics that may appear very important to some readers are omitted. Readers already familiar with certain portions of the field may find the treatment of some of the subjects incomplete. The point of view throughout is as elementary in character as adherence to fact and clarity have permitted. For this reason, the student is asked not to regard the book as a means of attaining mastery of the subject with which it deals. Having stated the purpose of the book, however,

the author feels that no apology is necessary for these shortcomings, all of which are admitted. He hopes that many who read it as a preliminary study will find themselves prepared to investigate some of the many excellent, although highly specialized, books in the field.

The need for a book of this kind has been observed by the author during several years of experience with advanced as well as elementary students of chemistry. Many excellent books dealing with selected topics, such as radioactivity or isotopes, may be recommended to students who are seeking sources of information. Such books, however, do not fill the need completely, and it became apparent that a single treatment which revealed more of the relationships of the individual subjects would be desirable. The book now offered by the author is the product of his contacts with students in a course that he has taught for several years at Indiana University. Lectures have taken the place of textbook in this course, since no one book was found to be sufficient or suitable. These lectures have been revised and extended to make this book.

To the students of this course the author wishes to express his appreciation of their keen interest in discoveries concerning the structure of matter, for it was their interest that encouraged him to undertake this work. He wishes to thank Dr. Robert C. Gore and Dr. John S. Peake for the many services that they have rendered at various times during the preparation of the manuscript. He also wishes to express his gratitude to Professors Victor K. La Mer, Eric Jette, Linus Pauling, Samuel Goudsmit, and A. H. Compton and to the Gaertner Scientific Corporation for permission to use certain drawings and photographs.

H. T. BRISCOE.

INDIANA UNIVERSITY,
March, 1935.

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THE STRUCTURE AND PROPERTIES OF MATTER

CHAPTER I

EARLY HISTORY OF THE ATOMIC CONCEPT

Introduction

This book deals with the forms of matter. These are myriad in number. But our present interest lies not in the larger forms which can be perceived by the senses but in the ultimate divisions which are the units of the more complex structures of matter. Our task is to organize and to interpret the information that we find available concerning the nature, and particularly the structural nature, of these smallest divisions.

The task is not easy. First of all, the lack of a satisfactory definition of matter is a handicap. Of course, we might state that "matter is that which occupies space and possesses mass." But what is space other than a convenient creation of our imagination, by means of which we locate different forms of matter with reference to one another? Even if matter is that which occupies space, what does such a statement tell us about matter? Again, we may say that matter is "that which possesses mass." But this definition, also, only postpones the answer to the question. At once, we are faced with the problem of defining mass, and this we usually do with the statement that "mass represents the quantity of matter" in a given body. Perhaps we should not expect to be able to say what matter is; any definition that we might give must be based upon the assumption that there is something more fundamental than matter itself and in terms of which matter can be described. So long as we have no knowledge of anything more fundamental in character than

matter itself, we must despair of being able to quote a satisfactory definition. It is not difficult to convince ourselves, or others, that matter is a reality. But it is impossible to go beyond this statement in explaining the character of the reality. Natural and experimental facts tell a great deal about the behavior of matter but very little about what it is.

In the second place, our study is difficult because of the multiplicity of ideas concerning the structure of matter and the kinds of ultimate units into which different forms of matter may be divided. We are faced with the problem of determining which of the divisions is the real unit. At one time, the question of the atomicity of matter as opposed to its continuously divisible character was the paramount issue. John Dalton appeared to have answered sufficiently this question in favor of the atomic concept. Then came the necessity of distinguishing between two very small and theoretically final divisions of matter—the atom and the molecule. Gay-Lussac, Avogadro, and Cannizzaro solved the problem, and the conviction that both atoms and molecules are realities finally appeared firmly established. But all that was real was the fact that these concepts best explained the facts then known concerning the behavior of matter. After a time, certain observations were made which indicated that atoms, which had previously been regarded as the smallest possible divisions of matter, are themselves complex. It appeared that they are composed of small particles which we now call protons and electrons. These particles are closely associated with electrical charge; indeed, we do not know that they have any existence aside from that which they have as electrical charges. Thus, the electrical charge which matter, at least in its ultimate state of division, possesses becomes as important a characteristic as its mass, its inertia, its gravitational effects, and its occupation of space.

Following the discovery of the complexity of the atom, many theories of atomic dynamics have developed. Some of these are based upon the principles of classical mechanics, and some are founded upon a new system of "atomic" mechanics. Many attempts have been made to visualize the parts of the atom and their relations to the structure as a whole. Some of these theories assign each electron (negative charge) a fixed position

in space with respect to the other electrons and with respect to the positive charge, which is thought to be concentrated in a small amount of space, called the nucleus, at the center of the atom. This nucleus contains both protons and electrons, but the former are always in excess of the latter; hence, the nucleus of every atom carries a positive charge. Other theories picture the electrons rotating in orbits around the nucleus. Considered in this light, the atom becomes a miniature "solar system" with a nucleus for its sun and electrons for its planets. All these theories are the results of efforts to explain the behavior of matter as manifested in chemical changes, in the emission of radiation, when exposed to radiation, under the influence of electrical and magnetic fields, etc. Some of the theories describe mechanical models of the atom, by means of which these externally observable phenomena, or at least some of them, can be explained. None of these has proved completely successful. Yet each theory has brought us a little nearer the final solution of the problem and has served some purpose even if that has been only to stimulate thought either for or against the point of view that it presented.

Modifications of our ideas concerning matter have been many in number and have followed in a rapid succession. Some of them have been revolutionary in character. We have seen many time-honored concepts give way to ideas arising from totally new and radically different ways of interpretation. Dissatisfaction with the "classical" methods of dealing with the problem has brought from some quarters the claim that our efforts to visualize the mechanism of atomic structure must always prove futile. We are told that our ordinary conceptions of space and time cannot be applied within the atom. It is possible, we learn, to explain atomic behavior only in terms of mathematical equations. These equations permit us to calculate the effects of changes within the atom, such as the frequency of the light that it emits; but they furnish us no information concerning the operation of the mechanism that produces these effects.

Amid these rapidly changing theories, the chemist has searched for some model of the atom, or at least for some treatment of atomic structure, that satisfactorily agrees with the known chemical behavior of matter in its different forms. An acceptable

theory must explain the valences that different kinds of elements exhibit. It must also account for the different kinds of valence which the chemist recognizes in different types of compounds. The valences in compounds such as sodium chloride, methane, and hydrated salts cannot possibly be identical in character. Such differences in combining power of the elements, and in the nature of the forces that bind atoms together, must be explained upon the basis of the structure of the atoms that combine. Furthermore, the chemist seeks a treatment of atomic structure that will explain isomeric compounds, allotropic forms, polymerization, electrolytic dissociation, double salts, variations in color, solubility, volatility, electric moments, magnetic properties, electrical conductivity, and many other related phenomena of elements and compounds. It is, perhaps, unnecessary for us to add that no physical, and certainly no mathematical, treatment of the subject proposed so far finds complete favor. And yet, we are sure that a great deal has been accomplished. It is our aim in this book to describe these physical and mathematical concepts concerning the structure of different forms of matter and to relate them to our knowledge of the chemistry of these same forms.

The purpose of these introductory remarks is to warn the reader of the purely theoretical basis upon which much of our discussion is based. The test of any conception that we shall present is the success of that idea in explaining behavior, which for us means particularly chemical behavior. We must discriminate carefully at all times between realities and the products of opinion and speculation. The facts of behavior are real. The frequency of a spectral line is real, and so are the combining capacities of different elements and all their other properties. The models based upon theories of atomic and molecular structures are not real. They are only surmises concerning the mechanism whereby such properties are exhibited. We shall leave open the question of the physical reality of the atom itself. After all, it is a question of *how real* atoms appear to each of us.

We cannot know man's first ideas concerning the nature of the world in which he lives or of the matter of which it is composed. We can only be certain that such ideas were among the first products of his slowly evolving intelligence. Our story must begin with the earliest written records of man's thoughts—records

made only recently in the history of his existence and at a time when his reasoning ability was well developed.

In this chapter, we shall discuss, first, the opinions of the Greek philosophers concerning forms of matter and their composition. This will be followed by a brief recounting of the story of alchemy and the beliefs of the early and middle Christian centuries. Later, we shall discuss the awakening of scientific thought and the beginning of the science of chemistry in the seventeenth and eighteenth centuries. This chapter briefly reviews, therefore, the thoughts of man concerning the forms of matter during a period of some twenty-four hundred years.

The second and third chapters will deal with the developments of chemistry during the nineteenth century. The remainder of the book is concerned, for the most part, with the discoveries and theories of our own century.

The material of these first chapters is, perhaps, largely of historical interest. It is of more significance than a bit of history, however, since one who hopes to follow the development of scientific reasoning in our own times must know how and from what our present ideas have developed. Only in this way can one become fully acquainted with the possibilities and limitations of our present position in the quest for the ultimate solution of the problem.

The Greeks

The idea that all matter is composed of ultimate divisions, which we call *atoms*, is almost as old as human thought; it is certainly much older than the science of chemistry. We can trace this idea as far back as the teaching of Kanada, who lived about 1000 B. C. The first definite expressions concerning atomicity, however, are to be found in the teachings of certain philosophers of ancient Greece. In considering the materials of which the world is composed, the idea that the division of matter must cease at some stage was the logical conclusion for these philosophers to reach. The idea of the infinite is not easily visualized, whether it be applied to the division of material bodies or to the extension of space and time. Common experiences indicate that there is a beginning and an end for everything. To the

Greek philosophers, therefore, the infinite divisibility of matter was not in accord with their experiences in other directions. It was far easier to imagine that somewhere in the process of dividing matter into smaller and smaller portions, one would reach a particle that could not be further subdivided.

The Greek conception of atoms, however, was different in many ways from our modern atomic theory of matter. They believed that "atoms are infinite in number and infinitely varied in the forms that they possess." They made no distinction between the "atoms" of simple (elementary) forms of matter on the one hand and those of complex forms on the other. They did believe, however, that there are certain elementary forms that combine in various ways and proportions to produce more complex bodies. In some cases, one finds the belief that a single kind of matter is the element from which other materials are made. To some of the Greeks, this element was water; to others, it was fire, air, or earth; to others, it was a certain primordial substance called *hyle* and unlike any freely existing form of matter; to still others, fire, air, earth, and water were all elements.

The Greek philosophers did not test their ideas by experiments as we do now. Experimentation, involving work with the hands, was below their social position. Aristotle, for example, said that "industrial work" lowers the standard of thought. Plato believed that all conclusions could be reached by reasoning without any information acquired through the senses. What these men thought, however, was based largely upon what they saw, or thought they saw, in life about them. Many of them thought that their observations of matter indicated collections of atoms in empty space, not something continuous and compact.

We must note that the use of facts as a basis for reasoning was not so easy in the days of the Greek philosophers as it is now, because not many facts were known at that time. In the absence of facts, they mixed metaphysics with scientific reasoning too freely. They depended too much upon well-ordered logic and too little upon well-ordered facts. Still, Aristotle insisted that all conclusions must agree with facts. Even he, himself, failed to apply this principle in his philosophy, for the very good reason, perhaps, that he found that any philosophy based solely upon

the few facts of nature then known would be very limited in its extent.

Because of their attitude and because of the conditions of their times, it is little wonder, therefore, that the success of the Greeks in explaining the great problems of astronomy and the structure of matter was very meager. The necessity of experimentation was not yet recognized. The world was not yet ready for any great scientific advances.

In the Greeks' favor it must be said that they first saw and stated many of the problems of science that we are still striving to solve. In their philosophies, we find for the first time the expressions of minds that were freed from mysticism and tradition. Theirs was the first approach toward the scientific study of natural phenomena. Theirs were the first attempts to arrive at conclusions by studying effects and their causes, to observe with the view of formulating general principles, and to reason inductively. Their influence in the direction of thought was felt strongly during the middle ages and even during the eighteenth and nineteenth centuries. It happened, however, that the strongest influence was exerted by the teaching of Aristotle, who did not accept the atomic concept of matter in which certain of his contemporaries and predecessors placed their faith. There is a lapse, therefore, of many centuries between the time of the Greeks and the revival of the atomic concept, which paralleled the revival of learning in other fields of knowledge.

The Opinions of Some of the Greeks

Thales (640–550 B. C.).—Thales was a native of the city of Miletus. To him water appeared to play an important part in the life of the world about him—more important, in fact, than that of any other substance. He observed water in all its changes of form. It revealed to him its ephemeral character in fog, rain, mist, dew, snow, ice, and the ever changing sea. What belief was more natural than that all substances are composed of water? For all things are ephemeral. Change is universal. Time flows on, and with it earthly forms of matter, organic and inorganic, spring into being just as the mist is born above the sea. In turn, they change into new forms, just as snow is changed into water.

To Thales, the earth was a flat disk floating in a great sea of water. Although his conclusions in these matters may indicate a feeble attempt at interpretation, this man made some very remarkable discoveries in other directions. It is said that he accurately predicted the date of an eclipse, determined the number of days in the year, and calculated the diameter of the sun. He also established several important theorems in geometry.

Anaximenes and Leucippus.—Anaximenes and Leucippus followed Thales as residents of Miletus. They looked upon air and earth as the elements of which all substances are composed. Air, earth, and water, however, were poetic symbols rather than the definite terms that the scientist of today uses in describing matter in its elementary forms. Anaximenes thought that the earth was a flat disk floating in a sea of air, through which the heavenly bodies moved in their rotations around the earth.

Heraclitus (540–475).—Heraclitus of Ephesus added fire as one of the elements. One may sit by the fire and observe the forms of many things. Then why should not fire be an element of which these things are made? All the world is just a picture in flames. All things are but moving pictures, which come and go through our minds, as pictures come and go among the flames.

Empedocles (490–430).—Empedocles taught that the four elements fire, air, earth, and water act under the influence of love and hate to form more complex substances. Bones consist of two parts of fire and one part each of earth and water. Flesh is a complex substance composed of equal parts of the four elements.

Democritus (470–360) and Plato (427–347).—Leucippus was the teacher of Democritus, who is sometimes called the founder of atomic theory. Democritus believed that the only existing things are atoms and empty space. The many different forms in which matter appears depend for their properties upon the number, size, and manner of aggregation of the atoms that compose them. The ideas of Democritus were modified by Plato, who, about 400 B. C., added geometrical forms for the atoms of the four elements and for the "atoms" of the substances that are formed from them. Atoms might be, according to Plato, tetrahedra, cubes, octahedra, dodecahedra or icosahedra—4-, 6-, 8-, 12-, or 20-point figures of symmetry. Some knowledge

of these beliefs has been left to us in "De Rerum Natura,"[1] written by the Roman poet Lucretius (100–55 B. C.).

Aristotle (384–322).—Aristotle, a pupil of Plato, rejected the Democritan theory of the atomic nature of matter and built up a school of philosophy which, so far as matter was concerned, was based upon the concept of infinite divisibility.

Aristotle replaced the four elements air, fire, earth, and water with the idea of one element hyle, which was the quintessence of all material objects. To this quintessence might be added essential qualities, or properties, which gave it the characteristics of one of the many different kinds of matter. Water, for example, was thought to consist of quintessence plus coldness and wetness. Fire was quintessence plus hotness and dryness. All substances were produced by the combination of these properties in different proportions with quintessence. It was logical to believe, therefore, that one form of matter could be changed into another if the proportion of essential properties was changed or if new properties were added to the quintessence.

Because, in part, of the tremendous influence of Aristotle's system of philosophy, the idea of the atom was abandoned. For sixteen centuries, chemistry became an Arabian art based upon the doctrines that Aristotle had proposed. If Aristotle had thought and taught differently concerning this problem, or if those who immediately followed him had interpreted his doctrines in a different manner, much more might have been accomplished during the early and middle Christian ages. Or was the world not yet ready? We cannot know. We can say only that, whatever philosophy had been accepted, scientific thought could not have moved more slowly toward truth than it did during the time which elapsed between Aristotle and the Renaissance, when attention was turned once more to some of the pre-Christian principles.

Alchemy

Alchemy owes its beginning and its fundamental principles to Aristotle. It was he who taught that all forms of matter contain

[1] Students of chemistry, and of the other sciences as well, will find much of interest in "De Rerum Natura." For an excellent translation, the reader is referred to the reference at the end of this chapter.

one fundamental kind of substance and that different substances consist of this plus essences, or properties. The original list of essences, consisting of dryness, coldness, wetness, and hotness, was expanded until, during the days of the alchemists, it came to include all the properties that substances were known to possess. Thus, if we followed this philosophy today, we should say that clay is red not because it contains ferric oxide but because it contains the essence of "redness." Living things possess the essence of life. Alchemists sought these essences, particularly the essence of life. They spent their lives attempting to extract essences from different substances and, by affecting the proper exchange of essences, to change one substance into another. If all the essences that make gold what it is, for example, could be obtained, and if these were added to lead, why could not lead be changed into gold?

In the beginning, alchemy was an Egyptian art. It was probably founded in Alexandria, a Greek colony, where, of course, Greek philosophy predominated. It was here that the earliest reliable records have been found. And it was here that the first personality became associated with the history of the art. He was the mythical author of many books and the "founder of science"—Hermes Trismegistos, the thrice great.

In the seventh century A. D., the Arabs conquered Egypt. From this time, alchemy became an Arabian art. Of the Arabs, Geber (721–813) was the outstanding alchemist. In many ways, he was a very remarkable man and a practical alchemist for his time. Unlike most of his contemporaries, he wrote of many chemical processes and of various forms of apparatus, such as furnaces and baths for sublimation, distillation, and crystallization. Geber's real name was Jabir Ibn Hayyan. He was a Persian by birth and a highly respected member of the court of Harun-al-Rashid. Geber believed that all metals consist of different proportions of mercury and sulfur. Mercury was thought to be that constituent of metals that gives them luster and malleability. Sulfur produces hard metals and causes them to change their form under the influence of heat. But Geber, too, was devoted to the search for the philosopher's stone, by means of which it was thought that transformations of matter might be accomplished and that even life itself might be added to

that which did not possess life. He offered no new ideas concerning the nature of matter.

Of the later centuries, we should mention four alchemists of note, Vinzenz Albert von Bollstädt, Roger Bacon, Arnaldus Villanovanus, and Raymundus Lullus. These men were of western Europe, and all were true disciples of Geber. Basil Valentine (fifteenth century), a German monk, followed Geber as the master of the alchemists. Valentine was an ardent seeker for the philosopher's stone and a true alchemist. In many ways, however, his work was different from that of most of the alchemists of his time. He was the first to describe a real element, antimony, and its compounds. Geber had thought that all metals were composed of mercury and sulfur. Valentine added salt—not sodium chloride but a certain something that made metals solid and able to resist fire.

Although the effect was quite unintentional on his part, it was Valentine who began the overthrow of alchemy. His work and writing on antimony and its compounds were much more like the chemistry of today than the usual work of the alchemists; they dealt with actual substances instead of unreal essences, and their objective was the accurate observation and recording of the methods of preparing, the properties, and the uses of definite substances.

If space permitted, we should also describe the work of other alchemists—von Helmont, Glauber, Agricola, Tacchenius—who helped to clear the way for chemistry. In a world steeped in mysticism and tradition, where men were seldom free to discuss even the evident truth, these men carried on in a scientific way as best they could and knew.

The records of alchemy are filled with strange names and queer stories. It was said that the art of changing base metals into gold was a secret that had been brought to earth sometime before the flood by certain demons from heaven. Certain biblical characters were claimed by the alchemists as members of their profession. Among these were Moses and John. Different alchemists wrote under the names of Democritus, Aristotle, Thales, Heraclitus, and Plato, in order to secure greater credence for their views. Many of the names were purely mythical. In some cases, the same name was used by many alchemists.

In fairness to the alchemists, we must admit that they tried to put their beliefs into practice. Not only did they think that gold is composed of quintessence plus certain qualities, but they attempted to produce gold by removing certain properties from other metals and adding those that belong to gold. Not only did they believe in the philosopher's stone; they tried to find it. They erred most certainly. Man's mind is always liable to error. But the alchemists kept right on erring in the same manner century after century.

Aristotelian philosophy alone was not the cause of the failure of scientific knowledge to advance during the early and middle Christian ages. Mysticism and superstition were revived and befogged man's mind. Furthermore, the church became the authority that dictated what men should study and what beliefs they should have about the natural, as well as the supernatural, world. Freedom to observe facts and to reason from them inductively was denied. In keeping with such dictates, it was only natural that the philosophy of Aristotle should prove the accepted guide to reasoning concerning the nature of matter and the material world. It was the path of least resistance and of greatest safety.

The Beginning of Chemistry

The End of Alchemy.—The downfall of alchemy and the beginning of chemistry were brought about largely through the efforts of alchemists who studied and prepared many compounds, usually with the idea that they might be of value in the treatment of diseases. Chief among these was Theophrastus Bombastus von Hohenheim, called Paracelsus for short. He was a physician, an alchemist, and a teacher. He regarded life as a chemical process and tried to find medicines to cure the ills that overcome man, when this reaction becomes unbalanced. He begged his contemporaries to cease their futile search for the philosopher's stone and to give their attention to the preparation of new inorganic substances that would be of practical value in medicine.

Francis Bacon (1561–1629) turned attention again to the Democritan doctrine of the atomicity of matter in his "Novum Organum." Later, Robert Boyle (1627–1691) formulated a

theory to account for the pressure exerted by gases. This theory was based upon the supposition that gases are composed of particles separated by empty space. In his "Sceptical Chymist"[1] and in "The Usefulness of Natural Philosophy," elements were defined as substances that had not yet been decomposed. He explained the changes that occur when two substances combine to form another substance as the combination of atoms of the two substances. In the "Sceptical Chymist," he introduced several well-defined terms to replace the very vague names inherited from Aristotle and the alchemists. Boyle, for example, clearly distinguished between compounds, mixtures, and elements, defining an element as a primitive substance which can produce compound substances by combinations with other elements. The "Sceptical Chymist" is one of the great milestones along the road of chemistry's development. It marks the end of alchemy. Isaac Newton (1642–1727), in his book entitled "Opticks and Principles," applied the theory of atoms to explanations of chemical affinity, gravitation, and magnetism. During the seventeenth century, therefore, the belief in chemical change as a reaction involving atoms was becoming more and more firmly established. A temporary halt in the development of these ideas was soon to come.

The Phlogiston Theory.—About 1670, there came into rather general use a strange theory concerning certain kinds of chemical change. This theory concerned the hypothetical substance known as *phlogiston*. This "substance" was described as a constituent common to all combustible materials; it was supposed to escape during combustion. The idea of phlogiston was first presented by Bücher (1669) and was later revived and extended by Stahl (1702). Pure hydrogen, which leaves no ash upon burning, was said to be composed only of phlogiston. Wood, which does leave an ash, was composed only in part of phlogiston. Air was thought to be necessary for combustion only because it acted as an absorbent of phlogiston. If air were not present, the phlogiston, of course, could not leave the original body that contained it.

[1] This work of Boyle is available in a volume of the Everyman Library. It should be read by everyone who expects to specialize in any branch of chemistry.

In 1669, Mayow had recognized the fact that air consists of more than one substance, one of which is active in supporting respiration and combustion. As early as 700, the Chinese seem to have had about the same information. This fact was not generally accepted, however, since it was in contradiction to the phlogiston idea of combustion. The latter, therefore, continued to dominate the situation until late in the eighteenth century. Even Priestley, who prepared oxygen by heating mercuric oxide (1774), did not recognize the gas that was liberated as an element and saw no relation between this substance and combustion. Priestley called the gas "dephlogisticated air." It caused substances to burn more brilliantly because it contained no phlogiston and was, therefore, a better absorbent than ordinary air, which is partially "phlogisticated." The fact that many substances gain in weight when they burn was not observed by the phlogistonists. One can scarcely imagine their failure to observe this effect in at least a few cases. It appears that their observations may have been "selected" to agree with previously drawn conclusions.

Lavoisier.—The overthrow of the phlogiston theory was due largely to the experimental work and writing of Lavoisier (1745–1794), who became interested in Priestley's dephlogisticated air. He showed that combustion results in a gain in weight rather than a loss, as the phlogiston theory would lead one to think. By gain in weight we mean that the products of combustion weigh more than the substances that undergo combustion. This leaves out of consideration, of course, the weight of the oxygen, which combines with the combustible substances or with their constituent elements. Lavoisier conclusively demonstrated the character of air and the part that it plays in combustion and similar chemical changes. He showed that Priestley's "gas" is an element and is identical with the active part of air.

Lavoisier insisted on the quantitative study of chemistry. By means of his own quantitative determinations, he established the law of the conservation of mass. It is for this reason that he is often spoken of as the "father of chemistry." He laid the broad foundations upon which chemistry as a quantitative science has developed.

Below, we give a list of the elements as compiled by Lavoisier. This summarizes, in a way, the chemical knowledge of his day.

By making allowances for a few mistakes, we note that 28 elements were known at this time (about 1790).

THE CHEMICAL ELEMENTS ACCORDING TO LAVOISIER

Light	Iron
Heat	Manganese
Oxygen	Mercury
Azote (nitrogen)	Molybdenum
Hydrogen	Nickel
Sulfur	Gold
Phosphorus	Platinum
Carbon	Zinc
Antimony	CaO[1]
Silver	MgO
Arsenic	BaO
Bismuth	Al_2O_3
Cobalt	SiO_2
Copper	Radical muriatic[2]
Tin	Radical fluoric
	Radical basic

[1] The formulas, of course, are ours. Lavoisier called these "elements" earths.

[2] Muriatic, fluoric, and basic radicals refer to what we now call chloride, fluoride, and hydroxyl ions, respectively.

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CHAPTER II

THE ATOMIC-MOLECULAR HYPOTHESIS OF THE NINETEENTH CENTURY

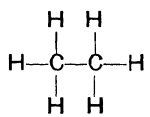
DALTON'S ATOMIC THEORY

The Law of Multiple Proportions.—In 1776, Bryan Higgins had suggested that two kinds of atoms combine to form particles of a compound. William Higgins, in 1789, published "A Comparative View of the Phlogistic and Anti-phlogistic Theories with Inductions." In this, he modified the suggestion of Bryan Higgins and postulated a theory of combinations between atoms in multiple proportions, the simplest and the most stable combination occurring when two atoms A and B combine to form a binary compound AB. Dalton later adopted this statement and incorporated it in his atomic theory. Cavendish, in 1767, had shown that a certain equivalency exists between the weights of metals and bases which neutralize a definite weight of a given acid. Richter, in his "New Aims of Chemistry" (1792–1802), extended the equivalency law of Cavendish, stating that "the ratio between the weights of two substances that combine with a fixed amount of a third substance is either equal to the ratio of the weights of the substances which combine with each other or is a small integral multiple or submultiple of this ratio." This became, in time, our law of combining proportions (by weight). Originally, Richter's law was applied only to reactions of metals and bases with acids, but later it was applied by Berzelius to elements and compounds generally.

At the beginning of the nineteenth century, there was still serious doubt concerning the atomic character of matter. Quantitative data were lacking. Even the principle of the definite composition of compounds and that of constant combining proportions were not acknowledged as valid by everyone. The law of multiple proportions, which had been suggested by William Higgins and which had attained some prominence by the quanti-

tative experiments of others, was by no means firmly established. Richter, in 1792, had shown that some metals form oxides that contain two proportions by weight of oxygen and metal. Lavoisier recognized the fact that a number of the elements combine with one another in different proportions to produce two or more compounds. Cavendish had analyzed three oxides of nitrogen. Proust, in 1799, had analyzed two oxides of copper. Clement and Désormes, in 1801, had proved that one oxide of carbon contains twice as much oxygen, for a given weight of carbon, as the other. It remained for John Dalton, however, definitely to establish the law and to provide a theory that would allow the science to develop along strictly quantitative lines.

In 1808, Dalton published "A New System of Chemical Philosophy." This publication was preceded by analytical work dealing largely with the hydrocarbons and the oxides of nitrogen. It appears, however, that Dalton may have made up his mind concerning the law of multiple proportions and the atomic theory before he did this analytical work. Close scrutiny of his data does not furnish absolute substantiation of the law in all cases. It is fortunate, too, that not many compounds of carbon and hydrogen were known in his day. He found that "olefiant" gas (ethylene) contains twice the proportion of carbon to hydrogen that is found in "marsh" gas (methane). Dalton assigned these compounds the formulas, therefore, of CH and CH_2, respectively. Ethane, C_2H_6, was not known, but if Dalton could have determined the ratio of carbon to hydrogen in this compound, he would have found one and one-third times as much carbon for a given weight of hydrogen as he found in methane and two-thirds as much as he found in ethylene. In other words, the law of multiple proportions (as formulated by Dalton) does not hold for ethane or for other compounds in which atoms of the same element are linked together, as the carbon atoms of the ethane molecule are united:



Similarly the law does not hold for naphthalene, $C_{10}H_8$, anthracene, $C_{14}H_{10}$, etc.

The Essential Principles of the Atomic Theory.—Dalton's atomic theory can be summarized by the following statements: (1) Atoms are the smallest divisions of an element. (2) These atoms are indivisible, compact units of matter. It was not thought in Dalton's day that they possess a structure. (3) Atoms of different elements have different masses, volumes, and forms. The atoms of any one element are identical in every way. There was no suggestion in the theory to account for different combining capacities of different kinds of atoms; it is doubtful, indeed, if Dalton realized that such differences exist, and, if he did, he was unable to explain them. (4) Atoms of elements combine to form the "atoms" of compound substances. Such combinations occur in accordance with the laws of definite and multiple proportions. (5) The simplest and most stable compound that two kinds of atoms combine to produce is a binary compound.

All except the first of the above statements fail either in stating the truth or in covering all the facts in an adequate manner. Even the first is open to some question, since the smallest particles of some elements, as they exist in nature, contain two or more atoms. The fifth statement, however, is incorrect in every way. For instance, the simplest and most stable compound formed by the combination of oxygen and hydrogen would be, according to Dalton, OH, the formula assigned to water. On this basis, hydrogen peroxide would have the formula HO_2. Ethylene would be given the formula CH; and methane, which contains twice as much hydrogen for a given weight of carbon, would be CH_2. Had he known of ethane, Dalton would have been forced by this reasoning to have assigned it the formula $CH_{1\frac{1}{2}}$, which would, of course, have been impossible, since such a formula indicates that one and one-half atoms of hydrogen react with one atom of carbon. Similarly, he would have given NH as the formula for ammonia, and NO for nitrous oxide. Dalton's theory, faulty as it was, definitely established the atomic concept of matter. Its most significant feature, perhaps, was its quantitative, although somewhat erroneous, expression of the manner in which atoms combine to form compounds. The atomic theory was inevitable when the law of multiple proportions was once accepted. This law proved that there is a definite minimum

weight of each element (based upon a fixed weight of a standard element) which is capable of taking part in a chemical change. If this minimum weight does not react, some multiple of it participates in the change. From this fact, the conclusion that either one atom or some whole number of atoms combine with one or more atoms of a second element naturally follows as the simplest explanation. The atom becomes, in accordance with this explanation, the chemical unit of an element.

Dalton's Atomic Weights.—If we consider Dalton's formulas of compounds and the relative weights that he assigned to different kinds of atoms, it becomes evident that he was thinking in terms of chemically equivalent weights of the elements rather than atomic weights. His weights were based upon a fixed weight of some reference element; he selected hydrogen as this reference and gave it a value of unity. Then, in accordance with the belief that the simplest and most stable combination of two elements is a binary one, he assigned the atomic weight of 8 to oxygen. This was based upon the combining proportions of oxygen and hydrogen in water which he thought should have the formula HO. The weights that he obtained by this method of reasoning, of course, are not our present atomic weights. The stumbling block that caused this confusion was Dalton's erroneous assumption concerning the binary compounds of different elements. Differences in the combining capacities of the elements (valence) had not yet been recognized. It was impossible to determine from the knowledge then available which compound, if any, contains an atom of one element combined with an atom of another. Dalton, perhaps, accepted the most reasonable conclusion in the light of his meager information. Wollaston and Gmelin realized the difficulties and proposed to call Dalton's values equivalent weights, as referred to a fixed weight of a standard, instead of atomic weights. Berzelius, however, followed Dalton explicitly and spoke of the weights expressed by Dalton's formulas as atomic weights. Because of the great influence of Berzelius and because of the somewhat stubborn attitude that he manifested in maintaining his personal views on the subject, confusion and doubt concerning the whole of the atomic theory became so widespread that, by 1850, the theory was practically abandoned.

The Atomic-molecular Concept during the Latter Half of the Nineteenth Century

Although the atomic theory had been well established early in the nineteenth century, its usefulness had never been completely recognized and was greatly impaired because of the controversies that arose concerning atomic weights. Everyone recognized that matter is atomic in character, but there were different views concerning the meaning of the word *atom* and just how much of an element the term should be used to represent. There was no distinction, either, between the atoms of elements and the "atoms" of compounds. The controversies on the subject were often so bitter and the contentions so contradictory that the use of the theory was practically prohibited. Some even went so far as to explain all chemical properties without any use of the atomic concept of matter.

The greatest difficulty in the path of further development lay in the failure of Dalton and his followers to realize that atoms of different elements possess different combining capacities. They did not know that different elements have different valences, as we should say today. Had these differences been recognized, the distinction between equivalent and atomic weights would have been evident. Dalton would not have assigned water and ammonia, for example, similar formulas, OH and NH. About fifty years was required for the accumulation of sufficient evidence by which differences in the combining capacities of the elements could be demonstrated clearly. Two discoveries which helped to advance knowledge in this direction are embodied in the principles introduced by Gay-Lussac and Avogadro. These principles are important because they led to the recognition of the molecular state of elements and compounds and finally settled the controversy concerning atomic weights.

Gay-Lussac's Law of Combining Volumes.—This law states that the volumes of different gases that take part in a chemical reaction and the volumes of the gaseous products of the reaction are all related to one another as small whole numbers. Thus, two volumes of hydrogen react with one of oxygen to form two volumes of water vapor. The volumes of the gases involved in this reaction bear the same relations to one another as the

series of small whole numbers 2, 1, 2. Similarly, one volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. In this case, the volumes are related in the same manner as the integers in the series 1, 3, 2. As a third illustration, let us examine the combining proportions by volume of hydrogen and chlorine. Here we find that equal volumes of the two elements combine and that the volume occupied by the product hydrogen chloride, which is also a gaseous substance, is twice that occupied by either hydrogen or chlorine alone. The volume relations in this case are, therefore, those expressed by the series of numbers 1, 1, 2.

The meaning and importance of Gay-Lussac's discovery are not difficult to understand. There can be but one explanation of the facts upon which the law of combining volumes is based. If equal volumes of hydrogen and chlorine react to form a volume of hydrogen chloride that is equal to the sum of their volumes, the following explanation appears to be justified: Let us assume that equal volumes of the two elements contain the same number of particles of the elements and that one particle of hydrogen reacts with one of chlorine. Let us also assume that a given volume of hydrogen chloride contains the same number of particles as are contained in an equal volume (same temperature and pressure) of hydrogen or chlorine. If these assumptions are granted, then one particle of hydrogen and one of chlorine must react to form two of hydrogen chloride. Since there are twice as many particles of hydrogen chloride as there were of hydrogen or chlorine, the volume occupied by the product of the reaction will be equal to the sum of the volumes originally occupied by the elements. Similarly, in the reaction between hydrogen and nitrogen to form ammonia, we assume that equal volumes of these three substances contain the same number of particles. Granting this assumption, the logical explanation of the volume relations in this reaction is that one particle of nitrogen reacts with three of hydrogen to form two of ammonia.

But to return to the reaction of hydrogen and chlorine: If one particle of each of the elements produces two particles of hydrogen chloride, this means that a particle of either element must consist of two equal parts. One part of a hydrogen particle reacts with one part of a chlorine particle to form a particle of

hydrogen chloride. The second parts of the hydrogen and chlorine particles form a second particle of the product. If this reasoning is valid, our explanation means that the units in which the elements hydrogen and chlorine exist in their natural state are not the units that combine with each other in a chemical change. It thus becomes necessary to distinguish between two very small divisions of elements. This conclusion was reached by Avogadro, who first offered the explanation, which we have discussed above, of the facts upon which the law of combining volumes is based.

Avogadro's Hypothesis.—In 1811, Amadeo Avogadro made two notable contributions to chemistry. He introduced the term *molecule* to represent the smallest particle of a compound and of an element in its free state. He also advanced the theory that equal volumes of all gases, when measured at the same temperature and pressure, contain the same number of molecules. Avogadro's conclusions were based upon the facts pertaining to the law of combining volumes. They were also supported by the facts pertaining to the relations of the volume, temperature, and pressure of gases.

The proof of Avogadro's principle is much easier now than it was at the beginning of the nineteenth century. At that time, it was not generally accepted. It has been found entirely in agreement with all known pertinent facts, however, and is now accepted universally as one of the most fundamental principles of the science of chemistry. For this reason, it may be worth while to give here mathematical proof of its validity. This proof is based upon applications of Boyle's and Charles' laws. Equal volumes of all gases, measured at the same temperature and pressure, are affected in the same manner by changes of temperature and pressure. It is equally true that two gases that exert equal pressures, when equal volumes at the same temperature are considered, show the same changes in pressure for equal changes in volume or temperature. Since the pressure of a gas depends upon the number of particles of the gas within a given space and upon their velocity, the identical behavior of different gases under changing conditions of volume, temperature, and pressure argues in favor of Avogadro's idea.

Let us take two gases G_1 and G_2. We select equal volumes of the two—let us say, one liter of each. We shall also hold them at the same tem-

perature. In the volume v_1 of the gas G_1, we shall place a certain amount of that gas. In a volume of the same size, which we shall designate as v_2, we shall place a sufficient amount of the gas G_2 so that the pressures p_1 and p_2 of the two gases will be the same. Now, let us say that there are n molecules of G_1 in the volume v_1, each molecule of which possesses the mass m and the velocity u. Let us think of the volumes v_1 and v_2 as two cubes, each of which has the length l as measured along one of the edges. A molecule in colliding with the walls of the cubical vessel, when moving with the velocity u, will strike the wall with a momentum equal to the product of its mass and velocity mu. According to the kinetic theory of gases, this molecule rebounds from the collision with the same velocity and, hence, suffers no loss in its kinetic energy. The momentum after the collision will still be mu but will be oppositely directed. The total *change in momentum* is equal to 2 mu. The distance between the walls of the cubical vessel is l; hence, the molecule will make u/l collisions with the walls of the cube in one unit of time. Each molecule, therefore, exerts an effect p upon the walls of the cube (in one unit of time) equal to

$$p = \frac{2mu^2}{l},$$

and the effect of all n molecules is

$$p = \frac{2mnu^2}{l}. \tag{1}$$

The cube's total inner surface against which the molecules strike is $6 \times l^2$. The pressure p_1 which is exerted on one unit of area is, therefore,

$$p_1 = \frac{2mu^2n}{l} \cdot \frac{1}{6l^2} = \frac{mu^2n}{3l^3}. \tag{2}$$

The volume of the cube is l^3; hence, substituting for l^3 the volume v for the gas G_1:

$$p_1 = \frac{mu^2n}{3v_1}, \tag{3}$$

and

$$p_1v_1 = \frac{mu^2n}{3} \tag{4}$$

Similarly for G_2,

$$p_2v_2 = \frac{m'u'^2n'}{3}, \tag{5}$$

where m', u', and n' represent, respectively the mass, velocity, and number of molecules of G_2 in the volume v_2, when the pressure is p_2 ($p_2 = p_1$). The temperature is the same for both gases. But since $p_2 = p_1$, $v_2 = v_1$, and $T_2 = T_1$ (T represents temperatures), the kinetic energies of the molecules of the two gases may be assumed to be equal in accordance with the kinetic-temperature hypothesis. Now, the kinetic energy of a molecule is defined as follows:

$$\text{K.E.} = \frac{mu^2}{2}, \tag{6}$$

where m is the mass and u the velocity of the molecule.
Hence, we may assume the following equality:

$$\frac{mu^2}{2} = \frac{m'u'^2}{2}. \tag{7}$$

Thus, all the corresponding terms in Eqs. (4) and (5) are equal, except n and n', which represent the number of molecules of the two gases G_1 and G_2 in the volumes v_1 and v_2, respectively. Since all the other corresponding terms are equal,

$$p_1v_1 = p_2v_2. \tag{8}$$

Substituting the value of p_1v_1 from Eq. (4) and the value of p_2v_2 from Eq. (5) in Eq. (8), we may write

$$\frac{mu^2n}{3} = \frac{m'u'^2n'}{3}. \tag{9}$$

Since

$$\frac{mu^2}{3} = \frac{m'u'^2}{3},$$

it follows that

$$n = n'$$

This means that equal volumes of G_1 and G_2 contain an equal number of molecules under the same conditions of temperature and pressure.

Other Proofs of the Corpuscular Nature of Matter

Thus far, the evidence that we have submitted in support of the idea that matter is composed of particles, or corpuscles, has been chemical rather than physical. The atomic theory proposed by Dalton was greatly aided, however, by certain other lines of evidence which gave to atoms a somewhat sounder physical basis of reality. We cannot discuss these except very briefly at this point.

The Kinetic Theory of Matter.—The behavior of gases cannot be explained except by assuming that they are composed of particles (let us call them molecules) separated by empty space. When this assumption is made, we can easily explain the pressure exerted by a gas and the manner in which it varies with changes in volume and temperature. The extremely great compressibility of a gas can be explained as the effect of added pressure in crowding the molecules closer together, thus reducing the

amount of empty space. If the molecules are far apart and exert little influence upon one another, the nature of the gas would not be expected to make any difference in this effect.

The tendency of a gas to diffuse into the space already occupied by another gas seems almost certain proof that both substances must consist of moving particles and that these lie far apart. The fact that a gas does not settle to the bottom of its container leads us to the same conclusion and also indicates that collisions of molecules with one another or with the walls of the containing vessel result in no loss of energy (average) in the colliding bodies.

If matter in the gaseous state is corpuscular in nature, the same must also be true of the liquid and solid states. The division of continuously divisible matter into discrete particles when a liquid changes into a gas, and the destruction of these particles when the gas condenses to the liquid again, is scarcely to be given any consideration, even as a remote possibility. On the other hand, the molecular nature of liquids and solids furnishes a satisfactory basis for the explanation of their vapor tensions. It explains particularly the fact that only limited quantities of a liquid, for example, will evaporate into a closed space and that the vapor attains a state of equilibrium with the liquid.

The solubility of liquids and solids in certain solvents also supports the molecular hypothesis. A solution, of course, is a mixture and as such resembles the mixture produced when one gas is allowed to diffuse into the space occupied by another. It is just as difficult to imagine that a continuous solid could mix with a continuous liquid as it is to think of two gases, which diffuse one into the other, as anything but collections of particles of matter separated by empty space.

The flow of liquids can be explained if we assume that molecules of the liquid slip and slide over one another in reaching a lower level. The tendency of a flowing liquid to form a stream, the ease with which this stream can be diverted into several channels, the breaking up of a liquid into small drops all argue in favor of a corpuscular structure. We could scarcely predict such behavior of matter that was not corpuscular. Similarly, the melting of a solid can be explained most satisfactorily as the separation of particles which in the solid state are held more firmly together than in the liquid. In short, the existence of matter in three

states is almost certain proof of its corpuscular, or molecular, nature.

Faraday's Law of Electrolysis.—In 1833, Faraday discovered that equivalent weights of different substances are deposited at the electrodes of an electrolytic cell when the same quantity of electricity passes through different electrolytes in solution or in their molten states. Thus, the passage of the same quantity of electricity through solutions containing different univalent metals, such as sodium, potassium, and silver, deposits at the electrodes of the cell weights of these metals proportional to their atomic weights. This may be explained if we assume that (1) the metals exist in solution as particles, (2) an atomic weight of each metal consists of the same number of particles, and (3) each particle of these three metals bears the same quantity of charge. This explanation is further supported by the fact that the quantity of electricity that liberates an atomic weight of an univalent element liberates only one-half of an atomic weight of a divalent element, such as zinc or copper. In the latter case, we assume that there is the same number of atoms of zinc or copper in an atomic weight as there is in an atomic weight of silver but that each zinc or copper atom carries a charge that is twice as great as the charge of the silver atom in solution.

The facts of electrolysis, therefore, support the contention that matter exists in definite units. They further show that definite quantities of electrical charge are associated with these units of matter. Thus, the charge on the copper atom, in solution, is a multiple of the charge carried by the silver atom. This indicates, of course, that electricity as well as matter is atomic in character. This idea is verified by other facts which will be discussed in later chapters.

Deviations from Boyle's and Charles' Laws.—Boyle's law states that the volume occupied by a gas at constant temperature is inversely proportional to the pressure. This relation is true, however, only for gases at ordinary pressures, such as that of the atmosphere. Even when the pressure is increased to a few atmospheres, the relation between volume and pressure is not valid. At first thought, this failure of the law might be considered as an argument against the explanation which is based upon the idea that gases are composed of molecules separated by

empty space. But a little further consideration will show us that this behavior is exactly what we should expect upon the basis of our explanation. The portion of the volume of a gas that acts in accordance with Boyle's law is the empty space between the molecules. At low pressures, the volume actually occupied by the molecules themselves is a very small part of the total volume and may be neglected. With increased pressure, however, the "free" space between molecules is greatly reduced, and the volume occupied by the molecules becomes a significant part of the whole volume. Under such conditions, we find, of course, that doubling the pressure does not reduce the volume to one-half of the former volume. Crowding the molecules together and actually compressing the volume that they occupy when crowded closer together are entirely different matters, of course, and cannot be treated in the same manner.

For gases under high, or even moderately high, pressure, the expression

$$pv = RT,$$

which combines Boyle's and Charles' laws, becomes

$$p(v - b) = RT,$$

where p is the pressure of the gas (expressed in dynes per square centimeter), v is the volume (in cubic centimeters) of a gram-molecular weight of the gas, T is the absolute temperature, and R is a constant which has the value 8.315×10^7 ergs per degree mole. The symbol b represents the correction of the whole volume for the volume actually occupied by the molecules themselves. The latter is actually four times this volume.

Even when the volume is corrected for the space actually occupied by the molecules of the gas, the laws still fail to hold. A second factor also appears to act in such a manner as to make the volume smaller than would be predicted. This factor concerns the attraction that exists between the molecules and that is responsible for cohesion. Whatever attractive forces exist between the molecules will tend to pull them close together; and when they are crowded close together, or when they are greatly compressed, these forces may cause considerable compression within themselves. The decrease in volume is not

inversely proportional to the change of pressure, therefore, since the increased molecular forces cause a shrinkage in volume that corresponds to a greater pressure than that which is actually applied. The complete form of the modified expression for Boyle's and Charles' law is called Van der Waal's equation:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

The real pressure p is increased by the term a/v^2, which we can regard as the "internal pressure," which is due to molecular attraction. Thus, it is shown that the gas laws may be applied more accurately to gases if allowances are made for certain effects of molecules. It should be stated, however, that for low temperatures and for pressures above 10 atmospheres, even Van der Waal's equation fails to hold exactly. Nevertheless, the fact that the gas laws may be more strictly applied under ordinary conditions if recognition is made of their molecular state seems to be as definite proof of the existence of molecules as is needed for the acceptance of the molecular hypothesis.

Is the Molecule a Reality?—We must admit that the molecule is not real if by reality we mean something which can be seen. Yet we cannot see sound or electricity. We cannot see the sender of a telephone message, nor, if we depended upon our ability to see, should we have reason to believe that the sound that came through our radio receivers have their origins in a real voice or a real instrument. In addition to the evidence of molecular reality presented above, further justification of the concept is to be found in the results of many other lines of investigation. Among these there is no stronger evidence than that furnished by Perrin's study of the Brownian movement.

There is, perhaps, no better evidence of the existence of a reality than exact and consistent measurements of its properties and dimensions. Different methods have given consistent values for the speeds of molecules, for their masses, energies, diameters, and the distances that they travel between collisions. With the help of these values, calculations have been made of the behavior of matter under certain conditions, *e.g.*, the specific heats of gases at constant pressure. These calculated values agree with those observed. So real, indeed, do molecules appear

that no serious doubt of their reality has been raised by either chemists or physicists for many years.

Diatomic Molecules.—Avogadro claimed that, since two volumes of water vapor are produced from one volume of oxygen, the smallest oxygen particle must consist of two equal parts.

Hydrogen + oxygen → water
2 volumes + 1 volume → 2 volumes
2 molecules + 1 molecule → 2 molecules

The smallest possible amount of water must contain one-half as much oxygen as the smallest possible particle of oxygen that exists in the free state. It was, therefore, necessary that a distinction be made between the oxygen particle and the parts composing it. The particle of oxygen that reacts to form two particles of water was called the molecule; and its two parts, atoms. The molecule of oxygen, therefore, is said to be *diatomic.* Two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. One volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. Now, each ammonia particle cannot contain one and one-half atoms of hydrogen; hence, it was decided that the hydrogen molecule must also contain two atoms. The ammonia molecule, evidently, must contain three hydrogen atoms and one nitrogen atom; this means, of course, that the nitrogen molecule also contains two atoms. Molecules of oxygen, hydrogen, nitrogen, and many other gaseous elements are *diatomic.* Some molecules of elements are, however, *monatomic* (He, Ar, Ne, etc.); others are *polyatomic* (S_8).

Differences in the Combining Capacities of the Elements.—At last, the combining powers of the different elements were shown to be different, and the means of demonstrating these differences was apparent. It was evident that one atom of oxygen combines with two atoms of hydrogen to form a molecule of water, while one nitrogen atom combines with three atoms of hydrogen to form a molecule of ammonia. The recognition of these differences also offered a means of accurately determining the atomic weights of the elements. The real atomic weight could be calculated, of course, by multiplying the equivalent weight of the element by a factor that represents the combining

capacity of the element as measured against the combining capacity of an element, such as hydrogen, taken as one. But the importance of Avogadro's theory was not recognized generally, and, for many years afterward, confusion continued. Berzelius and others persisted in the use of Dalton's original theory in its literal form and in the use of his atomic weights and formulas for chemical compounds.

In 1858, Cannizzaro wrote "The Sketch of a Course in Chemical Philosophy." In this publication, he revived and clearly established Avogadro's hypothesis, explained the distinction between atoms and molecules of the elements, and succeeded in explaining and reconciling the many contradictory results of experimental work that had accumulated since 1800. Special emphasis was placed in Cannizzaro's paper upon the fact that half of a molecule of hydrogen, oxygen, nitrogen, etc., really takes part in a chemical reaction, as Avogadro had argued 47 years previously. Cannizzaro stated that these "half-molecules," or atoms, are indivisible, "at least in the sphere of chemical actions." It is interesting to note that, even at this early date, this man was unwilling to say that the atom is indivisible in a physical sense. Cannizzaro felt that we can be sure of the atom as an ultimate division of an element only as concerns the chemical changes of the element.

Atomic and Molecular Weights.—With Avogadro's hypothesis as a basis, it was possible to determine the relative weights of different molecules. The method of such determinations is reviewed briefly in the paragraph that follows.

Equal volumes of gases contain an equal number of molecules, when the volumes are measured, of course, under the same conditions of temperature and pressure. Hence, if equal volumes of two gases are weighed, equal numbers of the two kinds of molecules are weighed. The ratio of the two weights expresses the ratio of the weight of all the molecules of one kind to the weight of the same number of molecules of the other kind; or we can say just as truly that it is the ratio of the weight of one molecule of one substance to the weight of one molecule of the other. If a number is arbitrarily selected as the molecular weight of a standard substance, the ratio of the weights of equal volumes of the standard and a second substance, if both are gases, will give

the molecular weight of the second substance. Cannizzaro chose hydrogen as the standard substance; but for reasons shown below, the present standard is oxygen.

In water, hydrogen and oxygen are combined in the ratio (by weight) of 1 to 8. Avogadro's principle and Gay-Lussac's law indicate, however, that two atoms of hydrogen are combined with one of oxygen in the water molecule. Hence, if we take one as the molecular weight of hydrogen, the atomic weight of that element will have to be one-half of 1, or 0.5, and that of oxygen will be 8. The molecular weight of water will be 9, and that of oxygen will be 16. In order to avoid atomic weights that are less than one, let us make oxygen the standard and fix its molecular weight as 32. On this basis, the molecular weight of hydrogen is 2 (really 2.016), and its atomic weight is approximately 1 (1.008). When the gram is used as the unit of weight, 2.016 g. is the gram-molecular and 1.008 is the gram-atomic weight. The atomic weight, or a multiple of it, is the smallest weight of the element ever found in the molecular weight of any of the compounds of the element. Thus, 1.008 g. of hydrogen is the smallest weight of hydrogen that has ever been found in the gram-molecular weight of any compound that contains hydrogen. The weights of hydrogen in the molecular weights of its compounds are either the same or multiples of this amount. Similarly, the least weight of nitrogen ever found in the molecular weight of a compound containing nitrogen is 14 parts per molecular weight of the compound; hence, 14 is taken as the atomic weight of nitrogen.

The molecular weight of the compound can be found, of course, in the usual manner by comparing the weights of equal volumes of oxygen and the compound, provided that the compound can be obtained in the gaseous state, and provided that the volumes are measured at the same temperature and pressure. The compound is then analyzed, and when this is done, the number of parts of the element whose atomic weight is desired, per molecular weight, can be calculated. Thus, nitric oxide, NO, is found to have a molecular weight of 30 (oxygen, 32). By analysis, it is found to contain $46\frac{2}{3}$ per cent of nitrogen, which means that $46\frac{2}{3}$ g. of each 100 g. of nitric oxide is nitrogen. In 30 g. of nitric oxide, $46\frac{2}{3}$ per cent of 30, or 14 g., is the amount of nitrogen. In

no other compound of nitrogen has less than 14 parts of that element per molecular weight of the compound ever been found. Hence, 14 must be the atomic weight of nitrogen, since it is the smallest weight of nitrogen that combines with other elements to form molecular weights of compounds, and since all other such weights of nitrogen are multiples of this amount. If anyone should find a nitrogen compound in which the parts of nitrogen per molecular weight proved to be, let us say, 21, then the atomic weight could no longer be taken as 14, since 21 is not a multiple of 14. In this case, the atomic weight would have to be changed to 7, since 14 and 21 are both multiples of that number. Other evidence (page 115), however, confirms 14 as the atomic weight of nitrogen and renders practically impossible the suggestion that any nitrogen compound can ever be prepared containing less than this number of parts of nitrogen per molecular weight.

Using the gram as the unit of weight, it has been found that 32 g. of oxygen occupies 22.4 l. when measured at 0°C. and 760 mm. of pressure. Hence, if 22.4 l. of any gaseous compound is weighed, this weight will be the gram-molecular weight of the compound. This volume, 22.4 l., is called the gram-molecular volume, since it is the volume occupied by the gram-molecular weight of any gaseous substance.

Other methods must be employed for the determination of the molecular weights of substances that are not readily obtained in the gaseous state. One of the most commonly used methods depends upon an application of Raoult's law. This law states that the vapor pressure of the solvent of a solution is directly proportional to the mole fraction of solvent. If 50 per cent of the molecules of a solution are solvent molecules, the vapor pressure of the solvent in the solution is 50 per cent of the vapor pressure of the pure solvent. It also follows from Raoult's law that the lowering of the vapor pressure of the solvent is directly proportional to the mole fraction of the solute. Thus, the vapor pressure of water in an aqueous solution of which 10 per cent of the molecules are sugar molecules is only 90 per cent of the vapor pressure of pure water. Since the boiling and freezing points of a liquid are dependent upon its vapor pressure, it follows that the lowering of the freezing point and the elevation of the boiling

point are also proportional to the mole fraction of the solute in the solution. The osmotic pressure of a solution is also proportional to the mole fraction of the solute. Raoult's law holds true only for ideal solutions, in which solute and solvent molecules are mixed and in which no chemical reaction occurs. If the solvent molecules react with those of the solute to form a third substance, the vapor pressure of the solvent cannot be directly proportional to the whole mole fraction; some of the solvent molecules have been changed into a third compound of the mixture. Speaking, therefore, of solutions as ideal mixtures, one mole of any substance in a given weight of the solvent should produce a solution in which the solvent has the same vapor pressure, boils at the same temperature, and freezes at the same temperature and for which the osmotic pressure is the same regardless of the nature of the solute. For aqueous solutions, the osmotic pressure corresponding to a concentration of 1 gram-mole of solute in 1,000 g. of water at 0°C. is 22.4 atmospheres. For a solution containing 1 gram-mole of solute in 22,400 g. of water, the osmotic pressure is one atmosphere. The freezing point of a solution containing 1 gram-mole of solute in 1,000 g. of water is -1.86°C.; the boiling point is 100.52° at 760 mm. of pressure. The molecular weight of any substance that does not undergo any chemical change when it dissolves can be determined from observations of the osmotic pressure, boiling point, or freezing point of its solution in a selected solvent. That weight of the substance is its molecular weight, which has the same effect upon the properties of the solvent in which it is dissolved as the molecular weight of some other substance produces when dissolved in an equal quantity of the solvent. If the substance for which the molecular weight is to be determined is insoluble in water, another solvent, such as benzene, may be used. In this case, the properties of a solution containing 1 gram-mole of solute in 1,000 g. of benzene are made the basis for the determination.

The Size of Atoms and Molecules

Although no one has ever observed a molecule or an atom, they appear real, because the behavior of matter seems to require them. Without them, the whole science of matter becomes unintelligible. So real do they appear, indeed, that various

determinations, such as the diameters, volumes, and masses of individual molecules and the number in a gram-molecular weight of any substance can be made. In the succeeding chapters, the dimensions of atoms and molecules and the methods by which they have been calculated will be discussed at different times. For the present, we attempt only to give some idea of how small they must be. Instead of individual molecules, we deal with gram-molecular weights of different substances. These weights contain, of course, the same number of molecules. This number is called *Avogadro's number* and, by different methods, has been found to have a value of about 6.06×10^{23}. This number, which may also be written as 606,000,000,000,000,000,000,000, is so large that we should have trouble in naming it, and still more trouble in using it in calculations, if we did not make use of the simplified system of expressing large numbers as small numbers multiplied by 10 raised to a certain power. The number is so large that we cannot visualize a collection of so many individuals. Yet, only 18 g. of water (approximately 18 cc.) contains this number of water particles. If you were offered a billion dollars to count them and were able to count 2 per second, working eight hours a day, and if you lived sixty working years, you would leave for others to count, when you were dead, 605,999,999,999,998,686,720,000 particles. You would have counted only a mere 1,313,280,000, or about the number in 0.000000000000004 cc. Not all the people in the world could win this billion dollars in sixty years. To count all these particles in this period of time would require the services of 480,000,000,000,000 persons.

Prout's Hypothesis, an Early Theory of Atomic Structure.—During the nineteenth century, atoms were regarded as solid, compact portions of matter and, hence, without structure. Not until the discovery of radioactivity did this conception of atoms give way to theories of atomic structure. We find, however, one idea of the early part of the century that was not in accord with the usual opinion. This was the idea of William Prout, a physician and chemist of Edinburgh and London. In 1815, Prout observed that the atomic weights of many of the elements are whole numbers as compared with the atomic weight of hydrogen, which is taken as unity. He interpreted this as

meaning that the elements, excepting hydrogen, are not simple substances and that their atoms are built up of different numbers of hydrogen atoms. Many of the early determinations of atomic weights, of course, were inaccurate, but on the whole the values known appeared, to Prout, ample justification of his hypothesis. His views were not shared, however, by his contemporaries. Later and more accurate determinations of atomic weights, particularly those made by Berzelius and Stas, proved, as it was thought at that time, that many elements have atomic weights that are not whole numbers. Prout's hypothesis was reasonable only as long as all, or nearly all, atomic weights were found to be multiples of the atomic weight of hydrogen. This followed from the Daltonian theory that the atoms of any one element are identical, a principle that no one questioned. Had the idea that the atoms of an element may not be identical occurred to any one, fractional atomic weights could have been explained as the average of the *whole-numbered values* of different varieties of atoms of the same element. This view would have preserved Prout's hypothesis. It appeared unreasonable, however, to think that an element may consist of two or more kinds of atoms. Even if this possibility were granted, it appeared even less possible that the different varieties should always be mixed in the same proportion to give the same average atomic weight. Prout's hypothesis appeared, therefore, out of agreement with the facts and was practically discarded until it was revived by the discoveries of the twentieth century.

Conclusion

This chapter has dealt with atoms and molecules as the units of which matter is composed. Except for the immediately preceding discussion of Prout's hypothesis, we have treated these units as discrete ultimate particles, possessing specific properties and consisting of definite kinds of matter. The idea has been accepted that molecules may be divided into atoms but that atoms are indivisible; atoms are simple portions of matter without structure. But all this was before the discovery of radioactivity and the electron.

The remainder of this book deals very largely with different theories of atomic and molecular structures and the lines of

evidence upon which they are founded. As these theories are discussed, certain defects in Dalton's atomic theory will become apparent. In a physical sense, the concept of the atom has been modified considerably. On the whole, however, we shall find that the atom today means about the same in a chemical sense as it did in the early nineteenth century. As more has been learned concerning the structure of the atom, it has become possible to explain its chemical behavior in a more satisfactory manner. But through all these changing concepts, the atom has remained the final state of division of an element in a chemical sense—the unit participating in chemical changes.

References

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Also Moore, Dampier-Whetham, Findlay, Von Meyer, Pattison Muir, and Stillman (see references at the end of Chap. I).

CHAPTER III

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

Attempts to Classify the Elements.—After the middle of the nineteenth century, there rapidly developed a vast knowledge of the chemical and physical properties of many elements and their compounds. This growth of chemistry called for a classification of the elements. The number of known elements was not great, and it was evident that many of these bore resemblances to one another. Chemical compounds could be classified most easily on the basis of the elements of which they are composed. For instance, one class of compounds consists of the oxides, another of the acids, another of the bases, etc. Elements were more difficult to classify, since the relationships among them were more obscure, although it was recognized that the number of elements could not be very large in comparison with the number of compounds. The difficulty of the classification was caused by the fact that no one knew just how many elements any correct classification should provide for.

Döbereiner, about 1825, showed that there are several triads of elements, the three members of each triad resembling one another to a marked degree. The properties of the middle member of each group represent a mean of the properties of the first and third. Examples of such triads are calcium, strontium, and barium of the alkaline earths; chlorine, bromine, and iodine of the halogens; and lithium, sodium, and potassium of the alkalis. A few years later, Dumas showed that these relations among the elements are not to be confined to triads but are much broader, each group including more than three elements. Thus, the alkaline earth triad can be expanded to include magnesium; the halogen group includes fluorine; and nitrogen, phosphorus, arsenic, antimony, and bismuth are members of the same group.

Following the explanations of Cannizzaro in 1858, Chancourtis arranged the elements, according to their atomic weights, along

TABLE I.—NEWLANDS' LAW OF OCTAVES

	No.		No.		No		No.		No.		No.		No.		No.
H.....	1	F	8	Cl	15	Co and Ni	22	Br ..	29	Pd .	36	I .	42	Pt and Ir	50
Li.....	2	Na ..	9	K .	16	Au	23	Rb	30	Ag	37	Cs . .	44	Tl ..	53
G	3	Mg	10	Ca ..	17	Zn	24	Sr ..	31	Cd	38	Ba and V	45	Pb	54
Bo	4	Al .	11	Cr	18	Y ..	25	Ce and La	32	U	39	Ta . .	46	Th .	56
C.....	5	Si .	12	Ti .	19	In	26	Zr .	33	Sn	40	W . .	47	Hg	52
N ...	6	P .	13	Mn . .	20	As	27	Di and Mo.	34	Sb..	41	Nb . .	48	Bi	55
O	7	S	14	Fe .	21	Se	28	Ro and Ru.	35	Te .	43	Au	49	Os	51

It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of 7; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves.—JOHN A. R. NEWLANDS, Aug. 8, 1865.

a helical curve, on which successive elements were separated by 16 units of length. When this was done, it was found that the elements that closely resemble one another were located one above the other. Chancourtis stated, therefore, that "the properties of the elements are the properties of numbers."

Newlands classified the elements in the order of their atomic weights into seven groups. The first member of each group was one of the first seven elements H, Li, Be, B, C, N, and O, omitting He, which should follow hydrogen. The other members of each group possessed properties similar to those of the first. Thus, the relationships of this classification were said to be in accord with Newlands' law of octaves, since, in a way, the seven groups were analogous to the musical scale. The elements H, Li, Be, B, C, N, and O correspond to the seven notes of the scale.

In 1869, Dmitri Mendelyeev made the most thorough study of the properties of the elements and their classification yet attempted and proposed the periodic law. This law states that *the properties of an element are a periodic function of its atomic weight.* There was no great difference between the classification of the elements that was proposed by Mendelyeev and that proposed by Newlands. Mendelyeev, however, first emphasized the fact that the most important recurring property of the elements is combining power, or valence. He showed that the elements can be classified into seven groups. All the members of a group possess approximately the same valence. The valences of the groups range from one to seven, respectively. Mendelyeev later added an eighth group, when Sir William Ramsay and Lord Rayleigh discovered the inert gases of the atmosphere. This was called the zero group, since these elements do not combine with other elements and, hence, possess zero valence. With only a few modifications, Mendelyeev's table serves as our present basis of classification and study of the elements.

The Periodic Table

The Short Series.—The arrangement of the elements in Table III reveals a number of striking relationships, the most important of which is probably the recurrence, or periodicity, of the properties of the elements. Starting with helium, the elements gradu-

TABLE II.—MENDELYEEV'S PERIODIC TABLE OF 1871

Group	I	II	III	IV	V	VI	VII	VIII
Formula of the oxygen compound	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Formula of the hydrogen compound			RH_5	RH_4	RH_3	RH_2	RH	
Typical elements	H(1) Li(7)	Be(9 4)	B(11)	C(12)	N(14)	O(16)	F(19)	
First period: Row 1 Row 2	Na(23) K(39)	Mg(24) Ca(40)	Al(27 3)	Si(28) Ti(50)	P(31) Va(51)	S(32) Cr(52)	Cl(35.5) Mn(55)	Fe(56), Co(59), Ni(59), Cu(63)
Second period: Row 1 Row 2	Cu(63) Rb(85)	Zn(65) Sr(87)	Yt(88)	Zr(90)	As(75) Nb(94)	Se(78) Mo(96)	Br(80)	Ru(104), Rh(104), Pd(104), Ag(106)
Third period: Row 1 Row 2	Ag(108) Cs(133)	Cd(112) Ba(137)	In(113)	Sn(118) Ce(138)	Sb(122)	Te(128)	I(127)	
Fourth period: Row 1 Row 2					Ta(182)	W(184)		Os(199), Ir(198), Pt(197), Au(197)
Fifth period: Row 1 Row 2	Au(197)	Hg(200)	Tl(204)	Pb(207) Th(232)	Bi(208)	Ur(240)		

TABLE III.—THE MODERN PERIODIC TABLE

Group → 0		I	II	III	IV	V	VI	VII	VIII
Period ↓ 1		H(1) 1 008							
2	He(2) 4	Li(3) 6 94	Be(4) 9 02	B(5) 10 82	C(6) 12	N(7) 14	O(8) 16	F(9) 19	
3	Ne(10) 20 2	Na(11) 23	Mg(12) 24 32	Al(13) 26 97	Si(14) 28 06	P(15) 31.027	S(16) 32 064	Cl(17) 35 46	
4	A(18) 39 91	K(19) 39.096	Ca(20) 40 07	Sc(21) 45 10	Ti(22) 47 90	V(23) 50 95	Cr(24) 52 01	Mn(25) 54 93	Fe(26) 55 84 Co(27) 58 94 Ni(28) 58 69
		Cu(29) 63 57	Zn(30) 65 38	Ga(31) 69 72	Ge(32) 72 60	As(33) 74 91	Se(34) 78 96	Br(35) 79 92	
5	Kr(36) 83 7	Rb(37) 85 44	Sr(38) 87 63	Y(39) 88 92	Zr(40) 91 22	Cb(41) 93 3	Mo(42) 96 0	Ma(43) ?	Ru(44) 101 7 Rh(45) 102 91 Pd(46) 106 7
		Ag(47) 107.88	Cd(48) 112 41	In(49) 114 76	Sn(50) 118 7	Sb(51) 121 76	Te(52) 127 61	I(53) 126 92	
6	Xe(54) 131 3	Cs(55) 132 91	Ba(56) 137 36	La(57)* 138 92	Hf(72) 178 6	Ta(73) 181 4	W(74) 184 0	Re(75) 186 31	Os(76) 191 5 Ir(77) 193 1 Pt(78) 195 23
		Au(79) 197 2	Hg(80) 200.61	Tl(81) 204 39	Pb(82) 207 22	Bi(83) 209 0	Po(84) 210	(85)	
7	Rn(86) 222	(87)	Ra(88) 225.97	Ac(89) 228	Th(90) 232.12	Pa(91) 234 ?	U(92) 238.14		

* The following elements, which are commonly called the *rare earths*, have atomic numbers between 57 and 72 La(57), 138.92; Ce(58), 140.13; Pr(59), 140 92; Nd(60), 144.27; Il(61), ?; Sm(62), 150.43; Eu(63), 152; Gd(64), 157 3; Tb(65), 159.2; Dy(66), 162.46; Ho(67); 163 5; Er(68), 165 2; Tm(69), 169 4; Yb(70), 173.04; Lu(71), 175. All of these elements have approximately the same properties and are regarded as occupying the same position in the periodic table.

Numbers in parentheses refer to the atomic numbers of the elements, *i.e.*, to their order in the table.

Numbers below the symbols of the elements refer to the atomic weights of the elements.

ally change from lithium, which is a very active metal, through beryllium, boron, carbon, nitrogen, and oxygen, all of which are increasingly non-metallic in character, to fluorine, which is an active and typically non-metallic element. The next eight elements—neon to chlorine—form a series each member of which resembles an element in the first series. Thus, the ninth (Ne) is like the first (He); the tenth (Na) is like the second (Li); and so on through the list. The properties of the elements of each pair are very much alike. Helium and neon are inert gases. Lithium and sodium are very active, univalent metals. Beryllium and magnesium, boron and aluminum, carbon and silicon, nitrogen and phosphorus, oxygen and sulfur, and fluorine and chlorine are other pairs of very closely related elements.

The Long Series.—The series following chlorine is much longer than those that precede it. It begins with argon, which resembles helium and neon. Potassium is much like sodium. But the resemblance toward the corresponding elements of the first two series decreases as we go along the third series. When we come to chromium and manganese, the differences become rather pronounced. These two elements only slightly resemble sulfur and chlorine, respectively. Iron, cobalt, and nickel in the middle of this series do not show any marked resemblances to any of the elements of the first and second series. They are placed, therefore, in a new group. Since they are very much alike, these three elements are made to occupy one position in the periodic table. Similar triads occur in the succeeding series; thus, the group 8 elements of the second long series are ruthenium, rhodium, and palladium; those of the third long series are osmium, iridium, and platinum.

After nickel in the first long series, the periodicity is taken up again with copper, which with its positive valence of one is somewhat like potassium, sodium, and lithium. The elements of the latter half of this series, however, do not resemble the elements above them in corresponding positions so closely as they resemble the elements in the same positions of the succeeding long series. Thus, copper does not resemble any of the elements that lie above it in group 1 except in the matter of valence; it does form compounds in which it has a positive valence of one. But even in its univalent state, the resemblance is not very striking; and

furthermore, the usual valence of copper is two, as in $CuCl_2$. Zinc is not much like calcium; zinc hydroxide acts as an acid as well as a base, while calcium hydroxide acts only as a base. Arsenic resembles nitrogen and phosphorus more closely, however—even more closely than it does vanadium, which is directly above it and in the first half of its own series. Similarly, selenium and bromine are very closely related to sulfur and chlorine, respectively, and are not very much like chromium and manganese.

The second and third long series are much like the first. The first half of each series starts out with elements that closely resemble the corresponding members of the first two (short) series. This likeness, however, changes as we progress toward the triad of elements in group 8; the elements more closely resemble the elements of the first half of the first long series. Thus, molybdenum and tungsten resemble chromium, and none of these is very closely allied to oxygen and sulfur. In the second half of each of these long series, the order of the first half is reversed. The first members resemble the elements of the last half of the first long series but not the corresponding elements of the two short series. Thus, silver and gold are like copper but not very much like the alkalis, although they do have a valence of one. The last members, however, resemble the corresponding elements of the two short series. Thus, tellurium and iodine resemble sulfur and chlorine more closely than they do chromium and manganese, respectively. It appears, therefore, that each of the seven groups is divided into two subgroups, as shown in Table III. Sometimes, the only likeness to be found among the members of the two subgroups is the property of maximum valence.

In the third long series occurs a group of elements—lanthanum to lutecium—called the rare-earth group. These elements resemble one another very closely—so closely, in fact, that for a long time they were regarded as a single element. Because of their great similarity, the rare earths are placed together in one position in the periodic table.

Some of the Features of the Periodic System.—Some of the more important conclusions to be drawn from an examination of the periodic classification and some of its defects are discussed briefly below.

1. Reading down in each group, the metallic properties of the elements become more pronounced, or, in other words, the nonmetallic character diminishes. Thus, radium is the most active metal in group 2. Iodine is most like a metal of all the halogens in group 7.

2. The middle groups contain nonmetals at the top and metals at the bottom.

3. There are 92 positions in the table. Each element may be assigned a number which represents its proper position with respect to other elements. These are called the *atomic numbers* of the elements. There is one blank in the table—No. 85. Claims for the discovery of this element have been advanced recently. Other blanks have been filled in fairly recent times; rhenium (75), masurium (43), illinium (61), and No. 87, which has not yet been named, all have been placed in the table within the last fifteen years.

4. Hydrogen is left out of the periodic arrangement. Its location is an interesting problem. Should it be placed at the top of group 1? It has the same valence as lithium and the other members of this group, but it does not resemble these elements in other respects, particularly in metallic properties. Or should hydrogen be placed at the top of group 7? Like fluorine and chlorine, it is a gas, but its usual valence is not at all like that of the nonmetals.

5. Many of the elements (reading across) differ in atomic weights by four or by multiples of four units. This is especially noticeable if we disregard the small fractions by which many of the atomic weights differ from whole numbers. We shall learn in a later chapter (page 115) that these may be disregarded. Thus, helium has the atomic weight of 4; carbon, 12; oxygen, 16; and neon, 20; magnesium and silicon differ by four units; argon and titanium, by eight units; and titanium and chromium, by four units. It is also strange that so many elements have atomic weights that are exact multiples of four.

6. In addition to valence and other chemical properties, the periodicity of the elements includes the recurrence of such physical properties as density, coefficient of expansion, hardness or softness, ductility, magnetism, melting point, malleability, conductivity of heat, and compressibility.

7. If we examine the table closely, we find that the locations of some of the elements are contradictory to the periodic law. If potassium and argon were placed in the table in the exact order of their atomic weights, argon would fall in group 1 and potassium in the zero group. This would place these elements in groups where they do not belong. Potassium is not like the members of the group of inert gases, and argon does not resemble the alkali metals. Similarly, inconsistencies exist in the positions occupied by iodine and tellurium and by cobalt and nickel. In cases where the arrangement of the elements according to their atomic weights does not agree with the chemical properties of the elements, atomic weights are disregarded, and the elements are placed in the groups to which their properties correspond.

Other defects of Mendelyeev's periodic table may be briefly reviewed. (1) There is no definite place in the table for hydrogen. (2) Several groups of elements, each group consisting of three members (Fe, Co, and Ni, for example), must be placed in group 8, although most of these never exhibit a valence of eight. (3) All the rare-earth elements must occupy the same position and, at best, are not very well taken care of in the table.

In spite of all these defects, however, Mendelyeev's table is without serious inaccuracies and has served as the foundation for the classification and organization of chemical knowledge during the development of the modern science of chemistry. It has stimulated research directed toward the discovery of "missing" elements which the table showed should exist but which had hitherto not been isolated or recognized. Then, too, it has served as a guide in the preparation and identification of the compounds of a great many of the rare and unusual elements. Since the positions of the elements in the table depend upon their atomic weights, the periodic arrangement has also stimulated careful analytical work to determine exact values for atomic weights.

The periodic classification aroused all sorts of speculation concerning the structure of atoms. The periodic feature of the table, the families and groups of related elements, the gradual transitions in properties through a series of elements with abrupt changes at the end—all these facts pointed toward a common origin of the elements. It became increasingly more evident that

atoms are not the ultimate subdivisions of matter. Atoms were shown to have properties that gradually change from element to element as the atomic weight increases. This gradation of properties finally ceases abruptly and then begins all over again. This suggested that the structures of the atoms gradually change, as if, perhaps, some structural unit were added, one unit at a time, until a certain part of the atomic model were completed. Another portion of the structure is then started by the addition of more of the same units. Mendelyeev, himself, did not see in the periodic law any reason for such speculation. But the fact remains that this law has been responsible for much of the investigation that has led to our present knowledge of the structure of atoms. We shall return to this subject at a later time, when we shall show why it is that the elements can be arranged in the various groups and why it is almost, but not quite, true that "the properties of the elements are periodic functions of their atomic weights."

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CHAPTER IV

RADIOACTIVITY AND THE RADIOACTIVE ELEMENTS

Radioactivity

The Discovery of Radioactivity.—In 1896, Röntgen discovered x-rays. Their peculiar properties stimulated many scientists to seek sources of the same, or similar, radiation among the elements and their compounds. X-rays affect the photographic plate; and so, many substances were studied in efforts to find something that would similarly exhibit photographic effects. Becquerel found that uranium potassium sulfate, when wrapped in paper, affects the plate in the same manner as x-rays and other forms of radiation. Further study proved that pure metallic uranium or any compound of uranium has the same effect and that the action does not decrease with age. Becquerel's observations amounted to the discovery of a new property for some forms of matter. This property was given the name of *radioactivity.*

Later, Madame Curie studied many of the elements and found one whose compounds act in the same manner as those of uranium. This was thorium. It was also shown that the activity of substances containing uranium is proportional to the number of uranium atoms present and is entirely independent of the other atoms in the compound. Evidence was also obtained that uranium minerals contain other radioactive elements. Their radioactivity is about five times as great as the number of uranium atoms present would indicate.

Madame Curie investigated a ton of material supplied by the Austrian government from its Bohemian uranium plant. This material consisted of pitchblende residues from which most of the uranium had been extracted. Pitchblende is a complex substance containing the oxides and sulfides of such metals as uranium, lead, calcium, iron, and magnesium; it also contains much silica as well as other compounds. From this residue, Madame Curie prepared compounds of an element that is much

more strongly radioactive than uranium. Madame Curie called this element polonium, from Poland, her native country. She also discovered a second element, radium, which is several thousand times as active as uranium. With her husband, Pierre, she prepared 0.1 g. of pure radium chloride. With this small amount of material, the spectrum of the element was studied, and its atomic weight was determined. Chemically, radium was found to resemble the alkaline earth elements magnesium, calcium, strontium, and barium. After the death of her husband, Madame Curie prepared pure radium and made many very thorough studies of this and other radioactive elements. She was twice the recipient of the Nobel prize, once alone, and once with Becquerel and her husband.

Several other radioactive elements have been identified. These are found either in minerals containing thorium or uranium or in preparations of compounds of certain other radioactive elements, such as radium and polonium. Some of these elements persist in their radioactivity for seemingly endless periods of time; the activity of others endures for only a few hours, minutes, seconds, or even fractions of seconds. Starting with a pure sample of a given element or one of its compounds, the activity decreases with time, and the rate of decrease is a characteristic of the element. Furthermore, it has been shown that as the activity of one element decreases, other elements appear. Hence, although we may prepare as pure a sample of one element as possible, other radioactive elements soon make their appearance and begin their characteristic radioactive changes. These facts indicate that the different elements are continuously produced and are, in turn, continuously disintegrating in the process of radioactivity. This is true of all the known active elements except thorium and uranium which, therefore, are regarded as the parent elements from which the others are derived.

In all, there are some 40 kinds of atoms that display the property of radioactivity and that have atomic weights greater than 200. These elements are members of three series. One series consists of those elements associated with uranium; a second, with actinium; and a third, with thorium. The members of the uranium and thorium families are independent, but the actinium

series appears to be either a branch from the uranium group or derived from a certain kind of uranium atom. In addition to these elements, potassium and rubidium are known to be feebly radioactive.

The ability of radioactive substances to affect the photographic plate was thought to be due to the radiation of energy by the atoms of the radioactive elements. The character of this radiation was not understood, although it was naturally assumed that it was like x-rays. It soon became evident, however, that three kinds of rays were emitted, although all three kinds were not emitted by any one element. The kind of ray and its properties were found to be characteristic of the element from which it was radiated.

One of the rays was absorbed by a layer of air a few centimeters thick; another was absorbed by a sheet of aluminum a few millimeters in thickness; while the third was found to pass through about 20 cm. of iron. The first of these was called the *alpha*, the second the *beta*, and the third the *gamma* ray.

Alpha Rays

Alpha rays are not true rays, like light and x-rays. They consist of particles of matter. A narrow beam of these "rays" is deflected toward the negative plate when it is passed between the two plates of an electrical condenser. The rays are also deflected by a magnetic field (Fig. 1). From the character of these deflections, it is evident that the particles that compose the rays carry positive electrical charges. Furthermore, they are found to ionize molecules of any gas between the plates of the condenser by dislodging negatively charged bodies, called *electrons*, from the molecules of gas with which they collide. The ions produced in this manner move toward the oppositely charged

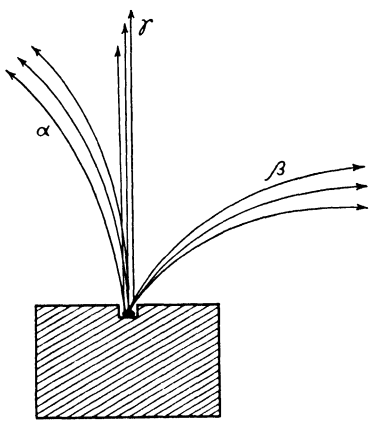

Fig. 1.—Effect of a magnetic field upon alpha, beta, and gamma rays.

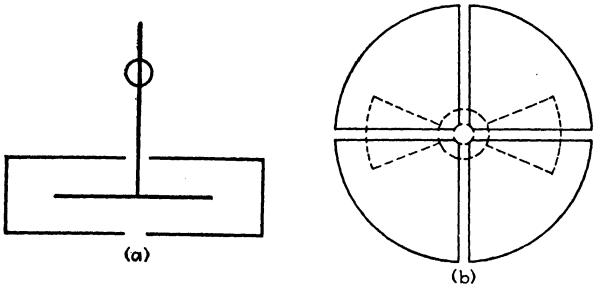

FIG. 2.—Electrometer. (*a*) The needle. Its rotation is observed by means of a scale and a telescope that is focused on the small mirror fastened to the wire that supports the needle. (*b*) The quadrants. The needle rotates on its suspension in a brass box, which is split into four quadrants. Opposite quadrants are connected and the two pairs of quadrants are oppositely charged. The needle is charged also and is attracted toward one of the pairs of quadrants and repelled by the other. The deflection of the needle is a measure of the difference of potential between the quadrants.

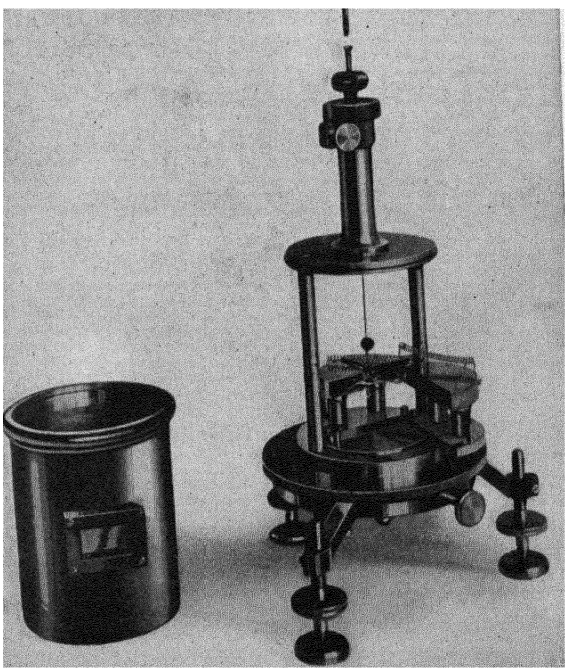

FIG. 3.—The quadrant (Dolezalek) electrometer. (*By courtesy of the Gaertner Scientific Corporation.*)

plate of the condenser, where they are discharged and thus lower the difference of potential. The plates are connected to an instrument (electroscope or electrometer, Figs. 2 and 3) that indicates the potential, or change of potential. By this means, the rates of discharge, and hence the relative intensities of beams of rays, are measured. If the rays pass through a space that is supersaturated with water vapor, the ions produced along the paths of the alpha particles act as nuclei for the condensation of water vapor. These paths, which are made up of tiny droplets of water, can be photographed and are sometimes called alpha-ray *fog tracks.* When alpha particles strike a screen covered with zinc sulfide, each particle produces a tiny flash of light as it strikes. If a microscope is focused upon this screen, the number of alpha particles emitted by a sample of radioactive material can be counted. Not all the alpha particles emitted strike the screen, of course, but if the area of the screen is known, and if the screen is considered as a part of a spherical surface entirely inclosing the source of the alpha particles, the total number of particles emitted can be calculated.

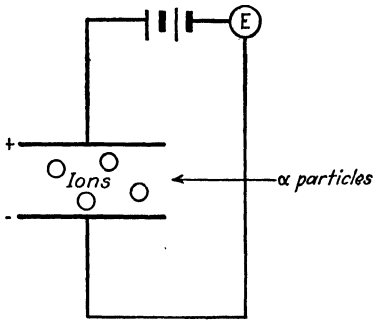

FIG. 4.

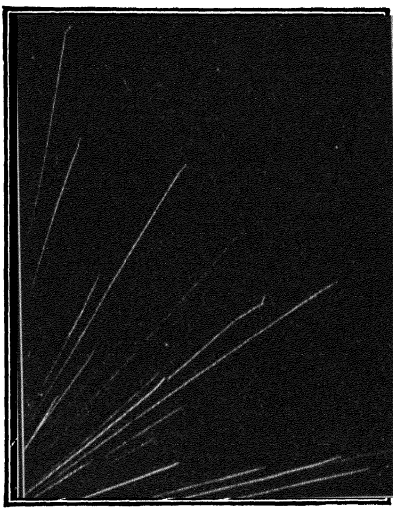

FIG. 5.

FIG. 4.—Ionization of a gas by alpha rays and the measurement of the ionization current.

FIG. 5.—Photograph of alpha-ray fog tracks. (*Reproduced by permission of the authors of Jette and La Mer's translation of Eucken's "Fundamentals of Physical Chemistry" and the McGraw-Hill Book Company, Inc.*)

The Rate of Emission of Alpha Particles.—The number of alpha particles emitted by a given substance in one unit of time can also be counted by means of a device called the Geiger counting tube (Fig. 6). The radioactive substance which is the source of the alpha particles is placed in the center of the spherical chamber *S*. This chamber is connected to the tube *T* by a small opening. Both the area of the surface of the sphere and that of the opening are accurately known. The tube contains a pointed wire, which is well insulated from the metallic walls. This wire is connected to the amplifying and phone circuits, as shown in the figure. When the voltage of these circuits is properly adjusted, each alpha particle that enters the

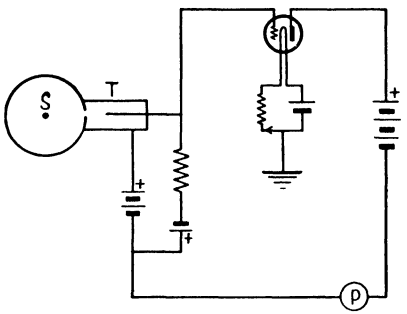

FIG. 6.—Geiger counting tube.

tube through the opening from *S* makes its presence known by a sound in the phones. This effect is due directly to the ions which the alpha particle produces in the tube. These move toward the wire, since they are positively charged, and thus produce a feeble ionization current. The number of particles that enter the tube can be counted for any known period of time. Then, from the surface of the sphere and the area of the opening, the total number of particles emitted by the substance in *S* can be calculated.

The Electrical Charge of an Alpha Particle.—It is also possible to measure the total charge that is carried by all the alpha particles emitted by any radioactive substance in a definite period of time. This determination is made by means of the Faraday cylinder (Fig. 7). Both the cylinder and the radioactive material are placed in an evacuated container to prevent ionization of gases by the alpha particles. Some of the particles

emitted by the source R pass through the opening O into the cylinder. This cylinder is connected to an electrometer E, by means of which the charge due to the entrance of the particles is measured. The area of the opening must be known. It is also necessary that we calculate the area of a sphere whose center is R and whose radius is the distance from R to O. With these facts known, it is possible to calculate the charge carried by all the alpha particles emitted by the radioactive substance in a definite period of time.

The number of alpha particles emitted by a given radioactive material per second and the total charge of these particles being known, it is easy to calculate the charge per particle. This has been found to be 9.54×10^{-10} e.s.u. This charge is twice as great as the charge of a single hydrogen ion in solution.

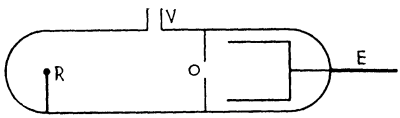

FIG. 7.—Faraday cylinder used in measuring total charge per second. The tube is evacuated by means of a pump connected at V.

The Nature of the Alpha Particle.—The ratio of the charge to the mass of the alpha particles can be determined from observation of the deflections of the particle in electric and magnetic fields. The method by which such determinations are made is discussed in the next chapter, since it has been most accurately applied to the determination of the ratio of the electron's charge to its mass. For the alpha particle, the ratio of e_1, the charge, to m_1, the mass, has been found to be 4.823×10^3 e.m.u. per gram. For the hydrogen ion in solution, the ratio e_2/m_2 is 9.573×10^3 e.m.u. per gram. Hence,

$$\frac{e_1/m_1}{e_2/m_2} = \frac{4{,}823}{9{,}573}.$$

But the charge of the alpha particle is twice that of the hydrogen ion:

$$e_1 = 2e_2.$$

Hence,

$$\frac{2e_2/m_1}{e_2/m_2} = \frac{4{,}823}{9{,}573}.$$

Simplifying this equation, we write

$$\frac{4{,}823e_2}{m_2} = \frac{19{,}146e_2}{m_1},$$

or

$$4{,}823m_1 = 19{,}146m_2.$$

Dividing each side of this equation by $4{,}823m_2$, we obtain

$$\frac{m_1}{m_2} = \frac{19{,}146}{4{,}823} = 3.97.$$

Hence, the mass of the alpha particles is 3.97 times that of the hydrogen ion. It appears, therefore, that the alpha particle is an atom of helium, since the atomic weight of helium (4) divided by the atomic weight of hydrogen (1.008) is 3.968.

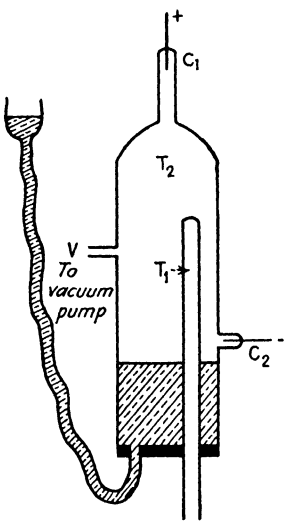

FIG. 8.—Apparatus used by Rutherford in showing that alpha particles are helium ions.

By means of the following experiment, Rutherford proved beyond any doubt that the alpha particle is an atom of helium (bearing a positive charge): He placed radium emanation (radon), which is a radioactive gaseous element, in the inner tube T_1 (Fig. 8). This tube was made of very thin glass, through which alpha particles ejected by radium emanation could pass. The outer tube T_2 was made of thicker glass through which the particles could not pass. Two electrodes were sealed into capillary tubes C_1 and C_2. The outer tube was practically filled with mercury. Any gas in this tube could be compressed by raising the level of mercury. The tube T_2 was evacuated as completely as possible, and the apparatus was allowed to stand for several days. Then the mercury level was raised, and the gas in T_2 was slightly compressed. An electrical discharge could now be made to pass between the two electrodes. The light from this discharge showed all the lines of the helium spectrum. It was necessary, of course, to prove that the radioactive gas contained

in the thin-walled inner tube did not contain helium which slowly filtered through the glass wall and into the outer tube. When pure helium was placed in the inner tube, no helium spectrum was obtained even after many days. The experiment proved, therefore, that the helium that appeared in the outer tube came from the penetrating alpha rays and that, in fact, these rays consist of helium atoms.

The Range of the Alpha Particle.—Alpha particles are shot out of radioactive atoms with very high velocities of 1.4×10^9 to 2×10^9 cm. per second. Because of their high velocities and their relatively great masses—the helium atom is four times more massive than the hydrogen atom and 7,400 times more than the electron—alpha particles possess tremendous amounts of kinetic energy for their size. They pass through some 200,000 molecules of oxygen and nitrogen in the air, knocking off electrons and ionizing the molecules as they go, before they lose their energy in collisions and are brought to a stop. Their range is the distance traveled in the medium before their energy is completely dissipated or at least becomes so small that the particles no longer possess ionizing power. This distance varies from about 2.5 to 11 cm. in air at 0°C. and 760 mm. of pressure, depending upon the radioactive element that emits the particles. For any one element, and under constant conditions of the atmosphere through which they pass, the velocity and range of all the alpha particles are the same.

The determination of the range of the alpha particles from a sample of radioactive material is important, since it offers a means of identifying the elements from which the alpha particles come. The range can be measured by means of a fluorescent screen upon which the particles produce scintillations when they strike. The maximum distance of the screen that permits scintillation is the maximum range of the particles. The range can also be measured by means of an ionization chamber, attached to an electrometer E (Fig. 9). The chamber is moved through different distances d from the source of the alpha particles. At each distance, a definite ionization current is measured by the electrometer. The current is proportional to the number of ions produced in the chamber by the beam of alpha rays. If the number of ions, or the strength of the ionization current, is

plotted against the distance between the chamber and the radioactive source, a curve (Fig. 10) is obtained. This curve rises steeply just before the distance reaches the maximum, and then

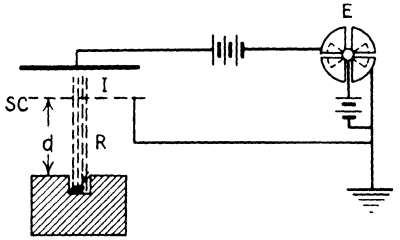

FIG. 9.—Ionization chamber used to determine the range of alpha particles. The radioactive material is placed in a small opening (*R*) in a lead block. The rays pass through the screen (*SC*) and into the ionization chamber (*I*).

drops sharply. The point at which this curve intercepts the *d* axis is, of course, the maximum range. This varies with temperature and pressure; hence, it is necessary, for comparison, that

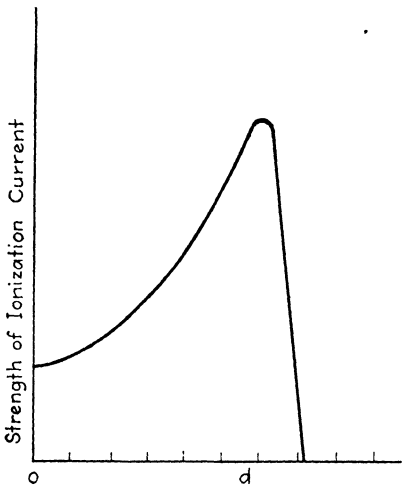

FIG. 10.—Relation of distance from source to the ionizing effects of alpha particles.

the maximum ranges of alpha particles from different sources should be determined under the same conditions.

It will be observed that an alpha particle produces the greatest number of ions not in the early part of its flight but near the end

when its energy has been largely spent. This may seem contrary to expectation. It is due, no doubt, to the very great velocities of the alpha particles when they are first liberated. Traveling as rapidly as they do at that time, they fly by atoms and molecules so quickly that there is not sufficient time for an electron (negative charge) to be dislodged before the alpha particle has passed beyond the effective range. After traversing a few centimeters of the gas, however, the alpha particles have slowed down considerably, and there is a longer period of time during which they may act to dislodge electrons from atoms near which they pass.

Avogadro's Number. A Method by Which It May Be Determined.—Since the number of alpha particles emitted by a radioactive substance can be counted by means of a fluorescent screen, and since the volume occupied by these particles can also be measured, it should be possible to make a direct determination of the number of molecules of helium in that volume and, hence, in any volume at the same temperature and pressure. Sir William Ramsay and Prof. Frederick Soddy measured the rate at which radium emits alpha particles as 158 c. mm. per gram per year at 0°C. and 760 mm. of pressure. Now, 1 g. of radium, in equilibrium with the short-life products that are found associated with it, emits 13.8×10^{10} alpha particles per second, or 4.35×10^{18} per year. This, therefore, is the number of atoms (or molecules, since helium molecules are monatomic) in 158 cu. mm. of helium under standard conditions. Since 1 cc. contains 1,000 cu. mm., 1 cc. contains $1{,}000/158 \times 4.35 \times 10^{18}$, or 2.75×10^{19} molecules. The gram-molecular volume, 22.414 l., should contain, therefore, $22{,}414 \times 2.75 \times 10^{19} = 6.16 \times 10^{23}$ molecules of helium or any other gaseous element or compound. This number is called Avogadro's number. Millikan's value (page 94) of 6.06×10^{23} is somewhat more accurate and is generally accepted.

Beta Rays

Beta "rays" are also streams of particles. These particles are negatively charged, as shown by their deflection toward the positive plate of a condenser and by their deflection in a magnetic field, which is opposite to that of the alpha particle (Fig. 1, page 49). They are called *electrons* and are identical as regards

mass and charge, whatever atom emits them. The mass of the electron is about 1/1,845 of the mass of the hydrogen atom.

Electrons, or beta particles, are emitted by radioactive substances with very high velocities, which range from about 30 to 97 per cent of the velocity of light. The velocity of the electrons emitted from any one radioactive element, however, is not constant but varies over a considerable range.

The Velocity of Beta Particles.—The velocity of beta particles is determined by means of the beta-ray spectrograph (Fig. 11). The whole apparatus is inclosed in a metal box, which is evacuated. The lower part of this box is filled with lead. A small opening O contains the source of the beta particles. At one end of the box, a photographic plate P is placed flush with the surface of the lead. Beta rays pass through a slit A at the top of the opening. The beam of rays is acted upon by a magnetic field acting at right angles to its path. The particles that have the smallest velocity are bent most by the magnetic field. Hence, they travel in an arc of greater curvature and strike the part of the photographic plate near the slit. The velocity of the particles that strike the plate at a definite distance d from the slit may be calculated from a knowledge of the magnetic force that acts upon the particles and the centrifugal force displayed by the particle in its circular path. The former is proportional to Hev, where H is the strength of the magnetic field and e and v are the charge and velocity of the beta particles. The latter is proportional to mv^2/r, where m is the mass of the beta particle and r is the radius of the circular path that the particles take. These two forces are equal. Hence,

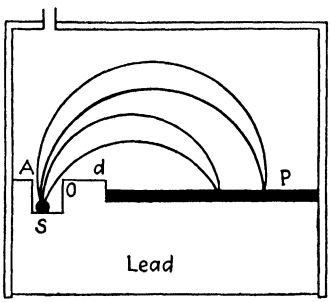

FIG. 11.—Beta-ray spectrograph.

$$Hev = \frac{mv^2}{r}.$$

From this equation, we calculate the value of v as follows:

$$Hevr = mv^2,$$
$$Her = mv,$$

and

$$v = \frac{Her}{m}.$$

The values of H, e, and m are known, and that of r can be determined from the lengths of the lines d and SA (Fig. 11). When the electrons possess high velocities, it is necessary to take into account the change of mass with velocity, or the "relativity mass," defined by the equation

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}},$$

where m_0 is the mass of a low-speed electron and c is the velocity of light (see page 95).

Investigations of the velocities of the beta particles ejected by different atoms lead us to the conclusion that these particles come from two different portions of the atomic structure and are liberated by different means. One group of beta particles appear to originate in the same portion of the atom as alpha particles; this is the very heart of the atom, its nucleus. The other group consist of particles that are liberated from the outer portions of the atom by the action of gamma rays. These rays, like light and x-rays, are capable of liberating electrons (or beta particles) from atoms upon which they fall. Thus, gamma rays liberate electrons from the atom in which they, themselves, originate.

Ionization by Beta Particles.—Although they have high velocities, the kinetic energy

$$\text{K.E.} = \tfrac{1}{2}mv^2$$

of beta particles is not very great as compared to the energy of alpha particles. The mass of the latter is some 7,400 times greater, and its velocity is about one-tenth as great as that of the electron. Beta particles possess sufficient energy, however, to ionize particles of the gas through which they pass. Hence, the paths of these particles can be photographed by the "fog-track" method. Because of their small momentum and kinetic energy, the particles suffer rather radical changes in the direction of their motion when they collide with molecules of gases contained in the space through which they travel. Their fog tracks, there-

fore, are not straight lines. Also, because they produce fewer ions to act as nuclei for the condensation of water vapor, the tracks of electrons are not continuous or solid lines, as are those of the alpha particles.

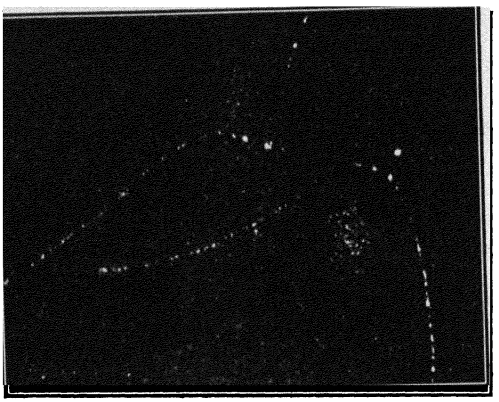

FIG. 12.—Photograph of beta-ray fog tracks. *(Reproduced by permission of the authors of Jette and La Mer's translation of Eucken's "Fundamentals of Physical Chemistry" and the McGraw-Hill Book Company, Inc.)*

GAMMA RAYS

Gamma rays are not deflected by magnetic and electrical fields. Like light and x-rays, they consist of electromagnetic radiation; they travel with the velocity of light and display other properties that serve to identify them with radiant energy. There is no evidence to indicate that they resemble alpha and beta rays in consisting of material particles, corresponding to electrons and helium atoms. Their frequencies are much greater than those associated with the spectrum of visible light, and their wave lengths are correspondingly shorter, ranging from 1.365 to 0.0047 Ångström unit (Å.). They have greater penetrating power than either beta or alpha rays.

The emission of gamma rays appears to be associated in some manner with the ejection of beta particles. Elements whose atoms eject beta particles during radioactive disintegration almost always emit gamma rays. Each element gives the complete gamma-radiation spectrum, but each also gives certain characteristic wave lengths.

The Theory of Radioactive Change

Radioactivity is independent of all chemical combinations of an atom. It is unaffected by external conditions such as temperature. It appears, therefore, that radioactivity is an atomic property which operates in accordance with the laws of probability.

Since they emit atoms of helium and electrons, it seems reasonable to believe that the atoms of the radioactive elements are composed, in part at least, of these particles. Now, the alpha particle and the electron are oppositely charged, and an atom may contain more of one of them than of the other. Let us assume that the particles are in motion and are closely packed. Tremendous electrostatic forces result from the charges of the particles, particularly since they are separated by very small distances. These forces are both attractive and repulsive in character; there is attraction between particles of unlike charge and repulsion between those of like charge. Under these conditions, we should expect that the particles would arrange themselves within the atom in such a manner that these forces are in equilibrium with one another. There may be several such arrangements. But there may also be one or more configurations into which electrons and alpha particles may fall which are unstable. For any one atom there is a certain number of chances that the particles which compose it will fall into an unstable grouping. When this happens, a particle of one kind or the other is expelled, and the arrangement assumes a more stable form. For a large number of atoms of the same kind, the same probability factor determines the percentage of atoms that fall into the unstable arrangement in a given period of time. This percentage will, of course, be different for atoms that contain different numbers of electrons and alpha particles. Another theory that attempts to account for the disintegration of the atoms of radioactive elements and the expulsion of particles from them is presented in the last chapter. This view of the problem is based upon a new system of mechanics for the atom, and its discussion is consequently postponed until the time when this system of mechanics has been presented.

Rutherford and Soddy's Theory of Transformation

If electrons or alpha particles are expelled from atoms during radioactive changes, it is evident that atoms of a different nature must result. In 1902, Sir Ernest Rutherford and Prof. Frederick Soddy suggested that the atoms of radioactive elements do disintegrate, forming the atoms of other elements. In confirmation of this suggestion, Rutherford found that radium produces a gaseous element which is not helium. He condensed this gas and found that it, too, is radioactive. Its activity was found to disappear, however, in a short time; a solid residue, also radioactive, next appears. Chemically, the gas is like helium and the other elements of the zero group. It was first called radium emanation, later niton, and is now called radon. Its molecular weight was found by Ramsay to be 222, which is also the atomic weight, since the elements of the zero group are monatomic. The atomic weight of radium is 226. Radium also liberates alpha particles, which have an atomic weight of 4 (helium). The conclusion that an atom of radium loses an atom of helium, thus changing into an atom of radon, naturally follows.

$$\begin{array}{ccccc} \text{Radium} & \longrightarrow & \text{radon} & + & \text{helium} \\ (226) & & (222) & & (4) \end{array}$$

Rate of Disintegration.—The intensity of the activity of any radioactive element is proportional to the number of atoms of the element that disintegrate per second. The number of atoms that disintegrate is proportional, in turn, to the total number of atoms of the element. To show the decrease in active elements with time, we may use the equation

$$\frac{N}{N_0} = e^{-\lambda t},$$

where N_0 and N are the numbers of active atoms at the beginning and at the end of the period of time t, e is the base of the Napierian system of logarithms, and λ is the transformation constant. This relation can also be expressed as

$$\frac{dN}{dt} = -\lambda N.$$

Here λ stands for the fraction of the atoms that disintegrate in the period of time *dt*. The quantity λ has a definite value for each radioactive element, but it is seldom used to identify an element. Instead, the time required for one-half of the atoms present to be transformed into atoms of another element is most generally used. This "half-life" period in the element is equal to $\frac{1}{\lambda} \log_e 2$.

To determine the half-life period of radium, for example, the number of alpha particles emitted by one gram of the element in a

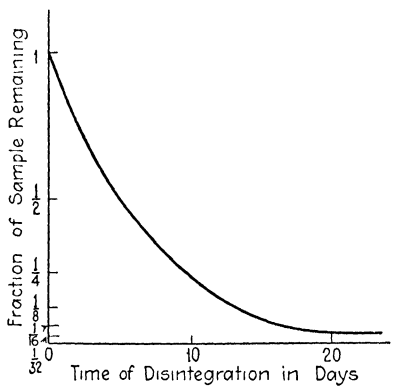

FIG. 13.—Rate of disintegration of radon.

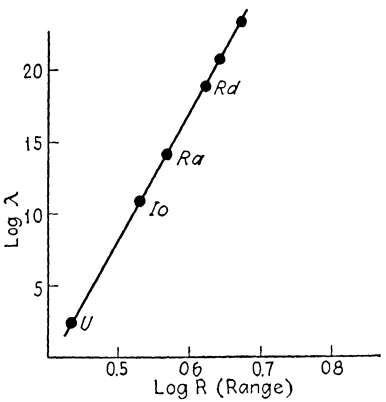

FIG. 14.—Relation of the range of alpha particles to λ the disintegration constant.

definite period of time is counted by means of the fluorescent screen. Since radium is very rare, only a very small fraction of one gram is actually used, but the results can be calculated upon the basis of one gram of the element. The number of alpha particles emitted divided by the total number of atoms in one gram gives the fraction that disintegrates in this period of time. From this fraction, the time required for half of the atoms to disintegrate can be calculated. This method requires that the radioactive substance be isolated from others. This separation is sometimes made by chemical processes, such as fractional crystallization, precipitation, volatilization, and electrolysis. The parent substances can be removed satisfactorily in this way,

but, of course, it is impossible to separate an element completely from its products, which are being formed at all times.

Another method that is used to determine the half-life period depends upon a general law of radioactivity which describes the relation between the life and range of the alpha particles emitted by the substance. According to this law, the logarithm of λ, the fraction of atoms disintegrating per second, is equal to the sum of the constant A and the product of the logarithm of the range R by a second constant B:

$$\log \lambda = A + (B \times \log R).$$

The constants A and B can be evaluated from cases in which λ and R are known. These constants, particularly A, depend upon the series to which the substance belongs.

If the logarithm of the range of the alpha particles is plotted against the logarithm of λ, a straight line is obtained (Fig. 14). Estimates of the half-life period of radioactive elements of very short duration can be made from this graph, provided that the range of the alpha particles expelled from their atoms is known. Thus, for radium C', λ is about 1×10^6. From Fig. 14, it will be noted that short-life elements eject long-range alpha particles. The relation between the life of the element and the range of particles that it ejects suggests that the velocities of the expelled particles depend upon the stability of the atoms from which they come. The shortest-life elements decay most rapidly and, hence, have the most unstable atomic structures; the alpha particles ejected by them have the highest velocities.

Isotopes

It was soon recognized that many of the radioactive elements, although widely different in radioactive properties, were identical in chemical behavior and, if once mixed, could not be separated. Soddy found that radium and mesothorium, for example, could not be separated by any chemical means. Likewise, thorium and ionium, radium D and inactive lead, and many other pairs, or groups of elements, are identical in a chemical sense, although in many cases the elements are members of different radioactive series and in all cases possess different atomic weights. Soddy gave the name *isotopes* to elements that differ radioactively and

in atomic weight but which have the same chemical properties and occupy the same position in the periodic table. Isotopes are more definitely defined as elements possessing the same atomic numbers. For the present, the atomic number of an element may be defined as the number (between 1 and 92) that states the relative position of the element in the periodic table.

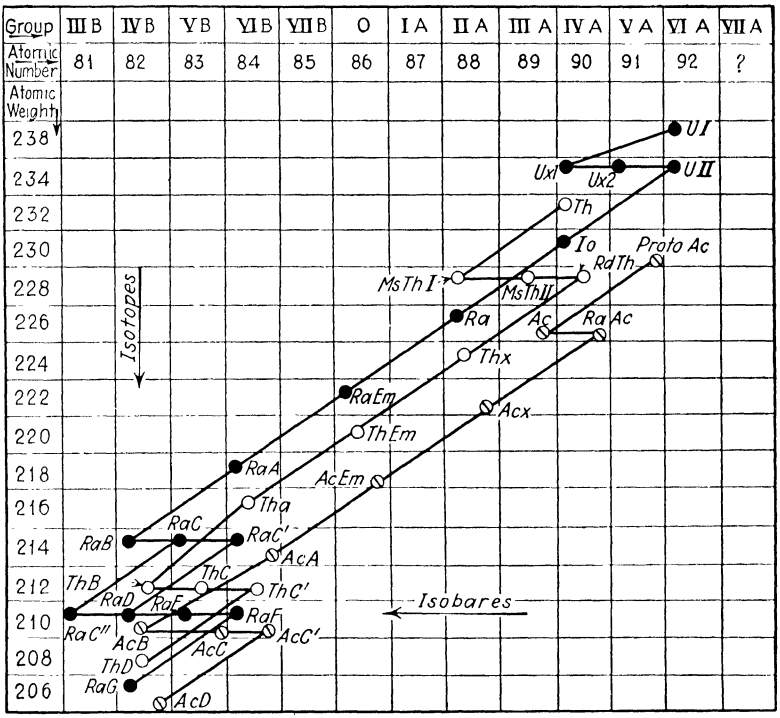

FIG. 15.—The three radioactive disintegration series of elements.

Further studies of the properties of the radioactive elements revealed the general fact that the loss of an alpha particle results in the formation of an atom of an element whose position in the periodic table lies two groups below the group to which the original element belongs. The loss of a beta particle produces the atom of an element that lies one group ahead. This means that the loss of an alpha particle results in a decrease in atomic number of 2 and the loss of a beta particle in an increase of 1. Thus, uranium I (Fig. 15) loses a beta particle in forming uranium

X_1; uranium X_1 then loses another beta particle and forms uranium X_2; the latter, in turn, loses an alpha particle and is converted into uranium II. Uranium I and uranium II have the same atomic number (92) and are isotopes. Uranium X_1 lies two groups below, and uranium X_2 one group below, uranium I and uranium II in the periodic table. The atomic number of uranium X_1 and uranium X_2 are 90 and 91, respectively. Radium loses an alpha particle in forming radon. Radium is a member of the alkaline-earth group (two) and has an atomic number of 88; radon is a member of the zero group and has an atomic number of 86. Here, as before, the loss of an alpha particle causes a shift of two places to the left in the table (to a position two groups lower) and a decrease in atomic number of two.

The shifts in periodic groups and in atomic numbers are shown by the line connecting the radioactive elements of the uranium series (Fig. 15). The data which have been compiled in making this table further show that the loss of a beta particle does not change the atomic weight. The product has the same atomic weight as the parent element; thus, uranium X_1 and uranium X_2 have different atomic numbers but the same atomic weights. There is a slight loss in weight, of course, since an electron is expelled from one atom in producing the other. But the weight of an electron is too small a part of the weight of the entire atom to be recognized by our usual methods of determining atomic weights. Furthermore, the loss is only temporary. The atom resulting from the expulsion of the electron is positively charged and is, therefore, an ion. This ion soon captures an electron and resumes its role as a neutral atom. The captured electron, however, does not enter the same portion of the atom's structure as that from which the original electron was expelled. We can assume that the captured electron enters the exterior structure of the atom, while the electron that was expelled came from an inner portion.

The radioactive elements (Fig. 15) fall into certain groups; the members of any one group are very much alike chemically, possess the same atomic number, and have very closely related physical properties. But these elements have different atomic weights and radioactively, at least, are clearly different elements.

TABLE IV.—RADIOACTIVE ELEMENTS

Element	Atomic weight	Atomic number	Half-life period	Kind of radiation emitted	Range of α particles in air, centimeters
Uranium I	238	92	4.5×10^9 years	α	2.7
Uranium X_1	238	90	23.8 days	β, γ	
Uranium X_2	234	91	1.15 min	β, γ	
Uranium II	234	92	2×10^6 years	α	3.28
Ionium	230	90	9×10^4 years	α	3.19
Radium	226	88	1580 years	α	3.39
Radon	222	86	3.8 days	α	4.12
Radium A	218	84	3.05 min.	α	4.72
Radium B	214	82	26.8 min.	β, γ	
Radium C	214	83	19.7 min.	α, β, γ	
Radium D	210	82	16 years	β, γ	6.97
Radium E	210	83	5 days	β, γ	
Radium F (polonium)	210	84	136.5 days	α	3.92
Radium G (lead)	206	82	Inactive		
Thorium	232	90	2×10^{10} years	α	2.9
Mesothorium I	228	88	6.7 years	β, γ	
Mesothorium II	228	89	6.2 hr.	β, γ	
Radiothorium	228	90	1.9 years	α	4.02
Thorium X	224	88	3.64 days	α	4.35
Thoron	220	86	54 sec	α	5.06
Thorium A	216	84	0.14 sec.	α	5.68
Thorium B	212	82	10.6 hr.	β, γ	
Thorium C	212	83	1 hr.	α	4.8
Thorium C″	208	81	3.2 min.	β, γ	
Thorium D	208	82	Inactive		
Protoactinium	230	91	1×10^4 years	α	3.67
Actinium	226	89	20 years	β	
Radioactinium	226	90	19 days	α	4.68
Actinium X	222	88	11.2 days	α	4.37
Actinon	218	86	3.9 sec	α	5.79
Actinium A	214	84	0.002 sec.	α	6.58
Actinium B	210	82	36 min.	β, γ	
Actinium C	210	83	2.16 min	α	5.51
Actinium C″	206	81	4.76 min	β, γ	
Actinium D (lead)	206	82	Inactive		

The elements of one of these groups are isotopes; their atoms are different kinds of atoms of the same element. All the different elements clustered about lead are different kinds of lead. The three radioactive gases radon, thoron, and actinon are also isotopes. These three elements occupy the position in the periodic table usually assigned to radon alone. It will also be noted that several of the elements, as shown in Fig. 15, have the same atomic weight but different atomic numbers. These are called *isobares*. One of the longer lists of isobaric elements consist of those for which the atomic weight is 210. Elements formed by the expulsion of beta particles are isobaric with the parent element.

One can observe from Fig. 15, and also from a consideration of the disintegration theory, that the end product of each radioactive disintegration series is an isotope of lead. In changing from uranium I to lead, a total of eight alpha particles are expelled. Since the atomic weight of uranium I is 238 and the atomic weight of helium is 4, the atomic weight of lead produced by the disintegration of the members of the uranium series should be 206. The change from thorium (atomic weight 232) to lead, at the end of the thorium series, calls for the loss of six atoms of helium. Hence, the atomic weight of lead produced by the disintegration of members of the thorium series should be 208.

Convincing argument in favor of the radioactive disintegration theory was obtained by the determination of the atomic weights of lead associated with uranium, of lead associated with thorium, and of lead of nonradioactive origin, *i.e.*, found in minerals that contain no radioactive elements. These determinations were made by Richards, Hönigschmidt, and Soddy. The lowest atomic weight of uranium-lead was found to be 206; the highest for thorium-lead was 207.9 (approximately 208); and that for nonradioactive lead was 207. The atomic weight of ordinary lead is 207.2, a value that indicates that ordinary lead is a mixture of the three isotopes. Clearer confirmation of the radioactive disintegration theory could scarcely be desired.

Radioactive Equilibrium.—Through a succession of changes, radium is produced from uranium I. Radium, in turn, disintegrates, forming radon. A given amount of uranium I will produce atoms of radium at a rate that is practically constant

over a period of many years, since uranium has a very long period because of the small degree of probability that governs the decay of its atoms. When radium atoms have been produced, they begin to form atoms of radon, at first very slowly, since there are only a few radium atoms present. It will be remembered that the rate of transformation of radium into radon is proportional to the number of radium atoms present and to the natural disintegration tendency, or probability of decay, of the radium atom. As time goes on, therefore, there will be more radium atoms, and a correspondingly larger number will disintegrate each day. After a comparatively long period of time, the number of radium atoms that disintegrate per day becomes equal to the number that is formed, and the total number of atoms of the element remains constant. This condition is said to represent a state of stable radioactive equilibrium between radium and the radioactive elements that precede it in the series. In like manner, each member of the series attains radioactive equilibrium when its atoms are produced from the immediately preceding member and are transformed into the element next following at the same rate. When a general state of radioactive equilibrium has been reached, each member is present in an amount determined by its natural disintegration tendency. The longer-life elements are present in large amounts, and the short-life elements in small amounts. This condition results from the fact that the number of atoms of an element that must exist in a mixture to produce a rate of disintegration equal to the rate of formation is determined by how rapidly the atoms disintegrate. The smaller the tendency toward disintegration the greater is the number of atoms that must be present to permit the number that disintegrates to be the same as the number that is formed at the same time.

Radioactive transformations are often compared with the flow of water from one vessel to others of successively lower levels through small holes in the bottom parts of the vessels. Let the water in the different vessels (Fig. 16) represent the different radioactive members of the uranium series. Let the size of the hole in the bottom of a vessel represent the rate of disintegration of the element with which the water in that vessel is compared. If water pours into the vessel at the top from a reservoir at a constant rate, it will empty into the vessels placed at successive

levels and, after a time, will come to a constant level in each of them. Water will enter and leave a container at the same rate, and the amounts of water in the different vessels will not change. The levels in the different vessels, however, will not be the same. If the hole at the bottom of a particular container is small, the water level will be higher in this container than in one in which the exit is of larger diameter. Similarly, at equilibrium, the amount of each radioactive element in equilibrium with the other members of its series is proportional to the rate of decay—to the size of the "hole," by which the atoms change from one element to those of the next element in the series.

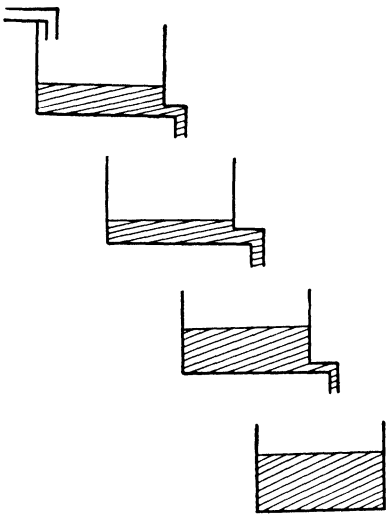

FIG. 16.—An analogy explaining the nature of radioactive equilibrium.

Radioactivity and the Age of the Earth.—The ratio of radium to uranium in an old mineral, in which equilibrium has probably been reached, is 3.3 parts of radium to 10,000,000 parts of uranium. In such minerals, there is also a definite ratio between any other pair of members of the series of radioactive elements. Since lead is the last member of the series, the amount of lead in an uranium-bearing mineral is accumulating at a definite rate. Hence, if the amount of lead in a given sample is known, as well as the amount of uranium in the same sample, it is possible to calculate, as Boltwood and others have done, the number of years that must have elapsed during the production of this quantity of lead from the calculated original quantity of uranium. This calculation should give an approximate age of the earth. Boltwood found minerals which appeared, on this basis, to be about 1,600,000,000 years old. At least, these figures lend some credence to the belief that the earth must be very old.

Since helium is a by-product of the disintegration of many elements in the three radioactive series, this gas is found in most

minerals and rocks which contain radioactive elements. The rate at which such minerals produce helium can be determined in the usual manner by the use of a fluorescent screen; from the number of particles that strike the screen in a given period of time, the rate at which helium atoms are produced can be calculated (page 52). Thus, the age of such rocks can be estimated from their helium contents. If we assume that these rocks are as old as the earth of which they are a part, we can arrive at an approximate age of the earth. This method of calculation is illustrated by the following determination: A certain radioactive mineral was found to contain 26 cc. of helium per gram of uranium and to produce 1 cc. of helium in about 16,000,000 years. At this rate of production, 416,000,000 years would have been required to produce 26 cc. of helium. This value for the age of the earth is much smaller than that which is calculated from its uranium-lead content. The discrepancies have not been accounted for completely. There are, however, several sources of error and uncertainty in all the methods employed. Thus, some helium may have escaped, and the observed volume may be, therefore, too small. Then, too, there is the possibility that not all the lead that is found in a mineral containing uranium has been produced by the disintegration of uranium and its products. It is *possible* that some lead may have been produced by another radioactive element, perhaps an isotope of uranium I, which because of its rapid rate of decay has long since disappeared completely.

The Production of Radium and Its Uses.—The first commercial source of radium was the uraninite deposits in Joachimsthal, Bohemia. Several grams of radium were extracted at great expense, since the amount of radium present was very small; for each 1,000 kg. of uranium, there was only approximately 300 mg. of radium, and, of course, not all of this could be extracted. The great value of the element caused an extensive search of the world's minerals to find those that contained workable amounts of radium. Small quantities of the compounds of the radioactive elements are found in most parts of the earth's crust. It is estimated that the average content is 2×10^{-12} g. of radium and 6×10^{-6} g. of uranium per gram of rock. But this, of course, is too small an amount to be recovered

at the cost that would be entailed; in fact, it is scarcely large enough to be recovered at any cost. Deposits of carnotite (potassium uranyl vanadate) containing about 2 per cent of uranium oxide were found in Colorado and Utah. Until about 1922, practically all the world's supply of radium was produced from these deposits of carnotite. Because of the small radium content and the labor and other costs involved in its recovery, the price was in the neighborhood of $125,000 per gram of radium. In 1922, however, rich deposits of pitchblende (U_3O_8 and other oxides and sulphides) were discovered in the Belgian Congo. These deposits were twenty times richer in radium content than the carnotite deposits of Colorado. Since 1922, therefore, most of the radium produced has come from this source. The price has dropped to around $70,000 per gram. In all, slightly less than one-half pound of radium has been produced up to this time.

The waters of many springs contain radioactive substances in solution and are said to possess curative properties. In this country, the waters from many springs possess marked radioactivity. The most famous of these are the Hot Springs of Virginia and Arkansas.

A large part of the radium produced is used in the form of its salts in the making of luminous paints. For this purpose, some radium salt and zinc sulphide are mixed in the proportion of 1 to 100,000. Radium is also used in the treatment of cancer and certain diseases of the skin. Radon is often used, however, for this purpose instead of radium. The gas is sealed in tubes, which are inserted in the flesh or placed in contact with it. The radiation is said to destroy "wild" growths of tissues, such as cancers, more rapidly than sound parts of the body.

Heat Emission by Radioactive Substances.—Radioactive substances are warmer than surrounding objects. This heat is produced by the absorption of the kinetic energy of the alpha and beta particles and the radiant energy of the gamma rays by the air molecules that surround the radioactive substance. The absorbed energy appears as heat. Madame Curie found that radium compounds produce about 100 cal. of heat per hour per gram of radium. Rutherford, later, determined the heat emission of radium as 134.7 g.-cal. per hour. He calculated the amount of heat emitted by 1 g. of radon during its whole life

period as 2.4×10^9 g.-cal. The heat emitted by any other radioactive element is also enormous and is of the same order of magnitude as that emitted by radon and radium. Knowledge of the enormous amounts of energy associated with the disintegration of the radioactive elements has led to much speculation concerning "atomic energy." The quantity of energy that is stored within the atoms of a few grams of matter is almost beyond our comprehension, since we are accustomed to think of energy in terms of the amount that can be made available, by ordinary means, from a ton of coal, or from a waterfall, or in terms of kilowatt hours of electrical energy. It is not within our power, however, to liberate the energy emitted by radioactive substances at any greater rate than that which they naturally display. Furthermore, the amount of radium available is too small to serve as a practical source of energy even if this energy could be liberated rapidly.

Can the energy that is locked within other atoms be released? And, if released, can it be controlled? These are problems of the future. Experiments that bring tremendous forces to bear upon the atom have been undertaken in attempts to answer these questions. Although these have not been successful, other experiments using still more concentrated forces will follow them. Some fear has been expressed that the experimenters if successful in liberating atomic energy will not be able to control it. It is thought that the liberation of such tremendous amounts in a small space will cause the disintegration of other atoms, releasing more energy, which in turn will explode other atoms, and so on until a general catastrophe results. Such fears seem ungrounded, however, for the experimenters, even if successful, can certainly not succeed in exploding very many atoms at a time, and the energy so liberated can be taken care of by the absorptive action of the surroundings. As regards the energy of radioactive elements, we might as well spend our time calculating the amount of work that each of us could do if we could spend the energy of a lifetime in a single day.

The quantity of heat that is liberated per hour by radioactive substances seems small, but if the radiation of the heat so produced in the interior of the earth is prevented by the relatively thin crust upon which we live, the accumulation of heat deep

down in the earth may lead to very high temperatures after long periods of time. Joly states that the heat liberated may produce a temperature of 1800°C. after a hundred million years. This temperature, with the high pressure that prevails deep down in the earth, may lead eventually, as Joly has suggested, to the melting of the crust, followed by the formation of another crust during a period of cooling, then by another period of slow accumulation of heat and rise in temperature, and so on through a cycle repeated over and over again. At least, knowledge of the heat which is emitted by radioactive elements within the earth has nullified the estimates of the earth's age which are based upon the rate of cooling.

Changes in the Atomic Theory.—The theory proposed by John Dalton led us to think of an element as a fundamental variety of matter, which was composed of a single kind of atom. It was this conception of the elements that caused the acceptance of the atomic weights, whether they were whole numbers or not, as the relative weights of different types of atoms. Contrary to this generally accepted interpretation, Prout had suggested that the atomic weights of all the elements should be multiples of the atomic weight of hydrogen. The radioactive properties of certain kinds of elements have furnished reasons for believing that Prout may have been nearer the truth than was thought by his contemporaries. There are evidently many elements among the members of the radioactive series that are chemically identical, and yet they are composed of different types of atoms and display different radioactive properties. Thus, there appear to be several different types of lead atoms, some of them radioactive and some not, and all differing in mass. The existence of isotopes of the same element is not confined to the radioactive elements, for we shall find that many of the stable elements are composed of two or more kinds of atoms. Furthermore, we find atoms that have the same relative masses but are not atoms of the same element (Fig. 15).

Thus, it becomes necessary to modify somewhat our notion of an element. All the atoms of an element are not identical as Dalton thought, and in this sense, at least, an element does not represent a single, fundamental variety of matter. Furthermore, we can no longer say with Mendelyeev that "the properties

of an element are a periodic function of the atomic weight," since atoms of the same mass have been found which have different properties, while atoms of different masses sometimes have the same properties.

What is it that atoms of an element, regardless of their masses, have in common? What is it, if not atomic weights, that determines the properties of the elements? How can we explain the periodicity which is so clearly demonstrated by Mendelyeev's classification? The answers to these questions must await our study of the structures of atoms.

Radioactivity portrays atoms in the process of disintegration. This, too, is contrary to the theory of Dalton, who regarded them as the simplest structures in nature. Particles that eject smaller particles must possess a structure; and so we are forced to discard the idea that the atom is a compact, continuous portion of matter of some one kind. Information of the sort furnished by the discovery and investigation of the radioactive elements naturally led to a great deal of speculation concerning the atoms of other elements. Many questions at once suggested themselves. Are other kinds of atoms the end products of other radioactive series, as lead is the end product of the uranium and thorium series? Or are they, themselves, very slowly, imperceptibly, undergoing disintegration? If helium atoms and electrons are present in the atoms of radioactive elements, do atoms of the more common elements also contain them? Can atoms of the inactive elements be decomposed? And if they can be decomposed, what kinds of particles should be liberated? Electrons and alpha particles? If helium atoms and electrons are ejected from atoms, can they, under other conditions, be made to combine again to form the same or other kinds of atoms? Is it possible that somewhere in the universe a process opposite to that of radioactivity is in operation and that there, atoms are created?

The discovery that electrons and helium ions are ejected from atoms led naturally enough to questions concerning the possible arrangement of these particles within the atoms. It was assumed, of course, that the ejected particles were present as such in the atom before the disintegration occurred and, therefore, were parts of its structure. These are the questions for

which answers have been sought during all the investigations of the structure of matter since the discovery of radioactivity.

Questions were also raised as to the possibility of other kinds of structural units from which atoms are built up. Prout's hypothesis was recalled, and the hydrogen atom (hydrogen ion) was strongly suspected as one of these possibilities. This idea was especially attractive since it provided the smallest particle, known to carry a positive charge, as the counterpart of the electron. If true, it meant that the alpha particle, itself, is not a simple body but is probably composed of four hydrogen atoms (ions) and electrons. Whether true or not, the examination of atomic weights appeared to show, however, that the helium atom—or ion—is present in many atoms. Many elements have atomic weights that differ, one from the other, by four or multiples of four units. This is the same difference that separates the atomic weights of two radioactive elements, one of which is transformed into the other by the loss of alpha particles. The supposition is, therefore, that the atoms of any two elements which differ by four units in their atomic weights contain one more or one less alpha particle. If we do not consider any portion of the atomic-weight figures except the whole numbers, we find many cases in which this difference is shown:

Li	B	C	N	O	Fl	Ne	Na	Mg	Al	Si	P	S	Cl
6	10	12	14	16	19	20	23	24	27	28	31	32	35

The difference between the atomic weights of many other elements of the periodic system is four or a multiple of four. This does not mean that carbon, for example, is formed, or can be formed, or was formed by the ejection of an alpha particle from the oxygen atom. It may, however, indicate that many of the different types of atoms, including those of carbon and oxygen, are built up in part at least of helium atoms. Oxygen, for example, may contain one more helium atom, or alpha particle, per atom than carbon.

Finally, one further question is suggested. If there are several kinds of lead atoms, can there not be different types of atoms of other elements as well? Are isotopes confined to those elements which are known to be radioactive? At first, no possible method of approaching the answer to this question could be thought of.

In a later chapter, we shall find how the study of isotopes was extended to include all of the elements and how isotopes of many of them were discovered.

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CHAPTER V

THE ELECTRON

Introduction.—The idea that electricity is atomic in nature is much older than the knowledge of the radioactive properties of certain elements. We have observed (page 26) that the results leading to the discovery of the law of electrolysis furnished the first experimental evidence of this sort as early as 1833. These results showed that an ion in the solution of an electrolyte carries one or more units of electrical charge, depending upon its valence, and that for ions of the same valence the charges are the same for all ions. It was thus demonstrated that the charges on ions appear as multiples of an elementary or atomic quantity of charge.

In 1874, Stoney suggested that the charge carried by an univalent ion, since it represented the electrical unit, should be called the *electron*. He computed this "atomic charge" by means of the relation between the quantity of current that passes through a solution of some silver salt and the weight of silver deposited at the cathode (negative electrode). This was found to be 0.001118 g. of silver per coulomb of electricity (1 amp. flowing for 1 sec.). The deposition of one gram-atomic weight (107.88 g.) of silver would require, therefore,

$$\frac{107.88}{0.001118} \times 1 = 96{,}490 \text{ coulombs.}$$

Now, 96,490 coulombs may be expressed as

$$9{,}649 \text{ e.m.u.,}$$

or

$$96{,}490 \times (3 \times 10^9) = 2.9 \times 10^{14} \text{ e.s.u.}$$

The charge on an individual silver ion can be determined by dividing the total number of e.s.u. associated with an atomic weight of silver by the number of silver atoms in this weight:

$$\frac{2.9 \times 10^{14}}{6.06 \times 10^{23}} = 4.8 \times 10^{-10} \text{ e.s.u.}$$

The value that Stoney obtained for the elementary charge was only about 0.3×10^{-10} e.s.u. His smaller value was due to the inaccurate value of Avogadro's number which he used instead of the more accurate value 6.06×10^{23}, which we have used in the calculation.

The suggestion offered by Stoney considered the electron as the unit of charge carried by both positive and negative ions. At present, however, we associate the term with negative charge alone and use it to represent a definite particle.

The products of the disintegration of radioactive elements have proved that the atom is not the ultimate division of matter that it was assumed to be in Dalton's atomic theory. From the atoms of these elements are liberated helium ions and other particles which bear negative charges. These negatively charged particles we call electrons. They are of special interest because they are the smallest particles of matter so far discovered. It is with them that we shall be concerned in this chapter. We are interested in the properties of the electron itself; we are still more interested in determining the relation of the electron to the atom as a whole and to the other particles of which the atom is composed.

We cannot describe definitely at this time the nature of the electron. We know how electrons can be liberated from various forms of matter. We know that they carry electrical charges; in fact, we know the magnitude of this charge and that it is the smallest charge yet discovered. We know that the charges of all electrons are identical. We know that their masses, however, vary with their velocities, increasing without limit as the velocity approaches that of light. We believe that the mass of the electron is of an electromagnetic character. But strangest of all is the behavior of electrons which makes it necessary for us to regard them sometimes as material particles and sometimes as waves like those of light.

So far as we know, therefore, the electron is a negative electrical charge. Farther than this, we cannot say; we do not know what a negative charge *is* or whether the electron has an existence that is separate from its charge. Of this much, however, we are

certain. Matter and electricity in the electron are more closely associated than we had previously believed. This relation, remarkable as it is, cannot tell us, however, very much about matter. It only ties matter more closely with charge, which we understand even less satisfactorily than we do matter itself. It is, however, a forward step in our knowledge of the constitution of material forms.

The Discharge Tube and Cathode Rays.—At ordinary pressures, gases are very poor conductors of electricity. A discharge may be obtained through a gas, however, if the pressure is reduced to a very low value. The usual device consists of a tube (Fig. 17) into which two wires, acting as the electrodes, are sealed; these wires are connected to the secondary of an induction coil. An electrical discharge passes between the two electrodes when the tube is exhausted by a vacuum pump. At first, the cathode

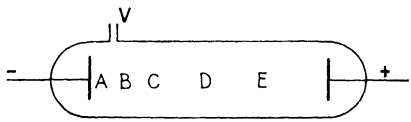

FIG. 17.—The discharge tube. The regions observable within the tube, beginning on the cathode side, are the cathode glow (*A*), the Crookes dark space (*B*), the region of negative glow (*C*), Faraday's dark space (*D*), and the positive column (*E*).

is covered by the Crookes dark space. Beyond this, there is a luminous region which is called the region of negative glow. Next comes another dark region, which is called the Faraday dark space. Beyond this and extending to the anode lies another luminous region called the positive column. The positive column is broken up into striae of light and dark layers. As the pressure within the tube is decreased, the Crookes dark space becomes larger and extends almost to the anode. The positive column, the Faraday dark space, and the negative glow are gradually pushed into the anode, or so it seems. In the Crookes dark space, streaks of bluish light appear. These seem to stream off the cathode and cause the glass walls of the tube opposite the cathode to glow with a green fluorescence. These are called *cathode rays*. They were first found by Plücker in 1859 and have since been studied by many others.

The following facts are known concerning these rays:

1. They travel in straight lines from the cathode. A solid object placed in front of the cathode casts a clear-cut shadow on the opposite wall of the tube.

2. They produce mechanical motion. A little pinwheel placed in the path of rays turns upon its bearings.

3. They produce fluorescence. The walls of the tube glow where the rays strike.

4. They produce a rise in temperature; hence, they possess energy which, when absorbed, is transformed into heat. If a concave cathode is used, the rays are brought to a focus. At this point, a piece of metal foil can be melted.

5. They are deflected by magnetic and electrical fields. The rays are deflected toward the positive and away from the negative plate, when they are allowed to pass between the two plates of a condenser.

6. They impart a negative charge to bodies upon which they fall. If the rays are caught in a Faraday cylinder which is connected to an electrometer, the negative character of their charge is easily verified.

7. They penetrate thin foils of metals.

8. They ionize gases through which they pass.

9. Fog tracks are produced when the rays pass through regions that are supersaturated with water vapor.

10. They blacken a photographic plate.

11. When cathode rays strike a target within the tube, x-rays are produced, provided that the difference of potential is sufficiently great.

Because of these properties, cathode rays are regarded as streams of small negatively charged bodies. This discovery opened up a rich field for investigation. Here was evidence of the existence of particles much smaller than any previously discovered. Many questions concerning them were suggested. What are they? How are they liberated? How much charge do they carry? What is their mass? Are the particles that are liberated from different substances identical?

There could be little doubt concerning the meaning of the discovery of cathode-ray particles. They definitely established the granular structure of electricity. This was not a new idea. As we have already observed (page 26), it was strongly suggested by the facts upon which Faraday's law of electrolysis is based. Stoney had explained such facts by assuming that each ion in solution carries an elementary charge or some multiple of it. He called the unit of charge, whether positive or negative, the *electron*. With the discovery of cathode "rays," the suspicion that the particles of which these rays are composed are electrons

became a likely probability. According to this view, the charge of a positive ion is due to the loss of one or more of these particles by an atom. If each atom in the atomic weight of an element loses one particle, 96,490 coulombs of electricity are required to liberate this weight of the element at the cathode; if each atom loses two particles, twice that number of coulombs are required; and so on. Similarly, the charge of a negative ion can be accounted for by assuming the absorption of one or more electrons.

Thomson's Cathode-ray Experiments.—Sir J. J. Thomson of the Cavendish Laboratory of Cambridge University undertook to determine the exact nature of cathode-ray particles. The tube used by him is shown in Fig. 18. The cathode rays stream off the

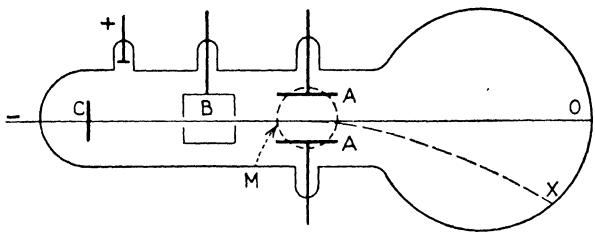

FIG. 18.—Thomson's cathode-ray tube.

cathode *C* in straight lines. Like all moving bodies, the particles in the stream that we call a cathode ray describe a straight line with constant velocity unless acted upon by external forces. A narrow pencil of the rays passes through the slits in the metal box *B*. This pencil of rays then passes between the plates of the condenser *A* and between the pole pieces of the electromagnet *M*. The magnetic field is at right angles to the electric field.

When a charged body moves through a magnetic field, its deflection is in the form of a circular path which lies in a plane at right angles to the field. Let us consider the path of the particle as a conductor, *v* cm. in length, carrying a current of strength *e*. The force acting upon such a conductor, and hence the radius of the circular path in which the particle is deflected, depends upon the mass *m*, charge *e*, and velocity *v* of the particle and upon the strength *H* of the magnetic field. The radius is small when the strength of the magnetic field is great, and the velocity of the particle is small; the charge and mass of the particle

may be regarded as constant. If r is the radius of the circular path,

$$r = \frac{mv}{eH},$$

and

$$\frac{e}{m} = \frac{v}{rH}. \quad (1)$$

Of the factors represented in the second of these equations, the strength of the magnetic field is known, and r can be measured. The pencil of rays, when deflected only by a magnetic field of definite strength, will strike the glass walls of the bulb B at the point X instead of the point O, where it strikes when there is no deflection. The radius r can be calculated, therefore, from the dimensions of the apparatus and the location of the point X. An arc of the path connects X and W (Fig. 19). Two lines are now drawn perpendicular to tangents at W and X, respectively. These lines intersect at F, and the point of intersection determines the center of the circle of which r is the radius. Now, if v can be measured, it will be possible to obtain a quantitative determination of e/m, the ratio of the particle's charge to its mass.

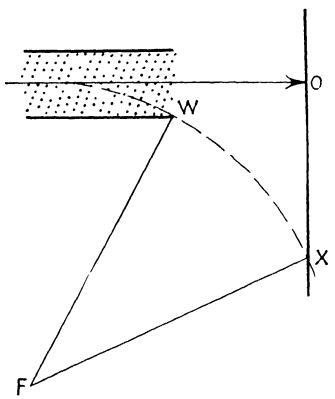

FIG. 19.—Determination of r. The dots represent cross sections of the lines of force of the magnetic field.

When acted upon by the electrical field alone, the pencil of rays is deflected and describes a parabolic path in the direction of the positive plate; thus, the pencil of rays may fall above point O. Now, if both magnetic and electrical fields are imposed simultaneously and of such strengths and direction that the two fields deflect the particle with equal forces in opposite directions, the pencil of rays will strike at the point O, just as if it had not been acted upon by any deflecting force. The magnetic force that acts upon the particles composing the pencil of rays is proportional to the product of the strength H of the magnetic field,

the particle's charge e, and its velocity v. The force exerted by the electrical field is proportional to the product of the strength of the field X and the particle's charge e. When both forces are imposed in such a way that the pencil of rays strikes at the point O, the forces are equal:

$$Hev = Xe.$$

Hence,

$$v = \frac{X}{H}. \tag{2}$$

The strengths of the electrical and magnetic fields are known; hence, v can be calculated. Now, if the value of v (Eq. 2) is substituted in Eq. (1),

$$\frac{e}{m} = \frac{X/H}{rH} = \frac{X}{rH^2}. \tag{3}$$

The velocity of the cathode-ray particles depends upon the difference of potential between the terminals of the tube and upon the pressure and character of the residual gas. For any one set of conditions, however, not all the particles possess the same velocity. This means, of course, that a single beam of rays is not deflected by the magnetic field to a single point. There are, in fact, as many points of deflection as there are velocities of particles.

Whatever the velocity, however, the ratio e/m remains unchanged. The electrons in cathode rays travel with a velocity that is approximately 10 per cent of the velocity of light. Slight changes in velocity of this order of magnitude do not affect e/m. For velocities much greater than this, e/m is found to vary, decreasing as velocity increases (see page 95).

The ratio is likewise constant for all working conditions of the tube and regardless of the nature of the electrodes and residual gas. It is also the same for beta particles ejected by radioactive elements and for electrons derived from any source (page 85).

Modifications of Thomson's apparatus have permitted a more accurate determination of the value of e/m than that secured by Thomson. One modification of his cathode-ray tube is shown in Fig. 20. A heated filament F emits electrons. These are accelerated by the potential of the tube toward the anode. At the

anode, a small beam passes through a slit and emerges in the magnetic and electrical fields imposed at E, through which they pass toward the screen S, which is covered with a fluorescent material. Another modification of Thomson's original apparatus simply secured a more complete evacuation of the tube. Unless a high degree of vacuum is attained, there is little deflection of the particles by the electrical field. This condition results from the ionization of the gas in the tube by the particles. The ions then move toward the plates of the condenser and discharge the potential. The cathode particles move, therefore, through a closed conductor and are not deflected.

The value of e/m secured by these improved methods is 1.77×10^7 e.m.u. per gram.

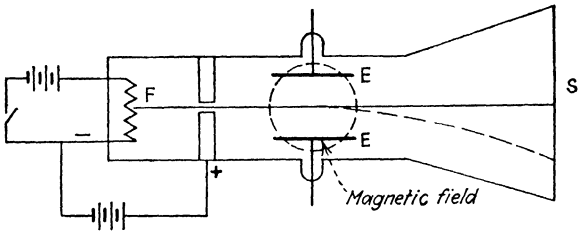

FIG. 20.—Modification of the cathode-ray tube using a hot filament.

Other Sources of Electrons. *Beta Rays.*—Rutherford showed that the beta particles expelled by certain radioactive elements are identical with the particles that compose cathode rays. The identity was established by showing that the ratio e/m is the same for both kinds of particles.

Thermal Emission.—Electrons, which move with very small velocities as compared with the velocities of beta particles, are expelled from certain hot bodies. The heated filament of the tube in Fig. 20 is such a source. Tungsten and certain metallic oxides that are deposited on platinum foil emit negatively charged particles when they are heated. It appears certain that these particles are electrons, since the value of the ratio e/m is the same as for beta and cathode-ray particles. In a similar manner, electrons are emitted by coats of oxides placed upon the filament of the radio tube. As the filament is heated by an electrical current from an external source, the oxides emit elec-

trons, which move through the space between filament and positive plate. This constitutes the flow of a small current.

Dissociation of Heated Gases.—When gases are heated to high temperatures, they dissociate to form ions of gaseous molecules and free electrons. The conductivity of the flame is due to the formation of these charged bodies.

Illumination.—The most strongly electropositive metals emit electrons when they are exposed to visible light; other metals act in the same manner in ultraviolet light; and still others expel electrons when exposed to x-rays. The expulsion of electrons from matter by the action of radiant energy is called the *photoelectric effect.*

Determination of the Mass of the Electron.—The value of the ratio e/m for the electron has been found to be 1.77×10^7 e.m.u. per gram. Now, the ratio of the charge of the hydrogen ion to its mass can be determined from accurate values of the charge and the mass. One gram-atomic weight (1.008 g.) of hydrogen is liberated at the cathode of a cell when 96,494 coulombs of electricity pass through a solution of hydrochloric acid, sulfuric acid, or other electrolytes containing hydrogen. The equivalent weight of any other element is liberated by the same quantity of electricity. It appears, therefore, that one gram-atomic weight of hydrogen, or the equivalent weight of any element or radical, carries this quantity of electricity as long as it exists in the charged, or ionized, state. Hence, for a gram-atomic weight of hydrogen, the charge is 96,494 coulombs, or 9,649.4 e.m.u., and the mass is 1.008 g.

$$\frac{e}{m} = \frac{9{,}649.4}{1.008} = 9{,}572 = 9.572 \times 10^3 \text{ e.m.u. per gram.}$$

If the assumption is made that a single hydrogen ion carries the same quantity of charge, but a charge of the opposite sign, as the electron,

$$\frac{e_{H^+}}{m_{H^+}} = \frac{9.572 \times 10^3}{1.77 \times 10^7} \times \frac{e_E}{m_E},$$

where e_E/m_E is, of course, the ratio of the electron's charge to its mass. Hence,

$$\frac{9.572 \times 10^3}{1.77 \times 10^7} = \frac{e_{H^+}}{m_{H^+}} \times \frac{m_E}{e_E}$$

and, since $e_E = e_{H^+}$

$$\frac{m_E}{m_{H^+}} = \frac{1}{1{,}848}.$$

On the basis of the assumption that the hydrogen ion and the electron carry the same quantity of charge, it appears that the mass of the electron is about 1/1,850 of the mass of the hydrogen atom. If the assumption is true, the cathode-ray tube experiments have led to the discovery of by far the smallest particle of matter known. However, we must note that Thomson actually determined only the ratio e/m. It was this ratio which was found to be identical, whatever the source and velocity of the particles composing the cathode rays. If the charge of one of these particles could be determined, and if it could be shown that all carry the same charge, then the existence of this smallest division of matter would be confirmed, and its mass could be determined. If even the assumption that Thomson had made could be proved valid, the mass of the cathode-ray particles could be calculated with a fair degree of accuracy.

The Charge of the Electron.—Many efforts were made to measure the charge of the electron. Much of the earlier work was done in the Cavendish Laboratory, where Thomson was the director. We have already mentioned the fact that water vapor condenses about charged atoms and molecules of gases which act as nuclei for the formation of tiny drops of water. Aitken showed that dust particles usually serve as condensation nuclei. He found that condensation occurs only when the supersaturation of the space with water vapor becomes eightfold if no dust and no ions are present. C. T. R. Wilson found that condensation occurs when the supersaturation becomes fourfold if negative ions are present. When positive ions are present, drops of water form when the supersaturation is sixfold. Ions can be produced in a space that is supersaturated with water vapor by means of x-rays, by means of radiation from radioactive substances, or by the exposure of a metal plate to ultraviolet light. Electrons that are liberated from metals by the action of visible and ultraviolet light do not ionize molecules of gases by knocking out electrons when collisions occur. No positive ions are produced. The velocity, and hence the kinetic energy, of such electrons is too small to ionize gases in this manner. But these electrons may be

absorbed by gas molecules and thus produce negatively charged ions.

Wilson formed a cloud of water droplets in a space in which electrons were liberated by the photoelectric effect of ultraviolet light upon metals. All the droplets in this cloud were of the same size. Each drop, of course, was negatively charged, since it had been produced by condensation upon a negative ion. The cloud settled slowly because of the action of gravity. But if it was formed between two plates placed one above the other, and if the upper plate was charged positively, the charged drops were acted upon by two forces which opposed each other. They were urged upward against gravity by the electrostatic attraction between the drops and the positive plate. When the strength of the electrical field was adjusted properly, these two forces, one urging the cloud of drops upward and the other downward, were exactly balanced, and the cloud remained stationary.

The velocity with which the cloud settled under the influence of the gravitational force was observed. From this velocity, which we shall call v, the radius r of one of the drops was then calculated by applying Stokes's law:

$$v = \frac{2gr^2}{9q},$$

where g is the gravitation constant and q is the viscosity of the medium through which the cloud falls.

In any experiment that deals with falling droplets, the velocity is found by dividing the distance d through which the drop (or cloud) falls during the time t, using the centimeter and the second as the respective units of distance and time, by t:

$$v = \frac{d}{t}.$$

When r has been found, the volume of the drop can be calculated. From this volume and the density of the liquid, which composes the drop, we can calculate its mass. The gravitational force that causes the drop to settle is proportional to the product of the drop's mass and g, the gravitation constant. The force that urges the drop (or cloud) upward and is caused by the electrical field is proportional to the product Xe of the strength of the field and the

charge on the drop. Hence, when the cloud neither falls nor rises,

$$Xe = mg,$$

and

$$e = \frac{mg}{X}.$$

Since m, g, and X are known, e can be calculated. For this purpose, the strength X of the electrical field may be defined in terms of V, the potential necessary to cause the cloud to stand still, and d, the distance between the two plates, the lower of which is earthed.

Many methods of determining e have been used. All these give the same value within the limits of experimental error.

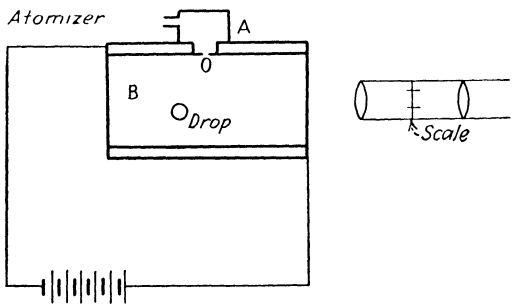

FIG. 21.—Millikan's apparatus for measuring the charge of the electron.

Robert Andrews Millikan has made the most accurate determination and has proved beyond any doubt that electrical charge is "atomic" in character. The main features of the apparatus used by Millikan are shown in Fig. 21. Instead of the cloud of drops used by Wilson and others, Millikan observed the behavior of a single drop in much the same manner as other observers had watched the movement of a cloud. In his many experiments, drops of good conductors such as mercury, of poor conductors such as water, and of nonconductors such as oil were used. By means of an atomizer, many tiny drops were introduced into the chamber A from which one (about 0.0001 in. in diameter) was allowed to find its way through the opening O into the observation chamber B. Here it was illuminated by a stream of light entering through a window. The drop was observed through a short-

focus telescope set at right angles to the stream of light. The drop appeared, of course, as a bright spot by reflection against a dark background. The eyepiece of the telescope was marked by two hairs separated by an accurately known distance. The movement of the drop over this distance was timed by a stop watch. The drop fell under the influence of gravity at the rate of about $\frac{1}{30}$ in. per second. When the top and bottom plates of the observation chamber were electrically insulated from each other and connected to a source of potential of several thousand volts, the rate of fall of the drop was altered. In some cases the drop fell more rapidly, and in other cases more slowly, than in the absence of the electrical field. Sometimes, the drop actually moved upward. The direction and rate of the drop's movement depended upon the quantity and the nature of its charge, assuming constant conditions within the observation chamber.

The drop carried a charge when it was introduced into the chamber. This charge was produced by friction when the drops were formed by the atomizer. Ions were produced between the plates by means of x-rays or by radium. Whenever a drop collided with an ion and absorbed it, the charge was either increased or decreased, depending upon the character of the charge of the ion and the original charge of the drop. Consequently, the velocity and, sometimes, the direction of the drop's movement in the observation chamber were changed. To add a positive charge, for example, the drop was allowed to fall until it was near the lower plate. The potential was then adjusted so that the force of gravity was exactly balanced, and the drop remained stationary. Ions were then produced from molecules of gas in the chamber by subjecting them to the action of a beam of x-rays. If the lower plate was negative, the positive ions immediately fell toward this plate, and the drop was subjected to a bombardment of positive ions, some of which it absorbed.

The results obtained by Millikan and his interpretation of them are illustrated by the following data taken from one of his experimental reports: He found that the average time required for the drop used in this experiment to fall through the distance between the two lines in the eyepiece of the telescope (0.5222 cm.) was 13.595 sec. in the absence of an electrical field. He also observed the rate at which the same drop rose when the potential

was 5,051 volts and the upper plate was negatively charged. The drop rose until it was above the upper line in the telescope. Then the electrical field was shut off, and the drop fell to a position below the lower line. The potential was now applied, and the drop rose again. In this manner, the several readings given below were obtained. Whenever a change in the charge of the drop occurred, because of the absorption of positive or negative ions, the rate at which the drop rose also changed.

Trial	Time required to rise, seconds	Explanation
1	12 5	Drop positively charged
2	12 4	No change in charge
3	21 8	Negatively charged ion, or ions, absorbed
4	34 8	Negatively charged ion, or ions, absorbed
5	84 5	Negatively charged ion, or ions, absorbed
6	85 5	No change in charge
7	34 6	Positively charged ion, or ions, absorbed
8	34 8	No change in charge
9	16 0	Positively charged ion absorbed
10	34 8	Negatively charged ion absorbed
11	34 6	No change in charge
12	21 9	Positively charged ion, or ions, absorbed

The gravitational force that causes the particle to fall is proportional to mg, where g is the acceleration of gravity and m is the mass of the drop. Hence, v_1, the velocity with which it falls, can be expressed by the equation

$$v_1 \propto mg. \tag{1}$$

The velocity with which the drop rises v_2 is proportional to the difference between the electrical force and the force due to gravity. These two forces, in turn, are proportional to Xe_d, the strength of the electrical field multiplied by the charge e_d on the drop, and mg, respectively.

$$v_2 \propto Xe_d - mg. \tag{2}$$

If Eqs. (1) and (2) are combined,

$$\frac{v_1}{v_2} = \frac{mg}{Xe_d - mg}.$$

Solving for e_d, the charge of the drop,

$$e_d = \frac{mg}{Xv_1}(v_1 + v_2). \tag{3}$$

All the factors on the right-hand side of Eq. (3) can be determined; hence, e_d, the charge on the drop, can be determined. The radius of the drop is determined by using a modified form of Stokes' law (page 88). With the radius known, the mass of the drop is calculated from the formula

$$m = \tfrac{4}{3}\pi r^3(d - \rho),$$

where $\frac{4}{3}\pi r^3$ is the volume of the spherical drop, d is its density, and ρ is the density of the medium (air) in which the drop is suspended. The strength of the electrical field is determined from the potential and the distance between the plates of the condenser. The velocities v_1 and v_2 are found from the observed time required for the drop to fall and rise through the distance of 0.5222 cm.

$$v_1 = \frac{0.5222 \text{ cm.}}{13.595 \text{ sec.}}$$

$$v_2 = \frac{0.5222 \text{ cm.}}{84.5 \text{ sec.}}$$ (For the fifth trip of the drop, page 91)

In another case, only 34.8 sec. was required for the same drop to cover the same distance; hence,

$$v_2 = \frac{0.5222 \text{ cm.}}{34.8 \text{ sec.}}$$

for this trip.

From Eq. (3) we find that the change in the charge possessed by the drop on these two occasions (preceding paragraph) is proportional to the change in the sum of the velocities v_1 and v_2:

$$\text{Change in } v_1 + v_2 = \left[\frac{0.5222}{13.595} + \frac{0.5222}{34.8}\right] - \left[\frac{0.5222}{13.595} + \frac{0.5222}{84.5}\right]$$

$$= \frac{0.5222}{34.8} - \frac{0.5222}{84.5} = 0.00891 \text{ cm. per sec.}$$

All other changes in the velocity, as for example, when v_2 changed from $\frac{0.5222 \text{ cm.}}{16.8 \text{ sec.}}$ to $\frac{0.5222 \text{ cm.}}{34.8 \text{ sec.}}$, are found to be 0.0178, 0.026,

0.0356, 0.04456, 0.05347, 0.06232, 0.07106, 0.08038, or some other multiple of 0.00891. None of the various possible changes in v_2 was smaller than 0.00891 cm. per second. This, then, represents the smallest possible change in velocity. Since change in velocity is proportional to the quantity of charge acquired, this minimum change in velocity is evidently produced by the absorption of the unit charge. All other charges that are added or subtracted from the drop are multiples of this minimum charge, since all velocity changes are found to be multiples of the smallest change in velocity.

The charge on any drop can be determined from Eq. (3) (page 92). Different drops, of course, have different values of e_d. But assuming, in accordance with the results just described, that the charge on the drop is always a multiple of the minimum charge, the smallest value of e_d found can be taken as the unit of charge—the charge of the electron. Millikan found some variation in the value of e with variations in the size of the drop. He explained these variations and made corrections for them upon the basis of the kinetic theory. The corrected values of e showed excellent agreement. Millikan's value for the electronic charge is 4.774×10^{-10} e.s.u.

Mass of the Electron and the Hydrogen Atom.—The value of the ratio of the electron's charge to its mass e/m is 1.77×10^7 e.m.u., or 5.304×10^{17} e.s.u. per gram. Millikan's value for e is 4.774×10^{-10} e.s.u.; this is the charge of a single electron. Therefore,

$$\frac{4.774 \times 10^{-10} \text{ e.s.u.}}{m \text{ (g.)}} = 5.304 \times 10^{17} \text{ e.s.u. per gram.}$$

Hence, the mass of the electron can be found by solving the above equation for m:

$$m = \frac{4.774 \times 10^{-10}}{5.304 \times 10^{17}} = 9 \times 10^{-28} \text{ g.}$$

Assuming still that the hydrogen ion carries a unit of charge, equal in magnitude to the charge of the electron,

$$\frac{e_{H^+}}{m_{H^+}} = 9.572 \times 10^3 \text{ e.m.u. per gram}$$
$$= 2.872 \times 10^{14} \text{ e.s.u. per gram.}$$

Solving for m,

$$m = \frac{4.774 \times 10^{-10}}{2.872 \times 10^{14}} = 1.662 \times 10^{-24} \text{ g.}$$

the mass of a single hydrogen atom. If this number is divided into the gram-atomic weight (1.008), the number of atoms per gram-atomic weight of hydrogen can be found. Half of this value is the number of molecules in 1.008 g. of hydrogen; or the whole is the number of molecules in 2.016 g. of hydrogen and in the gram-molecular weight of any substance. This is *Avogadro's number.*

The Nature of Mass

Matter is sometimes defined as that reality of nature that occupies space and possesses inertia. The quantity of matter which constitutes a body and which, therefore, determines the inertia of the body is called *mass.* These statements, of course, concern certain characteristics of matter and mass; they are practically worthless as statements of what matter and mass *are.* During the course of investigations extending over many years, we have learned a great deal concerning the behavior of matter; and from the knowledge thus acquired, we have drawn certain conclusions regarding the structure of different forms of matter. Similarly, many observations have been made which allow us to form certain conclusions regarding the nature of mass. Since many of these observations are based upon the behavior of the electron's mass, it is fitting that these conclusions should be briefly reviewed in this chapter.

Variations of the Electron's Mass with Velocity.—The ratio of the electron's charge to its mass e/m is constant only when electrons are considered that move with relatively low velocities. When electrons are produced in a discharge tube under a very high voltage, their speeds become very high; they approach the velocity of light. For such "high-speed" electrons, the ratio e/m is not constant but decreases as the velocity increases. The values of this ratio for electrons moving with velocities that range from about 10 to 90 per cent of the velocity of light are shown in the following table.

CHANGE IN e/m WITH CHANGE IN VELOCITY

Velocity,[1] Centimeters per Second	e/m Coulombs/G.
1×10^{10}	$1\ 77 \times 10^{8}$
$1\ 5 \times 10^{10}$	$1\ 77 \times 10^{8}$
$2\ 4 \times 10^{10}$	$1\ 3 \times 10^{8}$
$2\ 5 \times 10^{10}$	$1\ 17 \times 10^{8}$
$2\ 6 \times 10^{10}$	$0\ 97 \times 10^{8}$
$2\ 7 \times 10^{10}$	$0\ 77 \times 10^{8}$
$2\ 8 \times 10^{10}$	$0\ 63 \times 10^{8}$

[1] Velocity of light is $2\ 998 \times 10^{10}$ cm per second

The variation of e/m with velocity may be due either to an increase in mass or to a decrease in charge. Because the variation of mass is in accord with our theoretical opinions of the character of mass, this assumption rather than one involving a variable electronic charge is selected to explain the observed effects.

High-speed electrons are also liberated by certain radioactive elements. The variations of the mass of these electrons with velocity are shown in Fig. 22. The masses of electrons moving with different velocities are determined in this case, as before, by observations of the changing values of e/m. The results obtained in this manner agree with the calculations of the masses of electrons of corresponding velocities by means of the equation

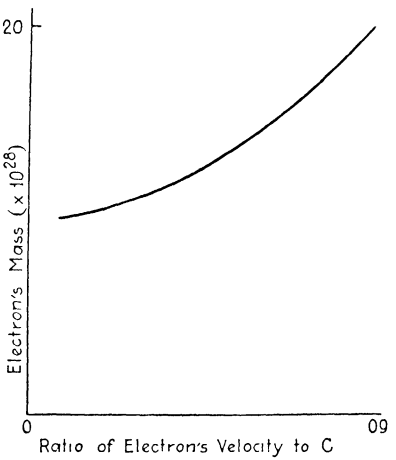

FIG. 22.—Variation of the electron's mass with the velocity. The velocity of light is represented by C.

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}},$$

where m is the electronic mass at the given velocity v and m_0 is the mass of an electron at rest or moving with a low velocity as compared to c, which is the velocity of light. This equation was

first derived by Lorentz from a consideration of the principles of classical electrodynamics as applied to the electron. It was also derived by Einstein, at a later date, upon the basis of his relativity system of mechanics. The equation states that m becomes infinitely large when v equals c. Hence, an electron moving with the speed of light would possess infinite mass and infinite kinetic energy. It is assumed, in accordance with this point of view, that no body can move with a velocity so great as that of light.

The conception of mass as a variable with velocity is contrary, of course, to the law of conservation of mass. The observations that have led to this law, however, have been based entirely upon bodies that are at rest or that are moving with relatively small velocities. Until the discovery of the electron, there was no opportunity to test the law as regards the masses of bodies that are traveling with velocities which approach that of light. We cannot accept the idea, however, that mass in the rapidly moving electron is created except at the expense of something else. We are not able to get away entirely from the principle of conservation. We believe that this increase in mass is due to an expenditure of energy; in turn, energy is liberated when the speed of the electron is retarded and the mass is diminished.

In accordance with the principles upon which the Lorentz equation (page 95) is based, it can be shown that the increase in the kinetic energy of a body, when it is acted upon by a force that changes its velocity from v_0 (zero velocity or state of rest) to v, is equal to $m_0c^2\left[\frac{1}{\sqrt{1-\frac{v^2}{c^2}}}-1\right]$, where m_0 is the mass of the body at rest and c is the velocity of light. Since c^2 is constant, the increase in kinetic energy corresponds to an increase in mass which is given by the equation

$$m - m_0 = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} - m_0.$$

Since v^2 is smaller than c^2, the value of v^2/c^2 is less than 1; and the value of $\sqrt{1-\frac{v^2}{c^2}}$ is likewise less than 1. Hence, $\frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$ is

greater than m_0. This means that the mass m_0 of a body at rest or moving with a velocity v_0 increases to the mass $m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$, when the velocity increases to v, according to our interpretation of the increase in the energy of the body. If E_0 is the energy of the body at rest, and E its energy when its velocity is v, we may express the relation between the increase of energy and the increase of mass by the equation

$$E - E_0 = (m - m_0)c^2.$$

Since $E - E_0$ represents a quantity of energy, and $m - m_0$ a definite mass, this equation may also be written as

$$E = mc^2.$$

This equation states that a system that contains the mass m also contains the energy E, and upon the basis of this deduction we assume that energy and mass must be closely related in nature. As the energy of a system increases with increasing velocity, there is a corresponding increase in mass. With diminishing velocity, E becomes smaller, and m likewise decreases accordingly. We may further assume that a quantity of energy corresponding to mc^2 may appear as radiation when the mass m disappears. As radiation, the energy thus liberated is not associated with the mass of a material system.

The Electromagnetic Nature of Mass.—The variation of the mass of an electron with velocity can be best explained by considering the electromagnetic field which surrounds an electron and moves along with it. The movement of an electron and its electromagnetic field may be compared to the movement of a body in water. Let us take the case of a log that is towed by a boat across a quiet lake. As the log is pulled along, it carries with it a certain quantity of water, because of the tendency of the water to adhere to the log and also because of the cohesion of the water itself. The moving system consists, therefore, of the log and the water which it drags with it. A part of the inertia of this system lies in the log and a part in the water. Likewise, when the system is set into motion, a part of its kinetic energy lies in the water that surrounds the log. As the speed with which

the log moves through the water is increased, more and more water is moved along with the log. The kinetic energy of the system increases, therefore, not solely because of the increase in the velocity of the log but because of the increase in the mass of the system as a whole. The case is similar to that of the moving electron. In the preceding section, we assumed that a quantity of energy equal to $c^2\left[\frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} - m_0\right]$ must be supplied to give the electron at rest a velocity equal to v. This was interpreted to mean that the mass of the electron increases from m_0 to $m\left(\frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}\right)$. Similarly, to provide a velocity v for the system of the log and water, a quantity E of energy must be supplied corresponding to

$$E = \tfrac{1}{2}(m + m')v^2.$$

The mass of the log is represented in this equation by m. But the kinetic energy of the moving system is greater than $\frac{1}{2}mv^2$, since the total mass is $m + m'$, where m' is the mass of the water that moves with the log.

Let us next turn to an explanation of electromagnetic mass which is based upon Faraday's theory of an electric field. According to this point of view, "electric lines of force" originate in a positively charged body and travel out in all directions. Similarly, with a negatively charged body we think of lines of force as entering from all directions (Fig. 23). Let us imagine an electron which is moving in the direction of A. Let us assume that it is a small sphere. Lines of force lie in the region around the electron and enter it from all directions. As these lines move past some point C which lies at an angle with the path along which the electron is moving, a magnetic field is produced in the region where C lies. The strength of this magnetic field is proportional to the speed with which the lines of force pass C. Since the energy of the magnetic field increases with its strength, the case becomes very much like that of the log and the water that moves along with it. Here, again, we express the energy of the system

by the equation

$$E = \tfrac{1}{2}(m + m')v^2.$$

This equation represents the total energy of the system as kinetic energy, *i.e.*, of the same nature as the energy possessed by the electron as a result of its mass and its velocity. This manner of dealing with the problem is entirely logical, however, since the energy of the magnetic field depends, also, upon the velocity of the electron. The term m' actually represents the inertia of that part of the moving system that consists of the magnetic field. To explain the inertia due to this field, we need only to recall its effect upon attempts to impart a velocity to the charged body when it is at rest or to stop it when it is moving. Thus, the

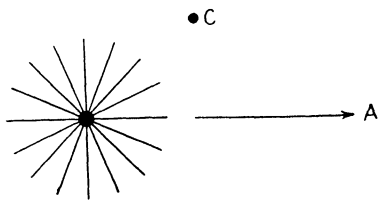

FIG. 23.—The electromagnetic field about a moving electron showing the lines of force according to Faraday.

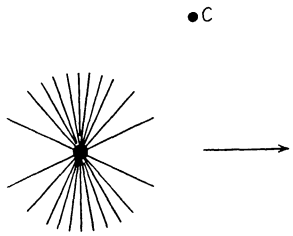

FIG. 24.—The effect of increased velocity of the electron upon the strength of its magnetic field.

field produces an electromotive force which opposes any effort to set the electron, at rest, into motion. When a force is exerted to stop a moving electron, this electromotive force tends to maintain the motion. This is the electromotive force of self-induction and corresponds, in a certain sense, to the inertia that is associated with a body of matter.

We may extend the explanation of electromagnetic mass, which we have based upon Faraday's electric lines of force, to include the effect of increases in velocity. If the electron moves with a very high velocity, the lines of force are, theoretically, crowded closer together in a direction that is at right angles to the path of the electron (Fig. 24). Now, only the lines that cut across the region C are effective in establishing a magnetic field. If C lay in the direction of A, *i.e.*, if B moved toward C, no magnetic field would be produced in that region. The effect of an

increase in the velocity of the electron, therefore, is to concentrate the lines of force in the region that lies at right angles to the electron's path and, hence, to increase the strength of the magnetic field in the region of C. The increase in the strength of the field results in an increase in the energy of the field that moves along with the electron. The total energy of the system is increased, and we assume that this means an increase in the "electromagnetic mass" m'.

An estimation of the electromagnetic mass of the electron can be made in the following manner: The quantity of energy in a small sphere, whose center lies at C in the electromagnetic field surrounding the electron, can be calculated from the charge e of the electron, the distance γ (Fig. 25), the angle ϕ, the velocity v of the electron, the volume u of the sphere, and the strength H of the magnetic field. The energy E_u of this sphere is defined by the equation

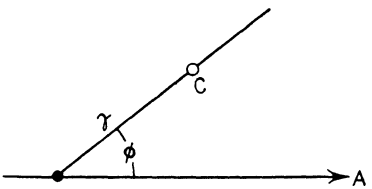

FIG. 25.—Estimation of the electromagnetic mass.

$$E_u = \frac{H^2}{8\pi} u.$$

Since

$$H = \frac{ev \sin \phi}{\gamma^2},$$

E_u can be further defined as follows:

$$E_u = \frac{e^2 v^2 \sin^2 \phi u}{\gamma^4 8\pi}.$$

The total energy E_{em} of the electromagnetic field is then the sum of the quantities of energy located in all the spheres of equal size in a region that extends from the electron to infinity. The summation of these quantities of energy can be expressed by the equation

$$E_{em} = \frac{e^2 v^2}{3a},$$

in which a is the radius of the electron.

In addition to the energy that is located in its electromagnetic field, the electron possesses kinetic energy because of its motion. The total energy of the moving electron, therefore, is the sum of its ordinary kinetic energy $\frac{1}{2}mv^2$ and the energy of the electromagnetic field that it generates in the space around it. The latter may also be regarded as kinetic energy, since it depends upon the velocity of the electron. There is no fallacy, therefore, in adding the two quantities.

$$\text{Energy of electron} = \frac{1}{2}mv^2 + \frac{e^2v^2}{3a},$$

or

$$\frac{1}{2}v^2\left(m + \frac{2}{3}\frac{e^2}{a}\right).$$

Thus, it appears that not only the ordinary mass m of the particle determines the energy but this mass is augmented by the quantity $\frac{2}{3}\cdot\frac{e^2}{a}$, which is called the *electromagnetic* mass of the electron.

Throughout the discussion, thus far, we have assumed that the mass of the electron consists of two parts. We may speak of these as the "ordinary" and the "electromagnetic" mass. The Lorentz equation (page 95) may be used to predict the variations of the electron's mass with velocity. This equation deals, however, only with mass that is electromagnetic in character. The observations of the change in mass with velocity give the same experimental results, nevertheless, as the results that can be calculated theoretically from the equation. This agreement indicates, therefore, that all the mass of the electron is electromagnetic in nature; the term "ordinary" mass thus becomes unnecessary.

In order to show that all the mass of the electron is electromagnetic in character, it was found that extremely high velocities must be imparted to the particle. Other particles of matter cannot be studied in a similar manner, since they cannot be made to move with velocities at which variations in their masses would become sufficiently appreciable to be detected. Nevertheless, the view is held that all matter consists in its final states of divisions of small charged bodies, including electrons and corresponding units which are positively charged but which possess

much more mass than electrons. All forms of matter are regarded, therefore, as electromagnetic in nature.

The Size of the Electron.—If the mass of the electron at rest is correctly expressed by the equation for electromagnetic mass, the radius of the electron can be calculated from the values of the mass m_0 and the charge e according to the equation

$$m_0 = \frac{2}{3}\frac{e^2}{a}$$

$$9.0 \times 10^{-28}\ \text{g.} = \frac{2(1.59 \times 10^{-20})^2\ \text{e.m.u.}}{3a}$$

$$a = 1.87 \times 10^{-13}\ \text{cm.}$$

This result, however, should not be regarded too seriously. To obtain it, we have assumed that the charge is concentrated upon a *sphere.* The size of this sphere is determined by the radius that we were forced to assume in the calculation of the electromagnetic mass of the electron. In other words, the derivation of the equation for electromagnetic mass *started with the assumption that the electron is a sphere.* We cannot be sure that the charge is distributed over the surface of such a sphere, even though our original assumption may be correct. In fact, we cannot know how the charge is distributed. The difficulty arises from the fact that we have no experimental evidence, and no means of obtaining such evidence, concerning the force exerted by the charge and the variations of that force with distance within the region nearest the electron.

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CHAPTER VI

PROTONS AND OTHER POSITIVE PARTICLES

Positive Particles.—The unit of negative charge is associated with an extremely small particle of matter. The unit of positive charge is of the same magnitude as the electronic charge. Until the discovery of positrons (see below), there was no known positive particle, however, that could be compared directly with the electron.

Positrons.—In 1932, Anderson announced the discovery of the positive electron, a name that he shortened to *positron*. These particles were identified from photographs of the fog tracks that they produced when they were released from atoms bombarded with cosmic rays. The positron has the same mass as the (negative) electron and a charge numerically equal but of opposite sign to the electron's charge. Its discovery adds one more kind of "building blocks" from which atoms are made in nature and into which they may be decomposed under certain conditions. The exact relation of the positron to the remainder of the units of an atom's structure remains, of course, to be determined. The argument has sometimes been advanced that quanta of cosmic or gamma radiation are converted, upon collision with atomic nuclei, into positrons. If this view is correct, as some hold, it means that energy is converted into matter. On the other hand, other scientists believe that the collision results in the disruption of the atomic nucleus that is struck and the ejection of particles that were present there before the collision occurred. This question, too, awaits a definite and convincing answer.

Kinds of Positive Particles.—Because of the small amount of information that we possess at present concerning positrons, we shall speak of positive particles in the older sense as positively charged ions. These are more like negatively charged atoms or molecules than electrons. Positive particles are found, therefore, in solutions of electrolytes, in discharge tubes, in gases that

have been ionized by alpha and beta rays, and under all other conditions where positive ions are produced. Wherever found, their charge is always equal to the electronic charge e or to a multiple Ne of this charge. The charge on a positive ion in solution seldom exceeds $4e$ and is usually e or $2e$. In the discharge tube, however, ions are found whose charges range from e to $8e$. The same kind of atom is sometimes found in a discharge tube with several different amounts of charge, all different multiples of e.

So far, we have considered only two positive particles, the hydrogen ion and the alpha particle. The first is an atom of hydrogen that has lost an electron; the latter is an atom of helium that has lost two electrons. There are, of course, as many kinds of positive particles as there are positive ions. The smallest of these is the hydrogen ion. Hence, this has come to be called the *proton*, the positive equivalent of the electron. The mass of the proton is approximately the same as the mass of the hydrogen atom. The mass of the electron is so small in comparison with the rest of the atom that its loss makes no appreciable difference in the mass of the particle expressed on the scale of atomic weights.

Positive Rays.—The discovery of cathode rays encouraged the search for positive rays which, it was thought, might emanate from the anode. Such rays were discovered, but they were found to originate in the gas within the tube rather than in the material of which the anode was composed.

When the pressure within a discharge tube is made very low, a region of violet glow is observed at a short distance from the cathode. Orange rays appear to start from this region and move toward the cathode. These can be demonstrated by the shadow cast upon the cathode when a screen is placed in the path of the rays. When first observed, they were thought to consist of "positive electrons." Goldstein, in 1886, using a tube containing a cathode that was pierced by a small cylindrical opening, found that a pencil of the rays passed through the opening and could be observed behind the cathode. The opening was called a *canal*, and the rays came to be called *canal rays*.

Sir J. J. Thomson investigated canal rays by the same methods that he had previously used so successfully in his studies of the electron. He found that they consist of positively charged

particles. The ratio of the charge to the mass of these particles was found to be much smaller than the same ratio for the electron, and its value varied with the nature of the small quantity of gas in the tube. The most likely explanation of the nature of these positive particles regarded them as electrically charged atoms and molecules. On the whole, the method used for cathode rays could not be applied to the determination of the ratio e/m for positive particles without encountering difficulties that made the results somewhat open to question. One of these difficulties is due to the kinetic energy of the particles, which is always relatively great because of the masses of the atoms or molecules. For positive rays, the kinetic energy of the particles is so great that their deflection by magnetic and electrical fields is very much less than that of the electron. Furthermore, the particles possess such great ionizing power that the residual gas between the electrically charged plates becomes strongly ionized. Hence, the particles are caused to pass through what is practically a closed conductor and are not deflected. To prevent this difficulty, that portion of the discharge tube beyond the cathode —this is sometimes called the camera—can be more nearly evacuated than the part of the apparatus in which the positive particles are produced.

Thomson's Positive Ray Tube.—Thomson designed a tube for the study of positive rays. The essential features of this tube are shown in Fig. 26. The anode A is located in a small side arm of the large bulb G. The gas from which the positive particles are produced enters through a small capillary tube B. The cathode is made of aluminum and is pierced by an opening through the center. A small copper tube is fitted into this opening; this is the canal through which the rays pass. The cathode is hollow and is cooled by water which circulates inside it. It is protected from the action of the magnet M by an iron jacket J. A soft-iron screen I shields the discharge tube from the magnet. The protection from the action of the magnet is necessary so that the particles will not be deflected before they enter the magnetic field proper. Deflection within the canal would be particularly undesirable. The bulb G is evacuated by means of a pump connected at D. A difference of potential of 30,000 to 40,000 volts is maintained between the anode and the cathode.

Electrons stream off the cathode in the direction of the anode, and if the difference of potential across this space is sufficiently high to give them the necessary velocity, they dislodge electrons from molecules of gas with which they collide in the bulb *G*. Thus, positive particles, or ions, are produced. These move toward the cathode, and some pass through the opening in the cathode and can be observed behind it. The velocity of each of the particles depends upon the distance through which it travels before it reaches the cathode. Like a body falling toward the earth, the particle moves faster and faster as it approaches the

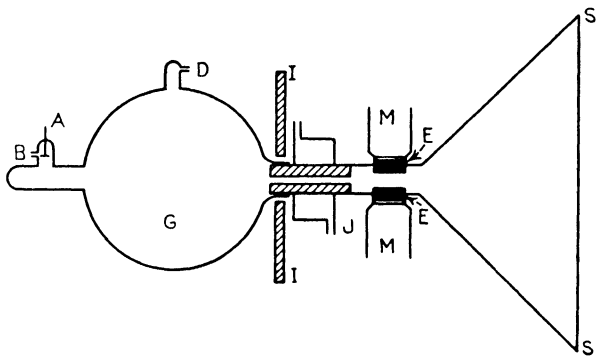

FIG. 26.—Thomson's positive-ray tube.

cathode. The velocity v, which a particle attains, depends upon the difference of potential V through which it falls and upon the charge E and mass m of the particle:

$$v^2 = 2\,\frac{VE}{m}.$$

Ions that are produced at different positions within the tube fall through different fractions of the total potential between the electrodes. Those positive ions that are produced near the cathode, therefore, will be traveling slowly, while those that are produced by collisions in the tube near the anode will possess much higher velocities at the time of their entrance into the canal. Hence, the pencil of rays that emerges behind the cathode, while consisting, perhaps, of particles of the same mass and the same charge, will contain particles that have many different velocities

up to a definite maximum. The maximum velocity corresponds to a fall through the total potential.

The pole pieces M of an electromagnet serve to produce a magnetic field through which the pencil of rays must pass after emerging from the canal. The ends of the iron cores of this magnet are insulated by sheets of mica, and the ends, so isolated, are connected to a set of storage batteries, thus producing an electrostatic field parallel to the magnetic one. The pencil of rays passes through the two fields simultaneously and at right angles to each.

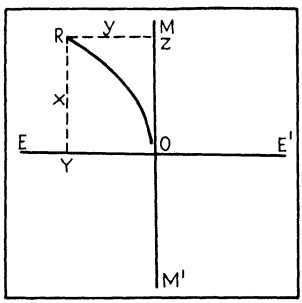

FIG. 27.—Magnetic and electrical deflections of positive particles.

The beam of positive rays may be detected by means of a photographic plate, a willemite screen, a thermocouple, or a Faraday cylinder. A photographic plate or a screen is usually employed. Whenever neither the electrostatic nor magnetic field is operating, the pencil of rays strikes the photographic plate or fluorescent screen SC at the point O—the point of no deflection. If only the electrostatic field is imposed across the path of the rays, any one particle in the beam will be deflected to the point E or E', depending upon whether the lower plate is positive or negative. The exact location of E or E' (the distance from O) depends upon the mass of the particle, its velocity, the strength of the electrical field, and the distance of the screen from the place where the deflecting force is imposed. If only the magnetic field is applied, the particle is deflected in the arc of a circle which lies in a plane at right angles to the field. Hence, the particle will strike the screen at a point M or M', the distance of which from the point O depends upon the kinetic energy of the particle, the strength of the magnetic field, and the distance of the screen from the magnet. A particle that is acted upon simultaneously by both the magnetic and the electrical fields will strike the screen at a point R, if the fields are so imposed that either alone would deflect the particle to M or E, respectively. All the positive particles in the beam, however, are not deflected to this point, although they may possess the same charge and the

same mass. Different particles possess different velocities. A slowly moving particle is deflected more strongly than one that is traveling faster. Hence, a path starting somewhere near O, lying between OE and OM, and passing through R should represent the location of all the points where particles of the same mass and charge strike the screen. Thomson found that the path was parabolic in character. This is the curve OR in Fig. 27.

Let us represent the strength of the magnetic field by H, that of the electrical field by X, the mass of the particle by m, its charge by e, its velocity by v, and the deflection by the magnetic field by OZ, or, more briefly, by x. We can define x as follows:

$$OZ = x = \frac{He}{mv} K_1 \tag{1}$$

where K_1 is a constant, the value of which depends only upon the dimensions of the apparatus, especially the distance from the magnetic field to the screen.

The deflection of the electrical field is OY, or y, which can be defined by the following equation:

$$OY = y = \frac{Xe}{mv^2} K_2, \tag{2}$$

where X is the strength of the electrical field, and K_2 is, again, a constant the value of which depends upon the dimensions of the apparatus.

Dividing Eq. (1) by (2):

$$\frac{x}{y} = \frac{HeK_1/mv}{XeK_2/mv^2} = \frac{Hemv^2K_1}{XemvK_2} = \left(\frac{HK_1}{XK_2}\right)v. \tag{3}$$

Since H and X may be maintained at constant values, HK_1/XK_2 is a constant; hence, x/y is proportional to v. Now, squaring (1) and dividing by (2), it can be shown that

$$\frac{x^2}{y} = \frac{H^2e^2K_1^2/m^2v^2}{XeK_2/mv^2} = \frac{H^2e^2mv^2K_1^2}{m^2v^2XeK_2} = \left(\frac{H^2K_1^2}{XK_2}\right)\frac{e}{m}. \tag{4}$$

Hence, x^2/y is proportional to e/m.

For any one kind of particle, let us say O^+, each of which carries one unit of charge, e/m is constant; hence, x^2/y is also constant. Since the velocity of all O^+ particles is not the same, x/y varies as v varies. All O^+ particles will strike the screen along one line at

all points of which x^2/y has the same value, and x/y varies with the velocity of the particles. Mathematically, these points should lie on a parabola if these two conditions are fulfilled. Thomson found such parabolas on the fluorescent screen or photographic plate *SC*. These are shown in Fig. 28.

Each parabola stops at a definite distance from *O*; the end of the curve corresponds to the maximum velocity and, hence, the minimum deflection of the particles. Some particles of each kind may have their charges neutralized by the absorption of electrons while passing through the canal of the cathode. They will have attained, however, a velocity that permits them to move on until they strike the screen. These neutral particles are not deflected, when they pass through the magnetic and electrical fields; they strike the screen, therefore, at the point *O*. Neutralization may occur, of course, in any part of the apparatus. If this occurs while the particle is passing through the deflecting fields, the extent of deflection will vary with the distance which the particle travels through the field before its charge is neutralized. This condition gives rise to so-called secondary effects, which must, of course, be taken into account and properly interpreted. They are less noticeable when the portion of the apparatus behind the cathode (the camera) is highly evacuated. Other particles may acquire a sufficient number of electrons to give them negative charges. These are spread out into a parabola which is located in the upper right-hand quadrant (Fig. 28). By reversing the directions of the magnetic field, the particles can be made to fall in the lower left-hand quadrant, thus completing the curves. When this is done, the lines on the plate clearly show themselves to be parabolas whose foci are located at *O*. The lines *EE'* and *MM'* can now be drawn through *O*.

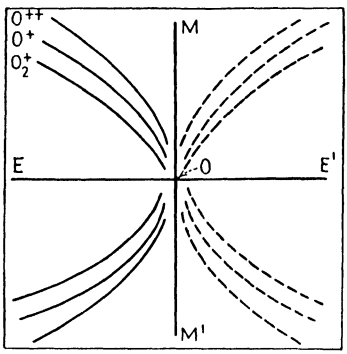

FIG. 28.—Deflection of particles of different charge and mass.

For the same particle with another charge, or for another kind of particle possessing a different mass and, perhaps, a different

quantity of charge, e/m will not be the same as for the O^+ particle. As many parabolas should be found on the screen as there are particles possessing different values of e/m in the beam. For the O^{++} particle, for example, e/m will be greater than for O^+, and all O^{++} particles will strike the screen along a parabolic curve, which lies above the first. For O_2^+ particles, e/m will be smaller; hence, these particles will strike along another parabola which lies below the first. Although the O_2^+ particle possesses the same quantity of charge as O^+, its mass is twice as great. The O and O_2 particles have the same kinetic energy, since each has the same quantity of work Ve done upon it. Their velocities, and therefore x/y, will vary, however, because of their different masses.

Now, let us consider two parabolas made by two kinds of positive particles A and B. We wish to show how the ratio e/m for one of these can be determined. Let us say that B is the particle of unknown charge and mass. The charge and mass of A are known. Hence, its parabola can be easily detected and can be used for the purpose of calibration. The particle that is often used for this purpose is the singly charged oxygen atom O^+. Draw a line (Fig. 29) from a point Q on one parabola through W on the other, perpendicular to the line EE' at U. The electrical deflection y is the same for the A particle which strikes at Q and for the B particle which strikes at W, but the deflections by the magnetic field x_A and x_B are different. For A, the distance of this deflection is measured by the line QU; and for B, by WU. Applying Eq. (4) (page 109),

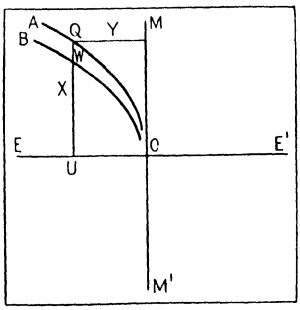

FIG. 29.—Comparison of e/m for two kinds of positive particles, A and B.

$$\frac{x_A^2}{y} = \left(\frac{H^2K_1^2}{XK_2}\right)\frac{e_A}{m_A}, \tag{5}$$

and

$$\frac{x_B^2}{y} = \left(\frac{H^2K_1^2}{XK_2}\right)\frac{e_B}{m_B}. \tag{6}$$

The value of $H^2K_1^2/XK_2$ is the same in both Eqs. (5) and (6); hence,

$$\frac{x_A^2}{x_B^2} = \frac{e_A/m_A}{e_B/m_B}. \tag{7}$$

The ratio of x_A and x_B is easily determined, since each is simply the length of a line between two definite points. If e_A/m_A is known, as we assumed in the beginning, e_B/m_B can be calculated. Furthermore, if e_A and e_B are equal, it is possible to calculate the value of m_B from the known value of m_A.

$$\frac{x_A^2}{x_B^2} = \frac{e_A m_B}{e_B m_A} = \frac{m_B}{m_A},$$

when

$$e_A = e_B.$$

Or if

$$m_A = m_B$$

$$\frac{x_A^2}{x_B^2} = \frac{e_A}{e_B}.$$

From the known values of e_A, x_A, and x_B, e_B can then be calculated.

Discovery of Isotopes of Nonradioactive Elements.—Thomson found that two parabolas were obtained whenever neon (atomic weight, 20.20) was present in the positive-ray tube. The value of e/m for the particles that fell on one parabola was $^1_{20}$; for the other, $^1_{22}$ as compared with the ratio for the singly charged oxygen atom $^1_{16}$. The latter might possibly have been due to molecules of carbon dioxide carrying two units of positive charge per molecule:

$$^2_{44} = {}^1_{22}.$$

This parabola, however, always appeared whenever neon was introduced into the tube and when every precaution was taken to exclude carbon dioxide and all carbon compounds. It was possible, of course, that the value $^1_{22}$ for the ratio e/m might be due to an ion containing one neon atom and two hydrogen atoms, NeH_2^+. Later and more refined investigations proved this explanation impossible.

The discovery of the two parabolas for neon was remarkable, and its effect upon our conception of the elements was revolutionary. The conclusion was inevitable. There must be two

kinds of neon atoms. One has a mass of 20 and the other of 22 as compared with the atomic weight of oxygen as 16. The value for the atomic weight (20.2) of neon which was accepted previously must be the average of these two values. This means, then, that there are isotopes of neon, just as there are of radon, another inert gas, and a member of the uranium series of radioactive elements (page 65).

The question of how general the existence of isotopes might be naturally arose. Were all the elements, especially those of fractional atomic weights, mixtures of two or more kinds of atoms?

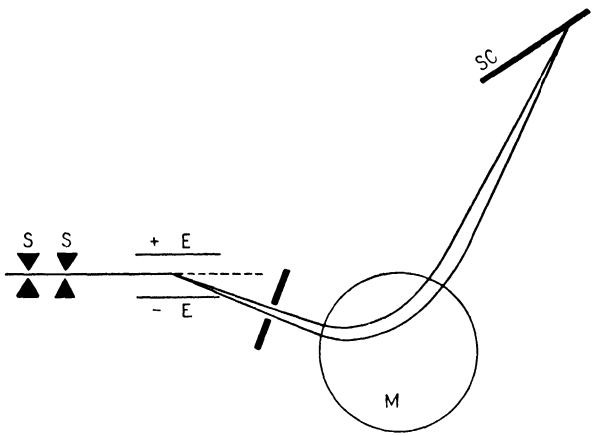

FIG. 30.—Aston's mass spectrograph.

The Mass Spectrograph.—F. W. Aston of the Cavendish Laboratory took up the investigation of the isotopes of the stable elements. He found that it was necessary to modify Thomson's original positive-ray tube in several ways in order to secure sharp lines by means of which accurate linear measurements could be made. He was also able to reduce the time required for exposure and to secure greater dispersion of the lines produced by different kinds of particles. The apparatus finally designed and used by Aston is called the *mass spectrograph.* It is shown in Fig. 30.

A ribbon of rays is secured by means of the slit system *SS* and is passed through the electrical field *EE*, where it is deflected. All the particles are not deflected through the same angle, of

course, and hence follow different paths after passing through the electrical field. The electric field breaks up the stream of positive particles into a *velocity spectrum;* all the particles, irrespective of the values of e/m, that fall through the same accelerating potential V_1 and which, therefore, possess the same velocity while passing through the electric field, are deflected through the same angle and would come to the same point.

After the deflection by the electrical field, the particles pass through the magnetic field M, where they are deflected in the arcs of circles which lie in a plane at right angles to the magnetic field. The particles finally strike the screen or photographic film SC. If the distances and the angles between the different parts of the apparatus and the strengths of the electrical and magnetic fields are properly adjusted, all particles that possess the same value of e/m, irrespective of their velocities, are brought to a focus. These strike the screen, or film, at the same point, the distance of which from some fiducial, or reference, point is a relative measure of the particles' ratio e/m. The focus of some known particle, such as O^+, serves for calibration.

A stream of positive particles is thus broken up, and a "spectrum" is obtained. The lines of this spectrum represent different masses, instead of different wave lengths, as in optical spectra. Aston, therefore, called his device a *mass spectrograph.* The lines of common particles, such as those of carbon dioxide, CO_2^+, carbon monoxide, CO^+, and oxygen, O^+ and O_2^+, can be located. These are used to calculate the values of the ratio e/m for other particles, which strike at other points on the film. When the value of e/m has been found for a given particle, m can be determined, provided that e is known or can be found.

If a particle of a given mass can possess more than one quantity of charge, there will be as many lines for that kind of particle as there are values for the ratio e/m. Naturally, there will be more particles that lose one electron and, hence, carry one unit of positive charge, fewer that carry two, still fewer with three units of charge, and so on. Since there are more particles that have lost only one electron than there are of any other kind, the line corresponding to these will be most intense. The other lines will show gradually diminishing intensity as the number of charges per particle increases. Because of these facts, and since the charge e

TABLE V.—ELEMENTS AND ISOTOPES

(Atomic weights or mass numbers are given to nearest whole number.)

Element's		Isotopes	Atomic weight (oxygen = 16) = mean atomic weight
Atomic number	Symbol		
1	H	1	1.008
2	Hi	4	4.00
3	Li	7, 6	6 94
4	Be	9	9 02
5	B	11, 10	10 82
6	C	12	12
7	N	14	14.01
8	O	16	16
9	F	19	19
10	Ne	20, 22	20.2
11	Na	23	23
12	Mg	24, 25, 26	24 32
13	Al	27	26 96
14	Si	28, 29, 30	28.06
15	P	31	31 02
16	S	32, 33, 34	32.06
17	Cl	35, 37	35.46
18	A	40, 36	39 88
19	K	39, 41	39 1
20	Ca	40, 44	40.07
21	Sc	45	45.1
22	Ti	48	48.1
23	V	51	51
24	Cr	52	52
25	Mn	55	54 93
26	Fe	56, 54	55.84
27	Co	59	58 97
28	Ni	58, 60	58 68
29	Cu	63, 65	63.57
30	Zn	64, 66, 68, 70	56 38
31	Ga	69, 71	69 72
32	Ge	70, 72, 74	72 38
33	As	75	74 96
34	Se	74, 76, 77, 78, 80, 82	79 2
35	Br	79, 81	79 92
36	Kr	78, 80, 82, 83, 84, 86	82 92
37	Rb	85, 87	85 44
38	Sr	86, 88	87.63
39	Y	89	88.9
40	Zr	90, 92, 94, 96	91
47	Ag	107, 109	107 88
48	Cd	110, 111, 112, 113, 114, 116	112.41
49	In	115	114.8
50	Sn	114, 115, 116, 117, 118, 119, 120, 121, 122, 124	118 7
51	Sb	121, 123	121 77
52	Te	126, 128, 130	127 5
53	I	127	126.92
54	Xe	124, 126, 128, 129, 130, 131, 132, 134, 136	130.2
55	Cs	133	132 81
56	Ba	138	137.37
57	La	139	138 91
58	Ce	140, 142	140 25
59	Pr	141	140 92
60	Nd	142, 144, 145, 146	144.27
80	Hg	198, 199, 200, 201, 202, 204	200.6
82	Pb	206, 207, 208, 209	207.2
83	Bi	209	209

is always an integral multiple of the electronic charge, the determination of the charge that the particle carries is never a difficult matter.

Aston has studied the atomic masses of nearly all the elements. Special means, such as electrically heated anodes coated with compounds of the elements, sometimes had to be used to secure positive particles of some of the elements in the discharge tube. A list of elements showing the isotopes which have been discovered for each, and the atomic weight of each isotope, is given in Table V. The results of Aston's earlier investigations were accurate to 1 part in 1,000. Greater accuracy was later attained with refinements in the apparatus. His later results are discussed in a later section (page 120).

The Separation of Isotopes.—A great many methods have been devised to separate the isotopes of different elements. One of these methods attempts to take advantage of differences in the rate of diffusion of gaseous isotopes through a porous tube. The rates of diffusion of different gases, according to Graham's law, are inversely proportional to the square roots of the masses of the diffusing particles. Hence, the residue of gas that remains after allowing as much of the lighter constituents as possible to diffuse through the tube should be slightly richer in the heavier isotope than the original mixture of the gas. Thus, Harkins has attempted to separate molecules of hydrogen chloride into two fractions by taking advantage of differences in the masses of the two isotopes of chlorine composing the hydrogen chloride molecules. He used 19,000 liters of hydrogen chloride and obtained two samples in which the chlorine differed in atomic weight by 0.055 unit.

Differences in the rate of evaporation of particles of different masses have formed the basis of other attempts to separate isotopes by allowing liquids to evaporate at low pressures. Many other methods have been used. Some of these depend upon differences in chemical activity and differences in the velocity of the ions of isotopes. No method has produced more than a very slight separation of an element into two fractions, except in the case of hydrogen (page 138). At the most, these fractions differ only by a few hundredths of a unit in atomic weights. Not even nature seems to have succeeded in a separation,

since the proportion of the isotopes of any one element is practically the same whether the element comes from the sea, from deep down within the earth, or is brought to the earth in a meteor from somewhere in outer space.

The Revival of Prout's Hypothesis.—The results of Aston's investigations revealed many interesting facts and relationships. Of perhaps greatest significance is the suggestion of these early reports that there are no isotopes of elements that have whole-numbered atomic weights. Thus, it appeared at first that there is but one kind of atom for oxygen, nitrogen, carbon, fluorine, sodium, vanadium, chromium, etc. On the other hand, the elements whose previously determined atomic weights were not whole numbers were found to consist of isotopes. The atomic weight of each isotope, however, appeared to be a whole number at least within the limits of 1 part in 1,000.

These results suggested at once that all atoms are aggregates of some structural unit, which on the scale of atomic weights (oxygen = 16) has an atomic weight of unity or a value very close to unity. Once again attention was focused on the suggestion made by Prout, in 1815, that all elements are composed essentially of one elementary kind of matter. The discovery of the isotopes of the nonradioactive elements and the facts of radioactivity that were already known provided the basis for something more than purely speculative opinions concerning the constitution of atoms. A means of unraveling the relationships of the elements, as revealed by the periodic system, was at last at hand. There was need, of course, for much more experimental evidence before the structure of atoms could be explained. Yet it was generally believed that so much had been learned that the rest would be solved without great difficulty. Theories were developed in great numbers, and physicists, who a few years previously had looked without hope to discover new fields for investigation, realized that the study of matter and also of energy was, perhaps, only in its infancy.

The Composition of Atoms

The Packing Effect.—If all atomic weights are whole numbers, as Aston's early results indicated, it should be possible to account

for the composition of all atoms as aggregates of different numbers of atoms of some truly fundamental variety of matter. On the scale of atomic weights (oxygen = 16), this element must have an atomic weight of 1. There is no element that has exactly this atomic weight. That of hydrogen is very nearly unity; it is 1.008, or, more exactly, 1.00778. The fraction, however, is a very real part of the atomic weight of hydrogen; Aston's results, for example, show that it is not due to experimental error in the determination of atomic weights. There is no other known particle, however, which can act as the structural unit for all other atoms. If the conclusion is accepted that the hydrogen atom, as the proton, is this unit, it becomes necessary to explain the loss of mass that must occur when protons and electrons are packed closely together to form the atoms of other elements. In accordance with this view of atomic composition, we may assume that the neutral helium atom, for example, is composed of four protons and an equal number of electrons. The alpha particle is electrically charged; it contains four protons and two electrons. The atomic weight of helium is 4, while the four protons, considered individually, have a total mass of 4.032 units on the scale of atomic weights. In the formation of one gram-atomic weight of helium, therefore, 0.032 unit of mass is lost. This loss of mass is often referred to as the *packing effect.* This loss is not caused by a decrease in the number of electrons. The four hydrogen atoms contain one electron each; they lose these in becoming protons, hydrogen ions. The neutral helium atom also contains, however, four electrons. There is no decrease in the actual number of particles, therefore, when the helium atom is built up, if this hypothesis is true, from protons and electrons. Furthermore, if all four electrons were lost and if the helium atom should consist of only four protons, the loss of 0.032 unit of mass would not be accounted for. Each electron has a mass which on the scale of atomic weights is only 0.00055; four would possess a total mass of only 0.0022 unit as compared to the theoretical loss of 0.032.

Assuming the packing effect to be real, we must account for the loss of mass that is associated with it. What becomes of the mass that disappears? The view now held is that it is converted into energy. The theory of relativity indicates a relation

between the mass and energy of a physical system that can be expressed by the equation (see page 97)

$$E = mc^2,$$

where c is the velocity of light. This means that any increase in the energy of a system is attended by an increase in mass and that a system that has the mass m also possesses a quantity of energy equal to mc^2. As in the case of the electron (page 97), we assume that the mass of the proton is also electromagnetic in nature.

We believe that electrons and protons are packed very closely together in the central cores of atoms. These cores are called the *nuclei* of the atoms. They contain all the protons and a certain number of electrons; the remainder of the electrons lie outside the atomic nucleus and at relatively great distances from it. It is not at all unreasonable to predict a certain degree of condensation of mass for those particles that are packed within the small confines of the nucleus. We must expend energy when an electron that lies near a proton is moved to a greater distance. This means that the energy possessed by the system as a whole is increased. It means, also, an increase in the inertia of the system and, therefore, an increase in mass, since inertia and mass are directly related. When electrons and protons are closely packed, the process is reversed. The electron is moved nearer the proton; hence, energy is released, the inertia of the system is reduced. This corresponds to a decrease in mass.

From the equation that expresses the relation between mass and energy, it can be shown that 7×10^{11} g.-cal. of heat is liberated when 0.032 g. is converted into energy during the formation of 1 gram-molecule of helium from hydrogen. The energy thus liberated has been suggested as the source of the heat that maintains the temperatures of the stars. The suggestion has also been made that this energy is radiated into space as cosmic rays, which consist of radiation of much shorter wave lengths than light, x-rays, or gamma rays. Other explanations of the phenomenon of cosmic radiation, however, have been offered, and the question of its origin is yet unsettled. To give a somewhat more concrete estimate of the quantity of energy involved, we may compare it with the energy obtained by burning coal. Upon

this basis, the energy that would be released when 1 g. of hydrogen is converted into helium would be equal to that which is liberated when about 100 tons of coal are burned. If we could heat our houses by the reaction

$$4H \rightarrow He + 7 \times 10^{11} \text{ g.-cal.},$$

instead of the reaction

$$C + O_2 \rightarrow CO_2 + 98{,}000 \text{ cal.},$$

our supply of fuel for the winter would consist of about 0.5 g. of hydrogen instead of 10 or 12 tons of coal.

The Packing Effect in Other Kinds of Atoms.—If all the atomic weights are whole numbers, it appears that the hydrogen atom must lose the same fraction of its mass, regardless of the atom that is formed. Furthermore, since so many of the atomic weights are exactly divisible by four, it appears likely that hydrogen atoms (really protons and electrons) are first "packed" to form helium atoms—or helium ions—and that the latter are then further packed to form more complex structures. Thus, we might assume that 16 protons, packed together as four helium groups, form an atom of oxygen. At least, this is what we thought until very recently, when more accurate determinations by a more highly sensitive method than the mass spectrograph revealed the fact that the relative mass of the oxygen atom is not exactly 16. These results were obtained by examination of the band spectrum of oxygen. They indicate that oxygen instead of consisting of a single kind of atom actually has three isotopes, which possess the relative masses of 16, 17, and 18, respectively. The usual atomic weights, therefore, are based upon a value of 16.0000 for the atomic weight of oxygen, which is really a mixture of the isotopes of mass 16, 17, and 18. If only the oxygen isotope of mass 16 were taken as the basis of atomic weights, all of our ordinary atomic weights would be increased by approximately 2 parts per 10,000. Thus, the usual value for the atomic weight of helium is 4.0013; on the basis of the oxygen isotope of mass 16, this atomic weight would become 4.0022.

The oxygen isotopes of masses 17 and 18 are present in such small amounts that the mean atomic weight differs from 16 by an amount that is far less than the experimental error that usually

attends our determinations of atomic weights by chemical methods. The extremely great preponderance of the oxygen atoms of mass 16 over those of masses 17 and 18 calls attention to the greater abundance and, hence, to the greater probability of formation of those atoms whose relative weights are exact multiples of four and which may be composed, therefore, of a definite number of alpha particles.

Nitrogen has been found to consist of two isotopes which have the atomic weights 14 and 15, respectively; the mean atomic weight is 14.008. In many other cases, the atomic weights that have been determined by newer and improved methods, even in the cases of isotopes, are found to differ from whole numbers by a few parts in 10,000. Aston has recently constructed a mass spectrograph which can be used to determine atomic and molecular masses with an accuracy of 1 part in 10,000. Some of his later results are given in the table below.

ATOMIC WEIGHTS BASED UPON ASTON'S LATER WORK

Helium	4 00216
Lithium	6 012 and 7 012
Carbon	12 0036
Nitrogen	14.008
Oxygen	16 0000
Neon	20 0004 and 22 0004
Chlorine	34 983 and 36.980
Krypton	77.926, 79 926, 80.926, 81.927, 83 928, 85 929
Iodine	126.932

The divergences of the atomic weights listed above from whole numbers can be explained on the basis of the packing effect. The results suggest, of course, that the effect of packing is slightly different in different atoms. The more closely protons and electrons are packed the greater the loss in mass. Thus, it appears that protons are more closely packed with electrons in atoms of chlorine, krypton, and iodine than in atoms of carbon, lithium, helium, oxygen, nitrogen, and neon. Aston's results show considerable variation in the mass of the proton with the atomic weight (or the mass number) of the elements in whose atomic nuclei it is packed. Figure 31 shows the average mass per proton in the nuclei of different elements upon the basis of the usual scale of atomic weights. The low points on this curve

correspond to low values of mass and, hence, to low values of mass energy (page 97):

$$E = mc^2.$$

These points, therefore, indicate the elements of maximum stability, since every system tends to attain its greatest stability when its energy content is at a minimum. The high points on the curve represent instability. Thus, the curve steadily rises in the direction of the mass numbers of the radioactive elements.

Before concluding the discussion of the masses of atomic nuclei, mention should be made of another suggestion which has been offered to explain variations such as those that we have described. According to this point of view, the mass of the

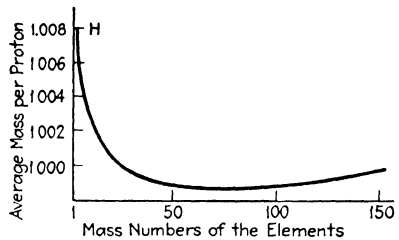

FIG. 31.—Variation of the packing effect with the atomic weights of the elements

atomic nucleus may be due entirely or partially to electrons which revolve in orbits with very high velocities. Since the mass of the electron increases with velocity, the electrons within the nucleus may constitute at least a considerable part of the mass of the atom.

This point of view, however, has not been considered very seriously, since it so far remains without any substantiation in fact. It is probably most conclusively contradicted by the liberation from atoms of relatively massive particles which can in no way be associated experimentally with negative charge.

The Atomic Nucleus.—According to our present ideas of atomic structure, all the protons and hence the positive charge of an atom are located in a small space called the *nucleus*. This nucleus, we believe, is composed of electrons and protons but contains a greater number of the latter than the former; hence, the nucleus of every atom carries a positive electrical charge.

This charge is always a multiple of the electronic charge e and can be represented as Ne, where N is the *atomic number* of the element.

The remaining electrons of the atom rotate about the nucleus in orbits that differ in size and in character; some may be circular, and some elliptical. The atom, therefore, is a porous body consisting of a central core of material and electrons which move through its outer regions in much the same manner as the planets move about the sun in our solar system. The complete atom is a particle which is electrically neutral to bodies external to it but within which powerful electrostatic, and probably magnetic, forces operate between the parts that compose its structure. The mass of the atom may be regarded as being almost entirely within the nucleus, since the total mass of the outlying electrons is so small that it may be neglected.

Concerning the arrangement of protons and electrons in the nucleus we know but little. The electrons may serve in some way as a means of binding the protons together. We shall discuss what little information we have on the subject in a later chapter (page 136). Experimental evidence shows that the nucleus of even the most complex atom is very small as compared with the space occupied by the atom as a whole. Tremendous forces must be in operation within this tiny space, where particles of the same and of opposite kinds of charge are packed very closely together. If these forces become unbalanced in any way, if electrons and protons fall by chance into an arrangement where the forces of repulsions are stronger than those that bind the parts together, one or more particles are ejected. This results in the disintegration of the radioactive elements.

The Composition of Atomic Nuclei.—The fact that alpha particles which are the nuclei of helium atoms are ejected by the atoms of certain radioactive elements indicates that these atoms are composed in part of helium nuclei. The fact that many atomic weights are divisible by four indicates further that the helium group is a very general positively charged unit of nuclear structures. On the other hand, there are many atomic weights that are not exactly divisible by four. These differ from multiples of four by one, two, or three units and indicate the presence of free protons, or groups of protons smaller than the

alpha particle, in such atoms. Upon the basis of these indications, it is possible to offer the following explanation of the production of complex atoms in nature: At first, four protons and two electrons are closely packed to form the nucleus of the helium atom. Different numbers of helium groups, together with free protons in some cases, and with additional electrons, are then further packed to form the nuclei of more complex atoms.

It has been suggested that the nuclei of the atoms of some elements whose atomic weights are multiples of four may be composed in part of helium nuclei, or alpha particles, and in part of neutral helium atoms. In speaking of the neutral atom, we refer, of course, to the nucleus plus the electrons that revolve around it. This suggestion is based upon the fact that several elements (in many cases we refer only to certain isotopes of the element) possess atomic weights that are multiples of four, but the charges of their nuclei cannot be accounted for on the basis of alpha particles and electrons alone. An alpha particle adds four protons and two electrons to the atomic nucleus of which it is a part, while each complete atom adds four protons and four electrons. Now, the nuclear charge of an atom is numerically equal to the *atomic number* of the element which determines the element's position in the periodic table. Hence, the presence of an additional helium atom or nucleus causes an increase of four units in atomic weight, while the atomic number remains the same if a complete helium atom is added but increases by two for each helium nucleus. If the atomic number of an element, whose atomic weight is divisible by four, is exactly one-half of the atomic weight, the assumption may be made that the atom is composed of helium nuclei. If the atomic number is less than half the atomic weight, we may assume that the atom contains whole atoms as well as nuclei of helium.

In accordance with the theory outlined in the preceding paragraph, the atomic weight of an element, when that atomic weight is exactly divisible by four, can be expressed by the following equation:

$$\text{Atomic weight} = n \times \text{atomic weight of helium} = n \times 4,$$

where n is an integer. All the elements of this group have even atomic numbers, a fact that confirms the idea that their atoms are

aggregates of helium atoms and nuclei, since the atomic number of helium itself is an even number (two). As Harkins has pointed out, most of the common elements of the earth's crust (Table VI) belong to this group.

TABLE VI.—COMPOSITION OF THE EARTH'S CRUST—LANDS, OCEANS, AND ATMOSPHERE

Element	Composition of the atomic nuclei[1] (theoretical)	Percentage of the earth's crust
Oxygen	4 He	50 02
Silicon	7 He	25 80
Aluminum	6 He 3 H	7 30
Iron	16 He	4 18
Calcium	10 He	3 22
Magnesium	6 He	2 08
Sodium	5 He 3 H	2 36
Potassium	9 He 3 H	2 26
Hydrogen	H	0.95
Others		1 81

[1] Where isotopes exist, that isotope whose mass number is a multiple of four is most abundant.

Another group of elements possess atomic weights that can be represented by the following equation:

$$\text{Atomic weight} = n \times \text{atomic weight of helium} + 3 \times \text{atomic weight of hydrogen} = (n \times 4) + 3.$$

Among these elements are lithium, $(1 \times 4) + 3$; fluorine, $(4 \times 4) + 3$; and sodium, $(5 \times 4) + 3$.

The elements of still another group possess atomic weights that agree with the formula $4n + 2$. Among these are nitrogen, $(3 \times 4) + 2$; neon, $(5 \times 4) + 2$; and zirconium, $(22 \times 4) + 2$.

There are also atomic weights that correspond to the formula $4n + 1$: The atomic weight of magnesium (one isotope) is $(6 \times 4) + 1$; and that of chlorine is $(9 \times 4) + 1$ or $(8 \times 4) + 3$.

It was thought for a time that single protons occur only in those nuclei whose relative weights agree with the formula $4n + 1$. In all other cases, it was thought that H^2, H^3, and H^4

particles constitute the massive units of the different nuclei. Because of the fact that H^2 and H^3 particles have not, until very recently, been observed experimentally among the products liberated by disintegrating atoms, their presence in atomic nuclei has not been regarded very seriously. There is now direct evidence of the existence of the H^2 particle, however, as an isotope of ordinary hydrogen, H, but whether or not this particle occurs within the atoms of other elements we cannot tell. There has been some evidence that H^3 particles are expelled from certain kinds of atoms under bombardment by rapidly moving alpha particles and are also present in the discharge tube. Such evidence, however, has not been sufficiently confirmed in an experimental manner to permit its general acceptance. Very recently, certain kinds of atoms have been found to liberate particles called *neutrons* which have approximately the same mass as protons. It is thought that a neutron is a bare nucleus containing one proton and one electron. We shall discuss the bearing of their discovery on theories of atomic structure in a later section (page 137).

We base our conclusions concerning the contents of atomic nuclei upon our knowledge of the kinds of particles that atoms liberate when they undergo disruption. The particles that we recognize in this connection are alpha particles, protons, neutrons, electrons, and positrons. So far as we are aware at the present time, these are the units of which all atomic structures are composed. All of them, or some of them, may be packed closely together, with accompanying reductions in the total mass of the system, within the nuclei of different atoms. Electrons alone form the outer structure of the atom.

The Number of Isotopes.—All the known isotopes of the elements are listed in Table V (page 115). This list is not necessarily complete. Further investigations with a more sensitive mass spectrograph or by other methods may reveal other isotopes of some or all of the elements. This table also shows the mean atomic weight, which is the value obtained by chemical methods. The number of extranuclear electrons is also given for each kind of atom; these are the electrons that revolve about the nucleus. This number also gives the nuclear charge in terms of e and is the atomic number of the element.

Physical Differences of Isotopes.—The isotopes of an element are nearly identical physically and chemically. This must mean that the structures of the atoms of isotopes differ only slightly. If we can determine how the atoms of isotopes are alike and how they are different, we should be able to say what part of the atom's structure is responsible for its chemical and many of its physical properties.

Isotopes do not have the same relative atomic masses. This means that there is a slight difference in their atomic nuclei, since the protons that are responsible for the mass of the atom are located in the nuclei. That atom which contains the largest number of protons within its nucleus possesses the greatest mass. Thus, there are two isotopes of lithium. The atoms of one have a mass of six on the scale of atomic weights (oxygen = 16), and the other a mass of seven. The former contains six protons per atom, and the latter seven, one for each unit of mass. Similarly, the chlorine isotope of mass 35 contains 35 protons, and that of mass 37 contains 37. But since the two isotopes of either of these elements have the same chemical properties, there can, evidently, be little relation between chemical behavior and mass, or nuclear structure. Furthermore, the chemical properties and many physical properties of the elements are periodic, but there is no evidence of periodicity in the structure of atomic nuclei. As we pass up the scale of elements in the periodic table from hydrogen to uranium, the mass gradually increases. There is a gradual increase in the number of protons in the nuclei of the atoms, and the difference between the numbers of protons and nuclear electrons increases one at a time. There is absolutely no evidence of a *recurrence* of *nuclear structures* corresponding to the periodicity which occurs among the elements and upon which the periodic table is based.

The position of an element in the periodic table is determined by its atomic number, which has been defined (page 123) as equal to the nuclear charge of the atoms of the element. Since all the isotopes of any one element must occupy the same position in the table, there is but one atomic number for all of them. Hence, although isotopes may differ as regards the number of protons in their nuclei, those nuclei that contain more protons must also contain a correspondingly larger number of electrons.

Thus, the atomic number of each of the isotopes of lithium is three. For the lithium atom whose mass is six, the nucleus contains six protons and three electrons. For the atom of mass seven, the nucleus contains seven protons and four electrons. The difference in the numbers of protons and nuclear electrons is the same for all the nuclei of the isotopes of one element.

If it is not the nucleus, then it must be the arrangement of the electrons which revolve around the nucleus that determines the chemical properties of the elements. It is in this extra-nuclear portion of the atom's structure that we must look for a periodicity of structural arrangement corresponding to the periodicity of the properties of the elements. We should expect to find that the arrangement of these electrons, whatever it may be, is the same for all the atoms of the isotopes of an element.

It is a remarkable fact that the isotopes of any element are always so mixed that the mean atomic weight of the element is the same, regardless of the source of the element, its history, and the chemical reactions in which the element may be involved. Thus, the two isotopes of chlorine, whose atomic weights are 35 and 37, respectively, are always so mixed that the mean atomic weight of chlorine never varies from 35.46. Even the 11 isotopes of tin are so mixed that the mean atomic weight is always 118.70. It is not difficult to understand why the mixture should remain unchanged when it is once prepared. The isotopes of any one element are so nearly identical in chemical and physical properties that when once mixed, they may always remain mixed in the same proportions. The strange thing about it all is that they were originally produced in the same proportion wherever and whenever the element was formed. The constant mean atomic weight argues in favor of the law of chance as the determining factor in the formation of different atoms. Thus, it appears that there is a definite number of chances that protons, alpha particles, neutrons, and electrons (and, perhaps, neutral helium atoms) may combine to produce the nucleus of a chlorine atom possessing the relative 35 and atomic number 17. There is also a certain number of chances that these same particles will also combine, under the same conditions and at the same time, to form an atom of mass 37 and atomic number 17. In the case of chlorine, the chances appear to be about three to one in favor of the chlorine

atom whose mass is 35. We also extend this principle of probability to include other atoms. When these common atomic constituents combine to form chlorine atoms, there is also a certain number of chances that they may combine in other proportions and in other ways to form atoms of other elements. Those elements of greater abundance such as oxygen, carbon, silicon, iron, magnesium, and calcium evidently possess the greatest number of changes of formation. It will be noted that all these most abundant, and therefore most probable, elements possess atomic weights that are multiples of four; or in those cases where there are several isotopes, that isotope is most abundant that has an atomic weight exactly divisible by four. It will also be noted that all of these elements have even atomic numbers. No element of an odd atomic number has more than two isotopes.

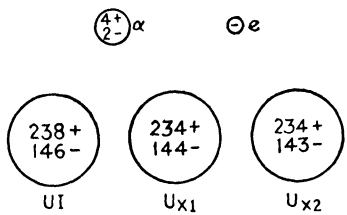

FIG. 32.—Disintegration of the radioactive elements.

Uranium I	Uranium X_1	Uranium X_2
Atomic weight 238	Atomic weight 234	Atomic weight 234
Atomic number 92	Atomic number 90	Atomic number 91

The atomic weights of the two isotopes usually, and above the atomic number nine always, differ by two units. The following pairs of isotopes are cited as examples: chlorine, 35 and 37; gallium, 69 and 71; rubidium. 85 and 87; and antimony, 121 and 123. Just what significance or meaning this may have is difficult to say.

The Isotopes of the Radioactive Series.—The loss of an alpha particle by a radioactive atom results in a decrease in mass of four units and a reduction of two in the atomic number of the element (page 65). These changes can be explained, of course, on the basis of the composition of the alpha particle. This particle contains four protons and two electrons; its atomic number, therefore, is two. The atom that results from the expulsion of the alpha particle (Fig. 32) contains four less protons and two less electrons than the atom producing it. These losses

account for the change in mass and nuclear charge, when an atom of radium, for example, is transformed into an atom of radon.

The loss of a beta particle, or electron, does not cause a change in mass, since the atom becomes positively charged and soon attracts another electron, which falls into the extranuclear portion of its structure; thus, the small, almost negligible, mass that is lost is regained. It will be noted, however, that the electron is lost by the nucleus and regained by the extranuclear structure. Hence, there is one less electron in the nucleus after the expulsion of the beta particle, and the atomic number of the product is one greater than that of the parent atom.

TABLE VII.—ATOMIC STRUCTURES OF THE ELEMENTS OF THE URANIUM SERIES

Element	Atomic Weight	Kind of particle ejected	Number of electrons in the nucleus	Atomic number
Uranium I .	238	Alpha	146	92
Uranium X_1	234	Beta	144	90
Uranium X_2	234	Beta	143	91
Uranium II. .	234	Alpha	142	92
Ionium .	230	Alpha	140	90
Radium.	226	Alpha	138	88
Radon . .	222	Alpha	136	86
Radium A	218	Alpha	134	84
Radium B	214	Beta	132	82
Radium C	214	Beta	131	83
Radium C′	214	Alpha	130	84
Radium D	210	Beta	128	82
Radium E	210	Beta	127	83
Polonium .	210	Alpha	126	84
Lead. .	206	.....	124	82

The nucleus of the uranium I atom contains 238 protons and 146 electrons. Its atomic number, therefore, is 92. In disintegrating to form uranium X_1, an alpha particle is lost; hence, the uranium X_1 nucleus contain 234 protons and 144 electrons and has the atomic number 90. An atom of uranium X_2 is next formed from that of uranium X_1 by the loss of a beta particle.

The loss of this particle causes a change of the atomic number from 90 to 91, since there is the same number of protons but one less electron in the nucleus. Next, the uranium X_2 atom forms an atom of uranium II by the ejection of another beta particle. Hence, the atomic weight of uranium II is 234, and its atomic number is 92, the same as for uranium I. Uranium I and uranium II are, therefore, isotopes. The relations between the atomic masses and atomic numbers of other elements in the uranium series are shown in Table VII. The atomic numbers of these elements show five sets of isotopes. Still other isotopes of these same elements are found among the members of the actinium and thorium series (page 65).

The Artificial Disintegration of the Nonradioactive Elements

It has long been known that electrons can be removed from the outer portions of all atoms. The resulting particle is always an ion of the same element. Such changes may result from the irradiation of the atoms of the elements by x-rays, ultraviolet light, or even visible light; by impacts of rapidly moving electrons, protons, and other small bodies such as alpha particles; by exposure to high temperatures; and by other comparatively simple means. But ionization cannot change the fundamental character of the atom; no new atom results from the change that occurs.

Many attempts have been made to remove electrons or other particles from the nuclei of atoms of some of the common elements, thus causing their disintegration and the formation of new elements. If, for example, the atoms of any of the stable elements could be made to eject protons in the same manner that radioactive elements eject alpha particles or electrons, the idea that all atomic nuclei are composed of protons would be experimentally confirmed. Many of these attempts to disrupt atomic nuclei have been successful in showing that protons can be ejected from atoms of many elements by bombardment with rapidly moving alpha particles. We shall describe the method used by Rutherford and the results that he obtained as typical experiments along this line.

Atoms and molecules of various elements were bombarded with alpha particles from radium *C*, whose range in hydrogen is 31 cm.

and in air about 7 cm. Radium *C* is deposited on the brass disk *D* (Fig. 33). The box BB_1 is filled with the gaseous form of the substance, which is to be studied, at any desired pressure. The opening in the end of the box is covered by a thin foil of metal, which has a known absorbing, or stopping, power for alpha rays. The absorbing power of the foil is expressed as the equivalent of a certain thickness of air, usually about 5 cm. Different numbers of these foils may be used when the "swift" particles have a great range in air. Those particles which pass through the foils strike the screen *SC*, which is covered with zinc sulfide and is, therefore, fluorescent. The scintillation produced by the striking particles is observed by means of the microscope

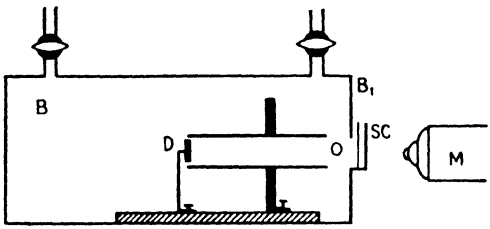

FIG. 33.—Rutherford's apparatus for the artificial disintegration of atoms.

M. By moving this screen through different distances from *O* or by placing different numbers of foils in the path of the particles, the maximum range of the particles can be determined. This range will have been measured when the conditions are such that the particles fall just short of reaching the screen.

When the box is filled with hydrogen, it is found that atoms of that element that are centrally struck by the alpha particles have a range (in hydrogen) of about 117 cm. By no means all of the struck particles, of course, have this great range. Those that are struck at a glancing angle are given a smaller velocity and, hence, travel smaller distances before they are stopped. When hydrogen compounds, such as hydrocarbons, are bombarded, long-range hydrogen particles, or protons, are also produced. That these are protons is shown by their ranges and by determinations of the value of the ratio e/m (page 82).

When the box is filled with nitrogen or air, swift particles are produced which have an average range of about 28 cm. in air.

This range is about four times as great as that of the alpha particles themselves and is approximately equal to the range of a struck hydrogen atom. Furthermore, the deflections of the particles in magnetic and electrical fields show that they possess the mass and charge of protons. But the only possible source of such protons is *the nucleus of the nitrogen atom.* Rutherford proved the absence of all contaminating sources which might have contained hydrogen. In studying the disruption of nuclei from which short-range particles were ejected, Rutherford further eliminated the possibility of the presence of protons from contaminating sources by observing the particles at right angles to the beam of alpha rays. Swift hydrogen atoms move only in the forward direction. Those observed at right angles to the beam must come from another source. He has further proved that oxygen, in experiments where air is used instead of pure nitrogen, does not serve as the source of any swift particles. The results must mean, therefore, that the nitrogen nucleus breaks up in the collision with an alpha particle and that one or more protons are ejected.

Rutherford found that long-range particles (protons) are liberated when atoms of the elements shown in Table VIII are struck by alpha particles. The ranges of the particles that were liberated in the experiments are also shown.

It will be noted that practically all of the elements in this list have atomic weights that are not exactly divisible by four. With the exception of argon, at least one isotope of every element has an atomic weight that cannot be expressed as a multiple of four. This suggests that protons are ejected only from atoms that contain free hydrogen particles and whose composition does not agree with the formula $4n$. Although the case of argon appears to be an exception, the suggestion in general is correct. In this connection, it is worthy of note that those elements whose most abundant and predominating isotope possesses a mass that *can* be expressed as $4n$ liberate few protons and that these have very short ranges (Table VIII). As examples, we may cite neon, magnesium, silicon, sulfur, and argon. It will be noted, also, that all of these elements possess even atomic numbers. On the other hand, every element of odd atomic number between 5 and 15 liberates protons that have relatively long ranges.

TABLE VIII.—RANGES OF PROTONS EMITTED BY ELEMENTS UNDER BOMBARDMENT BY ALPHA PARTICLES[1]
(Alpha particles from radium C)

Element bombarded	Atomic number	Atomic weights of isotopes	Range, centimeters	
			Forward	Backward
Boron	5	10, 11	58	38
Nitrogen	7	14	40	18
Fluorine	9	19	65	48
Neon	10	20, 22	16	
Sodium	11	23	58	36
Magnesium	12	24, 25, 26	18–30	
Aluminum	13	27	90	67
Silicon	14	28, 29, 30	18–30	
Phosphorus	15	31	65	49
Sulfur	16	32, 33, 34	18–30	
Potassium	19	39, 41	18–30	
Argon	18	40, 36	18–30	
Chlorine	17	35, 37	18–30	

[1] Data from the "International Critical Tables" and other scattered sources

The ranges of the particles produced by the bombardment of the atoms of different elements are shown in Table VIII. The maximum forward range of the particles liberated from nitrogen is about 40 cm. in air. This range corresponds to a kinetic energy of the ejected proton which is greater than that of the alpha particle that ejects it. The collision causes, therefore, a real disruption of the nucleus of the nitrogen atom. The only source of the additional energy that the ejected particle possesses is within the nitrogen nucleus; disintegration, as in the case of radioactive elements, is accompanied by the release of a certain quantity of the energy of the nuclear system.

Protons that have ranges up to 90 cm. (in air) are liberated when aluminum atoms are struck by alpha particles. As in the case of nitrogen, additional energy must be supplied from a source within the nuclei of the atoms. The energy released by the disintegration of aluminum atoms is greater than that which attends the breaking up of any other nonradioactive element yet investigated.

Other facts point toward the actual disruption of the nucleus. When hydrogen atoms are struck, protons are found to move

forward, usually directly forward. The protons expelled from other atoms, those of aluminum for example, move in all directions. This fact further indicates that the proton is not simply knocked out of the atom. The collision with an alpha particle actually disrupts the nucleus, and the proton is expelled because of the action of nuclear forces.

Rutherford believes that the protons ejected by atomic nuclei revolve as satellites about the main body of the nucleus. Since both the satellite and the remainder of the nucleus are positively charged, this view requires that within the limits of nuclear distances positive attracts positive. This force changes to repulsion at distances further removed. If the collision with an alpha particle drives the proton into this region where repulsive forces operate, the proton may be expelled from the nucleus and

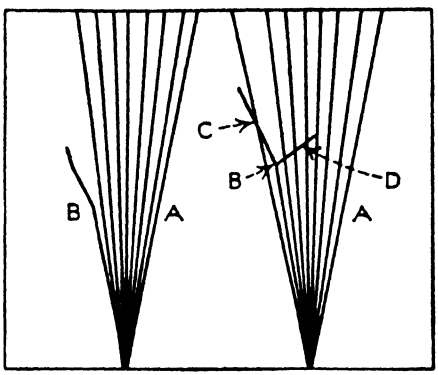

FIG. 34.—Disintegration of the nucleus of the nitrogen atom. *A*, fog track of alpha particle; *B*, point of collision of alpha particle and nitrogen nucleus; *C* and *D*, paths of proton and atom of oxygen isotope (17) after the collision.

be forced to move away with a high velocity. This explanation of the mechanism by which the proton is expelled cannot be supported, of course, by experimental evidence.

The question of what elements result when protons are ejected from different atomic nuclei has also been investigated. Cloud-track photographs (Fig. 34) have been made of swift alpha particles passing through nitrogen and other substances. Blackett, Harkins, and others have found that these photographs now and then show the results of a collision. Many photographs must be made before the desired result is obtained. It is estimated,

for example, that 1,000,000 alpha particles from radium C′ liberate about 20 protons when they are passed into and completely absorbed by nitrogen. About three times this number of actual disintegrations are observed when 100,000,000 of the slower alpha particles from polonium are allowed to bombard the aluminum atoms in a sheet of this metal which is thick enough to absorb all the particles that strike it.

The photograph of a disintegration (Fig. 34) shows two paths which diverge from the point where the collision occurs. One of these represents the path of the proton, and the other that of a particle which appears to be more massive than either the proton or the alpha particle. There is no path that corresponds to the movement of the alpha particle after the collision. Furthermore, the fact that never more than one path which can be ascribed to a proton is observed indicates that not more than one proton is liberated by a single collision.

Since the alpha particle does not appear after the collision, it must be absorbed by the atom that it strikes. If so, an atom possessing a relative mass of 18 and containing nine nuclear electrons is formed by the fusion of the two nuclei. The atomic number of such an atom would be nine; hence, it is an isotope of fluorine. After the proton is expelled, the atomic number of the residual atom is eight, and the mass is 17. The element that finally results from the collision, therefore, is an isotope of oxygen. The relative masses of the particles that travel the paths shown by the photograph are calculated from the angles that the paths make with each other. These angles depend upon the energy and momentum of the particles concerned, and these, of course, depend in turn upon the masses of the particles.

The suggestion has also been offered that the protons liberated by the collisions are produced by the disintegration of the alpha particles. This suggestion has not been received very favorably, however, since this view of the problem would predict the liberation of protons whenever alpha particles strike atoms of any kind. Rutherford's results, on the other hand, definitely indicate that collisions only with certain kinds of atoms result in the liberation of protons.

The Neutron.—Since 1930, it has been known that radiation of a very penetrating nature is emitted when alpha particles from

radioactive elements, such as polonium, fall upon beryllium or boron. This radiation was first interpreted as gamma rays. Later, it was shown that the radiation is far more penetrating than gamma radiation.

Chadwick, in 1932, showed by a series of convincing experiments that the radiation consists of particles that have approximately the same mass as protons but are uncharged. Since they carried no charge, Chadwick called the particles neutrons. He determined the mass of the particles within the limits of 1.005 and 1.008 on the scale of atomic weights (oxygen = 16.0000). Later, he decided upon the value of 1.0067. Lawrence of California claims that the neutron has a mass of only 1.0006, and Professor and Madame Joliot of France assert that the correct value is 1.012.

The neutron corresponds approximately to the nucleus of a hydrogen atom as regards mass; but since it is uncharged, this nucleus must contain an *electron* as well as a *proton*. It is, therefore, an atom of an element whose atomic number is zero; it is a bare, neutral nucleus. The neutron is extremely difficult to detect, since it may pass through matter or through magnetic and electrical fields without suffering deflection. For the same reason (it is uncharged), the neutron is a poor ionizing agent and, therefore, does not produce the customary fog track in a water-vapor chamber in the manner of other particles of like origin. Although the neutron itself produces very few ions, fog tracks of the ions produced by atoms that recoil from collisions with neutrons can be observed by the usual methods. The recoil atoms are particles that result from disintegrations of different nuclei when collisions with neutrons occur. It has been shown, for example, that several types of disintegration are produced by collisions of neutrons with atoms of nitrogen, in some of which the neutron fuses with the struck nucleus and in some of which it does not. Oxygen atoms, which have thus far resisted attempts to disintegrate them by alpha particles, have been disintegrated by neutrons.

Accepting the neutron as another kind of unit from which atoms may be built up in nature, we may offer the following interpretation of the beryllium atom: This element has an atomic number of four and an atomic weight of nine. The nucleus of a

beryllium atom, therefore, contains nine protons and five electrons. Four electrons revolve about the nucleus in the outer portion of the atom's structure. We may picture the nucleus as consisting of two alpha particles (eight protons and four electrons) and one neutron (one proton and one electron). The suggestion has also been advanced that protons and neutrons are added alternately in building up atomic structures. Thus, a proton constitutes the nucleus of an atom of hydrogen. The addition of a neutron gives the nucleus of an atom of the hydrogen isotope H^2. If another proton is added, the triple-weight isotope of hydrogen H^3, or the nucleus of an atom of an isotope of helium, is the result. An additional neutron then gives the nucleus of a normal helium atom (mass = 4). This rule holds with a fair degree of accuracy among the lighter elements. For the heavier atoms, we must assume that two neutrons are added one at a time and then two protons.

Instead of considering the neutron as a particle composed of an electron and a proton, we may find that it is more accurately defined as an elementary particle, which can be transformed under certain conditions into an electron and a proton. This kind of transformation may occur, for example, in the disintegration of an atom when a beta particle is ejected.

The full significance of the neutron, its bearing on the problem of nuclear structure, and its abundance as a free particle in nature yet remain, however, to be determined by future investigations. These may lead to observations of great importance. For the present, the discovery is significant because it has added one more element (No. 0) to the list of elements and because it has revealed a fourth unit from which atomic structures may be built up in nature.

The H^2 Isotope of Hydrogen.—Urey and his coworkers have found an isotope of hydrogen that has an atomic weight of approximately two. Liquid hydrogen was fractionally distilled, and the final residue consisting of the least volatile portion of the starting material was examined spectroscopically. The nature of the lines that appear in the spectrum of hydrogen, particularly the frequencies or wave lengths of the radiation corresponding to the lines, depends slightly upon the mass of the atomic nucleus. Urey found that instead of the single lines that one would predict

on the basis of a single kind of nucleus (mass = 1), two lines were observed. The second of these was always very weak, but it was in the very position that a line produced by an atom of mass 2 should occupy. The results have been confirmed by other investigators, and one of these, Bainbridge, has determined the mass of the H^2 isotope by means of the mass spectrograph. His value lies between 2.013 and 2.014.

We believe, at this time, that the nucleus of the H^2 isotope is composed of one proton and one neutron. This composition explains the mass and the atomic number (one) of the atom. We cannot predict, of course, that the mass of the neutron should be equal to the sum of the masses of a proton and an electron. The nucleus of the H^2 isotope has been called the *deuton*, although the name *diplon* has also been suggested (by Rutherford).

Double-weight hydrogen has come to be called *deuterium* and is represented by the symbol D, although some prefer to designate it as H^2. Rutherford has suggested the name *diplogen*. Its oxide, commonly called "heavy water," has the formula D_2O and is called deuterium oxide. Deuterium is now produced by the electrolysis of water, the heavier isotope being more concentrated in the last of the hydrogen to be evolved. By burning this hydrogen to form water and again taking the hydrogen from the last fraction to be electrolyzed, and repeating the process, the separation of H and H^2 is effected. A recently introduced method consists of dissolving zinc in dilute solutions of sulfuric acid. The H isotope is displaced by zinc more rapidly than H^2 (the ratio is about 4 to 1). The liquid consequently becomes richer in deuterium oxide.

Chemical studies of deuterium include the preparation of the iodide DI and the substitution of deuterium for ordinary hydrogen in hydrocarbons or their derivatives. Molecules corresponding to the formula HD have been prepared. These contain one atom each of deuterium and ordinary hydrogen. Heavy water in which all the hydrogen is deuterium is now prepared at Princeton. The specific gravity of this water is 1.1078 (25°). Heavy water has been used in many kinds of experiments which have been attempted to determine the difference between it and ordinary water. These experiments include the effect of heavy water upon the growth of cancer cells; its effect upon the life

processes of goldfish, mice, and other animals; its action as a solvent for salts and other substances; and many other types of experiments.

The Triple-weight Hydrogen Isotope.—Lord Rutherford and his fellow workers in the Cavendish laboratory have recently performed experiments which, as they believe, have resulted in the formation of triple-weight hydrogen H^3. Ammonium salts containing heavy hydrogen, or deuterium, instead of ordinary hydrogen were bombarded with deutons. Thus, deutons were bombarded with deutons. The products of this action indicated that two deutons were converted into two particles, one of mass 3 and one of mass 1. The heavier of these products may have been an isotope of hydrogen or of helium. In the first case, the lighter particle was undoubtedly an ordinary atom of hydrogen; and in the second case, a neutron.

$$(+\ -\ +)(+\ -\ +) \rightarrow (+\ -\ +\ -\ +)(+) \qquad (1)$$
$$(+\ -\ +)(+\ -\ +) \rightarrow (+\ -\ ++)(+\ -) \qquad (2)$$

Full explanation must await further investigation. Lord Rutherford has very recently announced the weight of this H^3 isotope as 3.051 on the scale of atomic weights. Experiments at Princeton, of the same general nature as those in the Cavendish laboratory, have also produced particles of mass 3.

Artificial Radioactivity.—An interesting discovery was recently announced by Prof. F. Joliot and Mme Irene Curie-Joliot, the daughter of Madame Curie. Boron was bombarded with alpha particles and was found to emit positrons. The activity or disintegration continues for some time after the bombardment has ceased. Boron is thus made artificially radioactive and behaves in a manner very much like that of the radioactive elements. The experiments have been extended by others to include bombardment of boron, carbon, magnesium, and aluminum by protons and by deutons as well as alpha particles. Boron has been found to lose one-half of its activity in 20 min.; carbon loses half of its radioactivity in 10 min.; aluminum does the same in 4 min.

In the case of the proton as the bombarding particle, it has been suggested that, upon entering an atom of the bombarded element, the proton forms a positron and a neutron. The latter

escapes from the atom at once, but the positron is retained. If retained by the boron atom, it causes an increase of one in the atomic number and produces, therefore, an atom of carbon. Similarly, the retention of a positron by a carbon atom makes an atom of nitrogen. The later activity is due to the delayed emission of these positrons. When alpha particles are used to bombard atoms of boron, it is thought that the boron atom and the helium molecules react to form a neutron and an unstable isotope of nitrogen (mass 13). The latter disintegrates radioactively to liberate a positron and gives an atom of an isotope of carbon (mass = 13).

The Evolution of the Elements.—Modern knowledge of the atom and the electron has led to much speculation as to how different forms of matter have come into existence. It appears that, during the lapse of millions of years, there has been an evolutionary change in the kinds of elements on the earth. Early in the history of the planet, protons, electrons, and possibly other kinds of particles probably were brought together under certain conditions in nature that permitted them to form atomic nuclei, first of the lighter and later of the heavier, more complex atomic forms. The law of probability determined the relative number of each kind of atom, not only of the different elements but of the isotopic forms of the same element as well. Some of the most complex of these structures have proved unstable. Because of the possible rearrangements of protons and electrons within their nuclei, such atoms disintegrate at a rate that depends only upon the probability that the unstable grouping may be formed; these are the atoms of the radioactive elements. It is possible that other more complex, more unstable, and hence more strongly radioactive elements may have existed at some time on the earth or may now exist in other parts of the universe.

More interesting still is the question of whether or not it is possible that somewhere, even now, protons and electrons are being packed together into helium nuclei and that, under other conditions and, perhaps, in some other part of the universe, helium atoms, protons, neutrons, and electrons are brought together to form the nuclei of other atoms. Another question also arises: If matter is converted into energy when atoms are

built up from protons, is it also possible that energy may be converted back again into forms of matter, such as neutrons, protons, positrons, and electrons?

The answers to such questions must remain for the present almost entirely in the field of pure speculation. Attempts to answer them have been encouraged by the discovery of cosmic rays and investigations of their nature.

Cosmic Rays.—Because of the action of alpha, beta, and gamma rays which emanate from the radioactive materials of the earth, it is to be expected that the air near the earth should be ionized to some extent. At elevations of about 1,500 ft., the ionization reaches a minimum, as one should expect if the rays causing the ionization have their source in the earth's crust. At higher elevations, however, ionization again increases slowly up to an elevation of 15,000 ft. Above this level, the increase is very rapid. The ionization of the higher layers of the atmosphere must be produced by rays that come from a source outside the earth's atmosphere. This radiation, which appears to come from the space outside the earth's atmosphere, is called *cosmic* radiation. These rays are very penetrating; they can be detected after passing through 6 feet of lead. The rays are not homogeneous, however, and not all of them have this great penetrating power. The more penetrating, or harder, portions of the radiation penetrate the earth's atmosphere more effectively than the softer parts. The more penetrating constituents have been found to pass through 600 to 700 ft. of water in snow-fed lakes high up in mountainous parts of the earth's surface. Considering the rays as having the same nature as x-rays, their frequencies appear to be some fifty times greater than the average frequency of gamma radiation.

Millikan suggests that cosmic rays are produced by a process in which protons are built up into the heavier elements. The spectrum of the rays reveals four bands of lines corresponding to four groups of wave lengths. In interpreting these bands, Millikan assumes that they are produced, respectively, by the synthesis (1) of helium, (2) of oxygen, (3) of silicon, and (4) of iron from hydrogen nuclei and electrons. He suggests that these changes occur in interstellar regions, where the temperature is near absolute zero. In such regions, the energy that is radiated

into space by the stars is converted into electrons and protons, which in turn are built up into atoms of the more complex elements.

Jeans has proposed a second explanation of the source of cosmic rays. He assumes that within the stars, electrons may "fall into" atomic nuclei, where they neutralize and annihilate protons. The disappearance of each proton results in the liberation of energy in the form of cosmic radiation.

These two views are directly opposed. Millikan's view proposes a universe that reconverts the energy dissipated into space by the stars into forms from which it may be liberated again. Jeans's suggestion is more in accord with our usual and older views of energy. It is possible, of course, that both Millikan and Jeans may be right—and both may be wrong. If energy is produced by the annihilation of protons and electrons in the interior of stars, then in the spaces between the stars this energy of radiation may be converted into protons and electrons once more.

The suggestion has also been offered that cosmic rays may not be radiation of the nature of x-rays and gamma rays at all. They may consist of electrons from the sun. Compton has recently gathered information concerning these rays from all parts of the earth. The variation of their intensity with altitude, with distances from the magnetic poles, with the passing of the hours of the day and night, and with every other conceivable condition has been investigated. If, for example, the rays consist of electrons (or protons), they should be deflected by the earth's magnetic field. Because of this deflection, we should find them concentrated near the magnetic poles. Millikan claims to find that the distribution of the rays is constant over wide ranges of latitude. Compton's results, however, tend to show that the distribution is not constant.

Others have suggested that the rays may be composed of neutrons. Further data must be secured before the question of their origin can be answered. No final solution is forthcoming, as this is written, although such a solution may be reached at any time. Compton's latest results, it may be said, however, do not greatly encourage the acceptance of the proposal of either Millikan or Jeans. It should be clearly understood, of course,

that we have no evidence that such changes as Millikan proposes are occurring in the universe. The proposal of Jeans is equally lacking in experimental verification, and at present the means of testing either suggestion experimentally is unavailable. Either scheme, or a combination of them, is contrary to our time-honored idea that the universe and all its parts are gradually being reduced to a state of complete inactivity. We have thought of the energy of the universe as undergoing a gradual dissipation and tending toward a final state in which it could no longer be used to do work. The idea now proposed assumes, on the other hand, that energy that is dissipated into space may be converted into forms of matter, which may at some future time and under other conditions mutually destroy one another to set energy free again. Because of our faith in the second law of thermodynamics, we are loath to accept this cycle of energy and matter as it is proposed. It is contrary to the behavior that we have learned to expect from our observations of the matter and energy of earth forms. Yet, because of our limited experience in dealing with questions on the scale of the entire universe, it is possible that we may be wrong and that the future may bring a revision of our conclusions in this regard.

The early nineteenth century found scientists in almost complete agreement in the belief that the atom is one of the ultimate realities of nature. For them, atoms could be neither created nor destroyed. Not only has this idea now been abandoned, but the first quarter of the twentieth century has left us in a state of quandary as to whether or not the *parts* of which atoms are composed can be created or destroyed.

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CHAPTER VII

THE ATOMIC NUCLEUS AND THE DETERMINATION OF NUCLEAR CHARGE

We have already (Chap. V) introduced the idea that the positive charge of an atom is located in a small central portion of the atomic structure, called the nucleus. This concept was discussed at that time without any mention of the experimental evidence supporting it, because the idea offered the most satisfactory basis of explaining the differences existing in the structures of the atoms of isotopes. We are ready to deal at this time with the evidence upon which the nuclear theory is founded. But let us first examine an earlier idea concerning the distribution of the positive charge of the atom.

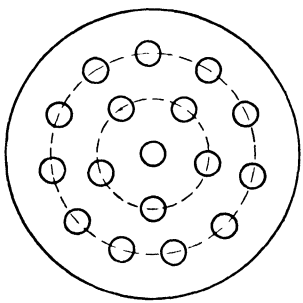

FIG. 35.—Arrangement of electrons in Thomson's sphere of positive electrical charge. A similar arrangement may be demonstrated by floating small corks in a dish filled with water and placed above a strong magnet.

The Positive-sphere Theory.—Sir J. J. Thomson pictured the atom as a sphere of positive electricity in which electrons are embedded (Fig. 35). The total charge of these electrons was assumed to be equal to the positive charge of the atom. Thomson showed the manner in which the electrons would arrange themselves within this sphere in stable groups. Thus, as many as 5 may lie in one ring. The sixth electron goes to the center, and under these conditions the ring is stable until it holds 8 electrons. The further addition of electrons produces two rings, one of 5 members at the center and an outer ring of 11. The seventeenth electron then goes to the center of the 5-membered ring and there starts still a third group, and so on. The periodicity of arrangement that results was interpreted as suggestive of the periodic grouping of the elements.

A positive electrical sphere, such as Thomson proposed, would possess an electrical field of maximum strength on the sphere's surface; the strength would approach zero toward the center. This conception of the distribution of the positive charge of the atom has not been generally accepted, or seriously considered, since it fails to explain many of the points concerning the atom's behavior, particularly the force with which it repels or attracts another charged particle. Furthermore, this model cannot explain the results obtained by spectroscopic studies of the light and x-rays emitted. On the other hand, this is a field of investigation in which the nuclear model of the atom has been extremely successful and helpful.

Rutherford's Nuclear Theory.—In 1911, Rutherford introduced the concept of the positively charged nucleus. There are several lines of evidence in favor of this view. Most of these have to do with the effect of various forms and kinds of matter in scattering alpha particles. The fog tracks (page 51) of alpha particles in air which is supersaturated with water vapor offer striking evidence in favor of the existence of atomic nuclei. These tracks show that alpha particles move in straight lines for some distance. They must pass through many thousands of atoms in doing so. Occasionally, a fog track shows a sudden change in direction, which indicates that the alpha particle has encountered a center of extremely strong repelling forces. These forces can be explained by the assumption that the atom is a very porous structure and that most of the mass and all of the positive charge of the atom are located on or within a very small portion of the atom, which we may call the nucleus. If an alpha particle encounters a nucleus in its flight, it is strongly deflected. If it does not, it passes through the outer portions of atoms and, therefore, encounters no repelling forces. The fog tracks of alpha particles offer no support for the idea that the atom is a sphere of positive electricity with electrons embedded in it.

The scattering of alpha particles by thin metal foils has been investigated by Rutherford, Geiger and Marsden, Chadwick, and others. If a narrow pencil of alpha particles from radium C, or some other radioactive source, is directed toward a screen of zinc sulphide (Fig. 36), a region of soft glow is produced upon the screen. This spot of light actually consists of many tiny

flashes, each of which is produced by the striking of a single alpha particle. By examining a definite area on the screen, it is possible to determine the number of alpha particles that strike this area in a given time. If a thin foil of metal is placed between the source of the alpha particles and the screen, the glowing spot becomes somewhat diffuse and of slightly greater area. When examined with the aid of a microscope, it is found that not so many particles strike the same area as before the metal foil was interposed. This means, then, that some of the alpha particles, and perhaps all of them, have been deflected during their passage through the foil. It is possible to calculate the fraction of all the particles that are deflected through different

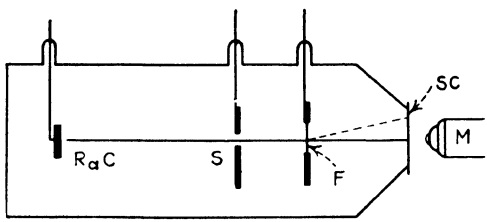

FIG. 36.—Rutherford's apparatus for studying the deflections of alpha particles by the nuclei of heavy atoms.

angles, by counting the scintillations produced in positions that lie in different directions from the original beam of alpha particles. The scattering through small angles appears to be in accordance with the law of probability, which, of course, would determine the final effect if each of the alpha particles were deflected slightly and in many different directions while passing through the foil. The fraction of particles thus deflected was found to be greater the greater the atomic weight of the metal used to scatter them. This number also increased with the thickness of the foil. These facts clearly indicate that the scattering effect is not due to surface reflection of the particles. A few particles are deflected through large angles of 30 deg. or greater (Fig. 37). In fact, some do not strike the screen at all, and some are deflected backward in the direction from which they came. The deflections that produce the scattering of alpha particles through small angles are explained as the results of encounters with the electrons which lie in the outer region of atoms. But large-angle deflections

cannot be accounted for as large deflections resulting from many small ones in the same direction. The number of particles deflected through large angles is far too great to be accounted for on this basis.

Rutherford assumed that the particles deflected through large angles encountered very intense deflecting forces within the atoms of the foil. Such intense forces as seemed to exist would require the concentration of the positive charges of the atoms in very small regions. They could not be explained if the positive charge was distributed over the entire atom. Of course, the attraction of electrons for the alpha particles would cause deflections, but such deflections would necessarily be small, because of the very great

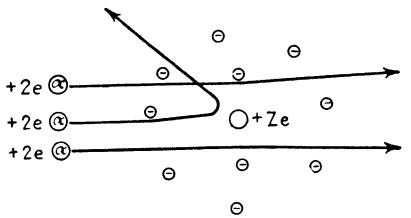

FIG. 37.—Deflection of an alpha particle upon passing through the space occupied by an atom of nuclear charge Ze.

kinetic energy of the alpha particles. Hence, Rutherford came to the conclusion that the positive charge is located at the center of the atom, the nucleus, which was assumed to have a diameter of something like 1×10^{-12} cm. Only a few alpha particles of several hundred thousand came close enough to a nucleus to be repelled strongly. If an alpha particle came very close to a nucleus, or struck it centrally, the alpha particle was deflected through such a large angle that it did not strike the screen at all and sometimes was turned back in the direction from which it had come. Those that did not pass so closely to nuclei were deflected strongly enough to throw them, perhaps, a considerable distance outside the original area of glow on the screen.

To aid the reader in visualizing the passage of alpha particles through matter, let us imagine alpha particles magnified until they are as large as airplanes. On this same scale, the foil is some 600,000 miles thick, and the nuclei of the atoms are something like 360 miles apart—farther apart than Chicago and

Cleveland and almost as far apart as Washington and Boston. Alpha particles, as large as airplanes, flying through this 600,000 miles of space at random would only occasionally pass near enough to a nucleus to be repelled and deflected by it. In the 360 miles of space between nuclei, there are, of course, electrons scattered here and there which slightly deflect the alpha particles. It is quite evident, however, that most particles can pass entirely

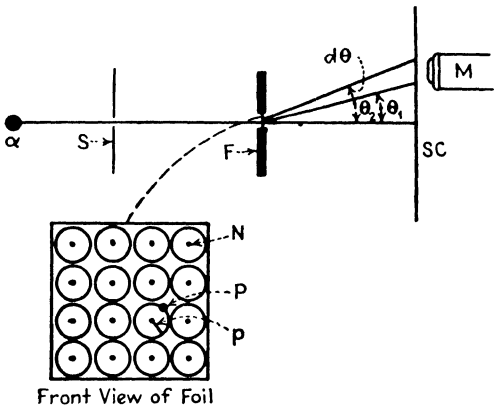

FIG. 38.—Deflection of alpha particles by metal foils. N, nucleus of the deflecting atom; P, point where the alpha particle strikes the foil; p, distance between P and N.

through the space without suffering much, or any, deflection from their original paths.

Determinations of Nuclear Charge.—Let the mass, charge, and velocity of the alpha particle be M, E, and v, respectively, all of which are known. Let Ze (a multiple of the electronic charge e) be the charge of the nucleus. The charge E of the alpha particle is equal to $2e$. Let p (Figs. 38 and 39) be the perpendicular distance from the center of the nucleus to the original direction of the alpha particle's path, and θ the angle through which the particle is deflected. Then, assuming that the force of repulsion between the two particles obeys the usual inverse-square law, and that the charges of the two particles act as point charges,

$$p = \frac{2Ze^2}{mv^2} \cdot \cot \frac{1}{2}\theta. \qquad (1)$$

The angle of deflection is smaller for larger values of p and v and for smaller values of Z.

The probability that a given alpha particle will follow a path that lies nearer or farther from the center of the nucleus than the distance p depends upon the number of nuclei per unit volume of the foil. The number of atoms and, hence, the number of nuclei per unit volume can be calculated from the mass of a unit volume and the mass of a single atom of the metal. Let n represent the number of atomic nuclei per unit of volume and t the thickness of the foil. Now, the chance that a particle in passing through the foil will approach a nucleus by a distance that lies between p_1 and p_2 and that it will be deflected through an angle between θ_1 and

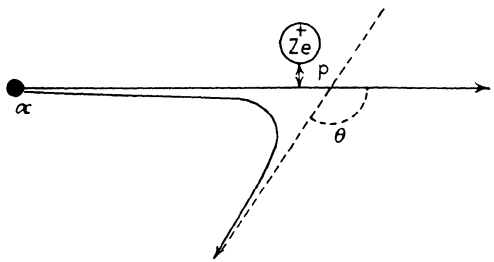

FIG. 39.—Deflection of an alpha particle by a heavy nucleus. The nucleus is regarded as remaining stationary.

θ_2 can be calculated from (The area of the circle whose radius is p_1) $\times$ (the number of such circles in the foil) $-$ (the area of the circle whose radius is p_2) $\times$ (the number of such circles in the foil). This can be expressed more concisely:

$$\text{Probability} = \pi p_1^2 nt - \pi p_2^2 nt = \pi nt(p_1^2 - p_2^2) \qquad (2)$$

Substituting the value of p from Eq. (1) in Eq. (2):

$$\text{Probability} = \pi nt \frac{4Z^2e^4}{m^2v^4}\left(\cot^2\frac{\theta_1}{2} - \cot^2\frac{\theta_2}{2}\right). \qquad (3)$$

Just as Eq. (3) gives the probability that a given alpha particle will be deflected through an angle somewhere between θ_1 and θ_2, it also gives the fraction of such particles out of a large number that will be so deflected within these limits.

Rutherford determined by actual experiment the fraction of a definite number of alpha particles that were deflected through different large angles between the value of θ_1, and θ_2, for example. The observed results checked closely with those predicted by

Eq. (3). He found, for example, that the number of particles deflected through any definite large angle was proportional to t, the thickness of the foil, as the equation demands. The relation between velocity and the fraction of particles deflected at a given angle was also verified; the fraction so deflected was found to vary with $1/v^4$, m remaining unchanged. The theory of the nuclear atom was remarkably substantiated, since Eq. (3), which is based upon the assumption that the positive charge Ze is located at the center of the atom, fully accounts for all the results observed.

The nuclear charge Ze can be calculated from Eq. (3) if the fraction of a given number of particles passed through the foil and deflected through angles between θ_1 and θ_2 is known, since all other values in this equation are known or can easily be determined. It was suggested, by Stoney, that the nuclear charge determined in this manner is equal to the *atomic number* of the element of which the foil is made. Previously, the term atomic number had been used in referring to the position of the element in the periodic table. If the atomic numbers of all the elements could be determined, it was evident that a much more complete and accurate periodic system than that based upon atomic weights could be formed. Furthermore, it should be possible to determine the exact number of elements between hydrogen and uranium in the periodic system. From the results of scattering experiments, the charges on the nuclei of copper, silver, and platinum atoms were found to be 29.3, 46.3, and 77.5, respectively. These numbers correspond to the atomic numbers of these elements, and the agreement is fairly satisfactory. Thus, the positions of gold, silver, and platinum in the periodic system are 29, 47, and 78 places, respectively, above hydrogen.

Atomic Numbers

A very accurate method for the determination of the atomic numbers of the elements was soon developed after the nuclear theory of atomic structure was definitely established. This method involves the study of the wave lengths of the characteristic x-rays emitted by the elements. It is necessary, therefore,

that we next turn our attention to the subject of x-rays, what they are, and how they are produced.

X-rays. Their Nature and Origin in Terms of Electromagnetic Theory.—While working with cathode rays in 1895, Röntgen noticed that surfaces coated with barium platinocyanide became luminous when placed near the tubes. This luminosity was not due to the direct action of cathode rays, since it was observed in positions out of reach of these rays, which, of course, travel in straight lines. It soon became evident that a new form of radiation had been discovered and that it originated in the portions of the glass walls of the tube that were exposed to the action of cathode rays. This radiation was called *Röntgen rays*, or *x-rays*.

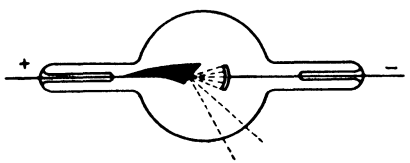

FIG. 40.—X-ray tube.

With a few modifications, the cathode-ray tube became a Röntgen-ray tube. The cathode was made in the form of a concave mirror so that the cathode rays might be brought to a focus at a point within the tube. At this point, a platinum or tungsten plate, called an anti-cathode, was introduced. The Röntgen rays were produced when the cathode-ray particles struck the anti-cathode. These rays travel in straight lines from the surface of the anti-cathode and penetrate the walls of the tube. They affect the photographic plate, even when the plate is covered with materials that are opaque to visible light.

Röntgen recognized the extremely great penetrating power of x-rays. Investigations of the relation of the tube potential to the character of the rays showed that the penetrating power, or hardness, of the rays increased with increasing potential. Other properties of the rays were soon determined. These included their power of ionizing gases through which they pass; of exciting secondary x-rays when they fall upon different substances; of affecting a great many chemical reactions, such as freeing

iodine from iodoform; and of stimulating biological activity in some cases and of destroying cells in others.

The properties of Röntgen rays and the absence of any evidence that they are corpuscular in character suggest that they are of the same nature as light. It was learned that these rays, like light, can be polarized and diffracted. In accordance, therefore, with the accepted theory of light (of that time), they were regarded as electromagnetic waves. According to this view, the kinetic energy of the rapidly moving electrons in the beam of cathode rays is converted into the energy of electromagnetic waves.

An electron in motion—like all moving electrically charged bodies—is surrounded by an electromagnetic field. When it is

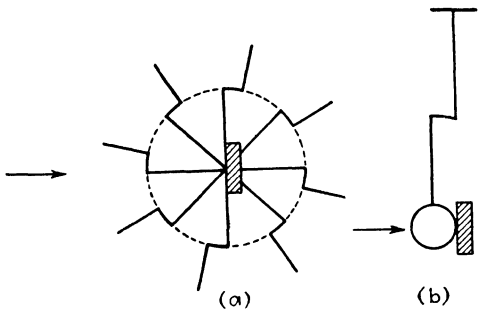

FIG. 41.—Production of an electromagnetic pulse. (*a*) Electron and lines of force; (*b*) the analogy of a ball and an attached string.

at rest, the electron is surrounded only by an electrostatic field. When a moving electron is stopped, or when its motion is retarded, therefore, a disturbance arises in the electromagnetic field and travels out from the position of the electron at the point of retardation in all directions. Thus, a single electromagnetic pulse is said to be produced. The mechanism by which this pulse is produced can be explained if we think of a moving electron surrounded by lines of forces (page 99). These lines extend from the electron in all directions and move along with it. If the electron is suddenly stopped, the ends of the lines attached to it are also stopped. The outer portions of the lines, however, maintain their original velocity. The case is very much like that of a stretched string which is attached to a moving ball (Fig. 41). When the ball is brought to a sudden stop, the end of

the string which is attached to the ball also stops. But all of the string does not stop at the same time. Instead, a displacement, or kink, travels out along its length with a definite velocity, as if the rope were jerked suddenly.

In a similar manner, "kinks" are produced in all the lines of force about an electron. These kinks represent disturbances, or displacements, in the electrical field of the electron. Now, any displacement in the electric field acts in a manner similar to that of a moving charged body in producing a magnetic field that lies at right angles to its motion. Hence, as the kinks, or electrical displacements, move out from the electron, a magnetic field is produced and also moves out along the lines of forces as the displacement is propagated farther and farther from the electron.

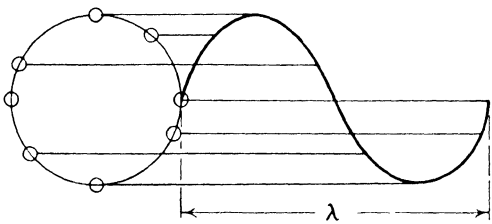

FIG. 42.—Oscillation of the electron about a fixed point, λ represents one wave length.

Since both electrical and magnetic fields are thus involved, we speak of the disturbance, as a whole, as an electromagnetic wave. We may think of this wave as constituting the surface of a sphere which expands into larger and larger spheres as the displacement is propagated away from the electron with a velocity that depends upon the magnetic permeability and the dielectric constant of the medium.

An electromagnetic disturbance of the kind just described constitutes a single electromagnetic pulse. We assume that a pulse of this character is produced when an electron strikes the anti-cathode in a Röntgen-ray tube. If, instead of stopping suddenly, an electron oscillates about a fixed position, the direction of its motion is continuously changed (Fig. 42). The electron is stopped in one direction only to move off in another. In this manner, a series of pulses are produced with the vibrating electron as the source. The frequency of these waves is deter-

mined by the number of times that the motion of the electron is reversed per second, *i.e.*, by the period of vibration of the electron. The wave length is the distance between the successive pulses, or the distance traveled by the electromagnetic disturbance during the time required for a complete vibration of the electron.

The explanation outlined above is not the only theory of the origin of light, x-rays, and other forms of radiation. The explanation given is based upon the classical electromagnetic principles of Faraday and Maxwell and has led to what is usually styled the wave theory of light. This theory was extremely successful in explaining many of the properties of light, such as reflection, refraction, polarization, and diffraction. Serious difficulties were encountered, however, when the theory was applied to the explanation of the action of radiation upon matter and to the problem of the origin of spectral lines. Our conception of the nature and origin of radiation has changed considerably since the time of Maxwell. The wave theory, although not entirely discarded, has been changed radically by the incorporation of new principles. In fact, it appears necessary at times to regard light not as waves of electromagnetic character but as corpuscular radiation. We leave a consideration of these matters to a later chapter, where the newer theories will be compared more freely with the old.

The Diffraction of Light.—The use of x-rays in the determinations of atomic numbers is the principal reason for our interest in this form of radiation at the present point in our discussion. This use depends upon the *diffraction* of x-rays. Before undertaking the discussion of this subject, it may help if we first become familiar with the diffraction of light. Since the wave theory offers a satisfactory explanation of diffraction phenomena, we shall continue to treat light as electromagnetic waves resulting from electronic vibrations.

The Diffraction Grating.—A grating for the diffraction of light is made by ruling many lines, 5,000 or more per centimeter, on a glass plate, thus producing a number of small parallel slits. If light of a definite wave length and from a slit source falls upon this grating, each slit acts as the source of a new wave (Fig. 43). Let us suppose that plane waves fall upon the grating G. On the other side of the grating, the new waves spread out in all direc-

tions but, for the sake of simplicity, let us consider only the direction between the grating and the screen. All of the wave trains originating at the grating are in the same phase at the apertures. New wave fronts may be represented as advancing in directions that form many different angles with the original direction of the plane waves; let us consider the wave front that advances in the direction indicated by the line R_1R_5. In order that the wavelets along this front may be in phase the distance traveled by the wavelet originating at one slit must be one full wave length longer or shorter than the distance traveled by the wave originating at an adjacent slit. This condition will be fulfilled at the point R_1, for example, if the distance S_1R_1 is equal to two full wave lengths and if the distance S_2R_1 is equal to three wave lengths. If a lens is used to gather up all the rays that move out with this wave front, they may be brought to a focus and will produce a bright spot of light at the point O_1. At other points, there is no light, since the wavelets are not in the same phase for other angles; hence, they destroy one another by interference. There is, however, another direction S_1T_7 along which a new wave front may advance, the rays of which may be focused by a lens at the point O_2. The wavelets that start from the apertures reach points along the new wave front two wave lengths behind or in advance of the wavelets from adjacent apertures. The spots O_1 and O_2 are called the first- and second-order images, respectively. If the source of light had consisted of several wave lengths, each would have given rise to its own

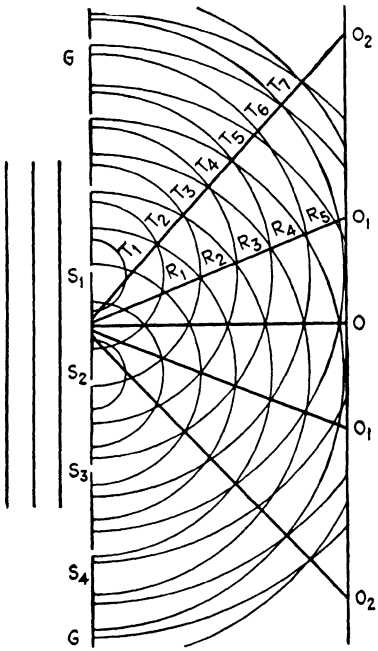

FIG. 43.—The diffraction of light. Points O, O_1, and O_2, appear as regions of light on the screen. The regions between these points are dark because of destructive interference.

first- and second-order images, corresponding to wave fronts at different angles from the path of the incident beam. For each wave length, there are, of course, other orders of images, such as O_3, O_4, etc.

The angle at which the wavelets from the different apertures of the grating reinforce one another depends upon the ratio of the wave length to the distance between successive apertures. It can be shown that reinforcement occurs when

$$\sin \alpha = \frac{\text{wave length}}{\text{distance between apertures}} = \frac{\lambda}{a},$$

or when

$$\sin \alpha = n\frac{\lambda}{a}.$$

Thus, for the wave front, S_1R_5, $n = 1$; for S_1T_7, $n = 2$; and so on. This assumes, of course, that there is a single wave length in the incident beam. If white light is allowed to fall upon the grating, each wave length (or color) produces its own series (first, second, third order, etc.) of spectral lines. Let us confine our attention to the spectrum of the first order. Since λ is different for each of the various wave lengths in the beam, and since a is the same in all cases, different values of α will be required to fulfill the conditions of the equation $\sin \alpha = \lambda/a$. Hence, the different wave lengths will be propagated, after diffraction, along wave fronts that make different angles, one for each wave length, with the original path of the incident light. The beam of light, therefore, is spread out into a spectrum in which all of the colors are separated. The width of the spectrum and the dispersion of its lines depend upon the dimensions of a as compared to those of λ. The dispersion increases as a decreases. Hence, it follows that the lines must be very closely ruled on the grating if the different wave lengths are satisfactorily separated.

The Diffraction of X-rays.—Since the wave length λ of an x-ray is very much smaller than the wave length of any portion of visible light, the distance a between successive apertures of a grating that would diffract x-rays would have to be exceedingly small. This means, of course, that the lines would have to be ruled very closely together, about one million to the centimeter. Recently, x-rays have been successfully diffracted by means

of ordinary gratings. This has been accomplished by making the angle of incidence at which the rays fall upon the grating very large (almost 90 deg.).

In 1912, Laue suggested that a grating for the diffraction of x-rays could be had in the crystalline form of a substance, such as sodium chloride. This idea was investigated experimentally by Laue in collaboration with Friedrich and Knipping. A small beam consisting of parallel monochromatic x-rays was allowed to fall upon a stationary crystal which was about 1 cm. square by 0.5 cm. in thickness. A photographic plate was placed behind the crystal (Fig. 44). Since the crystal remained stationary,

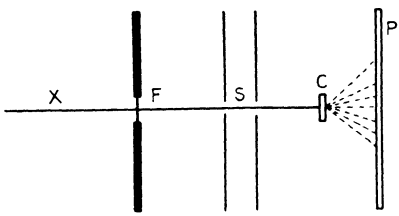

FIG. 44.—Apparatus used by Friedrich, Knipping, and Laue in diffraction of x-rays by a crystal. *X*, the incident x-ray beam; *F*, filter made of aluminum foil, *S*, slits; *C*, the crystal; and *P*, a photographic plate.

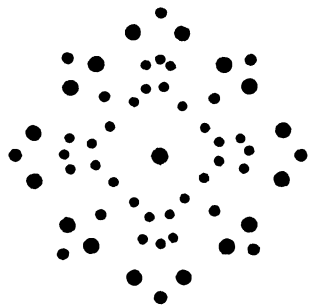

FIG. 45.—Laue spots produced by means of a crystal possessing cubic symmetry. The incident beam of x-rays was parallel to a fourfold axis of symmetry.

the x-ray beam was "reflected" only in certain directions and produced, therefore, spots upon the plate (Fig. 45). The symmetry of the arrangement of these spots reflects, in a certain sense, the symmetry of the crystal.

So that we may better understand the effects of crystals upon x-rays, we shall next consider some of the principles concerning crystal forms. This study is called crystallography.

Crystallography.—The symmetrical external forms of crystals suggest that their interiors are also symmetrically constructed. When a crystal forms, each particle assumes a fixed position in space with respect to other particles. These particles may be atoms, ions, or molecules. Different kinds of particles take different positions relative to one another. Patterns of different

geometrical forms result. A crystal unit consists of the smallest number of particles required to complete a given pattern. The structure of a crystal consists of the repetition of this crystal unit throughout the entire volume. The pattern of the unit is called a *space lattice* and represents the distribution of particles in three dimensions. Two-dimensional lattices are simply planes containing certain sets of particles within the unit. Certain of these planes constitute the *planes of symmetry* of a given crystal unit and serve as a basis for the classification of the different crystal patterns. The symmetry of the crystal is the same, of course, as of its space lattice. Upon the basis of this classification, crystallography recognizes six groups of crystal patterns.

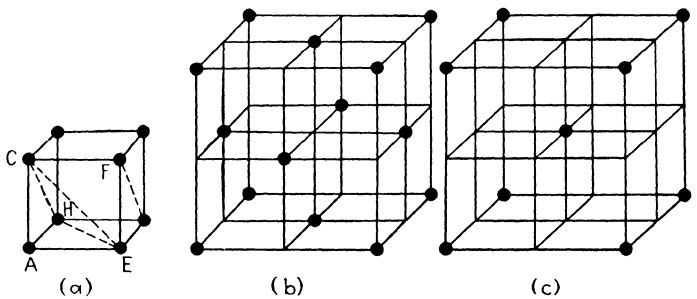

FIG. 46.—Types of cubic space lattices. (*a*) Simple cubic lattice; (*b*) face-centered cubic lattice; (*c*) cube- or body-centered cubic lattice.

The six groups are further subdivided into 32 classes. Thus, there are three kinds of patterns all of which belong to the group of the cubic system of space lattices. These three kinds of cubic patterns are called the simple, the face-centered, and the body-centered lattice (Fig. 46). Any one of these lattices possesses nine planes of symmetry. Three of these are designated as the principal planes. These planes are at right angles to one another and form three faces of a simple cube. The three cubic forms are also similar in that each possesses three rectangular axes of equal length. The forms of the crystal structures built about these axes are not always the same, owing to the development of different faces. In this way, the external form of the crystal may be that of a tetrahedron, a cube, an octahedron, or a dodecahedron. If, for example, the crystal grows in such a way that the face *CEH* (Fig. 46*a*) is developed, an octahedral form

results. If the face *AECF* is developed, the form will be that of a cube.

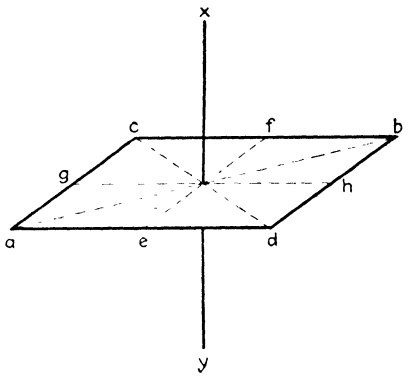

FIG. 47.—A fourfold axis of symmetry, showing the intersection of four planes of symmetry with a plane that is normal to the fourfold axis in a cubic lattice. Axis, *xy*; intersections of planes, *ab*, *cd*, *ef*, and *gh*.

The axes of a crystal are described with respect to the number of planes of symmetry that can be drawn through the axis. Thus, the edge of a cube in a cubic lattice represents a so-called fourfold axis of symmetry. Through this edge, four planes may be drawn. The intersections of these four planes with a plane that is normal to the axis are shown in Fig. 47. A threefold axis of symmetry for a cubic lattice is represented in Fig. 48, by a line drawn perpendicularly to an octahedral face of the crystal or connecting opposite corners of a cube. A line joining the midpoints of opposite edges of a cube is a twofold axis of symmetry. The center of a cube is a center of symmetry, since two lines drawn from it in opposite directions locate identical points in the cube.

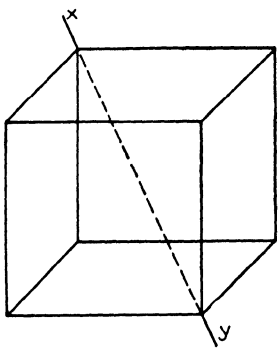

FIG. 48.—A threefold axis of symmetry of a cubic crystal.

In the examination of crystals or in the description of the passage of a beam of light or other form of radiation through the crystal, it is always important to know the direction of the passage of light with respect to some axis of symmetry.

Let us, then, look at a simple cubic lattice in the direction of the fourfold axis of symmetry. From this point of view, let us describe certain planes containing particles of the pattern. It will be understood that each plane that we shall describe is a

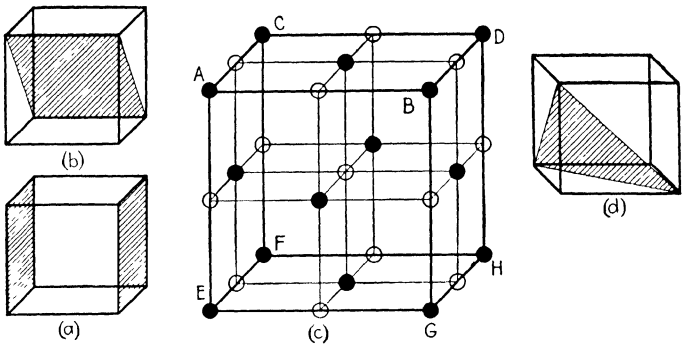

FIG. 49.—Kinds of atom-bearing planes in the cubic space lattice. (*a*) planes of the type *AECF*; (*b*) planes of the type *ABFH* or *CDEG*; (*c*) a complete unit of the crystal of sodium chloride, showing how the small cubes, such as those shown in (*a*), (*b*), and (*d*), are associated in a large crystal. (*d*) planes of the type *AFG*.

member of a set of planes that could be drawn for a large crystal. The planes of each series are parallel and lie at the same distance from one another. The distance between planes is different, of course, for the different series. Thus, we have shown in Fig. 49 the arrangement of particles in three planes of a simple cubic lattice and the manner in which the various planes are related to one another. Figure 49*c* shows the structure of a larger portion of a crystal, while *a*, *b*, and *d* show three of the smallest possible cubic structures, all of them identical and each a crystal unit. In the three crystal units, we have drawn three kinds of planes: *AECF* or *ACBD*; *AFG*; and *CBFG*. In the larger crystal (Fig. 50), the intersections of a series of parallel planes with the face *BGDH* are shown. The intersections of the same planes with face *BGDH* are shown for a still larger crystal in Fig. 51; these are the planes designated by *y*. Similar, but differently spaced,

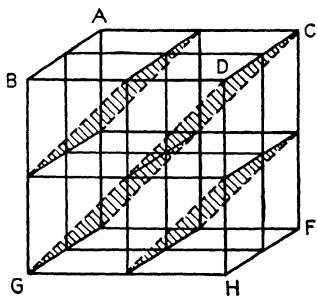

FIG. 50.

sets of planes (x, w, and z) are also shown. The intersections of a series of parallel planes with the face *AEBG* are shown in Fig. 52. Besides these, many other series of planes can be visualized.

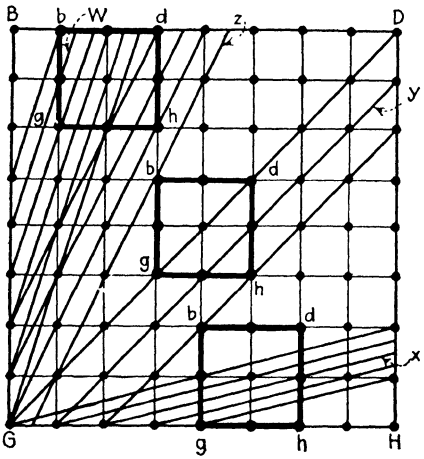

FIG. 51.—Some of the sets of planes that are perpendicular to a face of a cubic crystal. y, Planes parallel to plane *CEDG* of Fig. 50; x, w, and z are other sets of planes perpendicular to face *BDGH*. Note the differences in the distance d between adjacent planes of the four series

There is, for example, a series each plane of which is parallel to plane *BEH* and intersects face *EFGH* (Fig. 53).

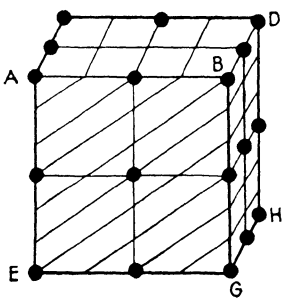

FIG. 52.

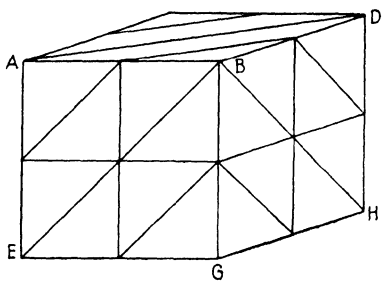

FIG. 53.

The Crystal as a Diffraction Grating for X-rays.—The structure of crystals will be considered in greater detail in the next chapter. At this time, we are interested only in the action of a crystal as a space lattice where particles act as diffraction centers

for a beam of x-rays. With the understanding that we now have of space lattices, we shall proceed to a discussion of the diffraction that they produce.

Sir W. H. Bragg and W. L. Bragg developed a method, following the discovery of Laue, that depends upon the "reflection" of x-rays from the surface of a crystal. This method is used to separate a beam of x-rays into its constituent wave lengths.

Let us confine our attention, for the present, to one series of planes. The plane that forms one face of the crystal is one of these. The x-ray beam falls upon the face and penetrates the crystal for a short distance before its energy is entirely absorbed. A part of this energy is used in the production of secondary x-rays. When a train of waves, represented by A_1B_1 in Fig. 54,

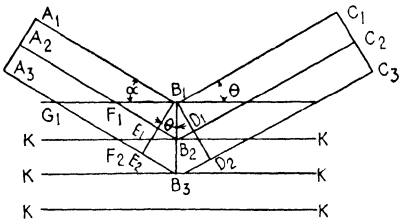

FIG. 54.—The Bragg method of determining the frequencies of the x-rays and the spacing between the planes of crystals.

strikes an atom in the uppermost plane (the face), a secondary train of waves originates and is propagated outward in all directions around B_1. Another train A_2B_2 strikes the face at F_1, and a part of the energy of the waves is consumed in producing a secondary wave which starts out from this point. The train of waves penetrates to the second plane, however, and there produces another secondary ray when it falls upon an atom at B_2. This secondary ray spreads out in spherical form around B_2 and overlaps the ray originating at B_1. Now, at B_1, two things may happen. Either the two rays, one from B and the other from B_2, may coincide, crest falling upon crest and trough upon trough, or they may fail to coincide, in which case the crest of one wave falls upon the trough of the other. The first condition results, of course, in reinforcement and increased intensity. The second results in interference and reduction in intensity, or perhaps, complete destruction. Other wave trains are produced

from F_1, G_1, etc., and may be reinforced or suffer interference by similar trains starting from F_2 and G_2, etc., respectively.

The spherical waves originating from these various points, B_1B_2, for example, combine to make a wave that advances along the straight wave front C_1, C_2, etc., so that the angles α and θ are equal. When the wave trains from B_1 and B_2 are in the same phase (waves coincide, crest to crest) and reinforce one another, a strong, or intensified, wave advances along this wave front. This means that the reflection at the angle θ is intense. But if they are exactly opposite in phase, the wave is destroyed, and there is no reflection at this angle. If they only partially interfere, the reflection is proportionally weakened. As a matter of fact, almost no reflection is obtained when the two wave trains are only slightly out of phase.

The term "reflected beam of x-rays" is used here in the sense that the angle between the entering train of waves and the planes of atoms in the crystal is equal to the angle between the same planes and the departing, or reflected, beam, as in the case of the reflection of light from a plane surface.

The secondary rays produced by atoms that lie at a depth of 1 mm. or greater below the surface are absorbed by the layers of atoms between their place of origin and the surface. Hence, the reinforced beams that are actually observed are those that are produced near the surface. In this sense, also, the effect is similar to that of reflection from a surface. Of course, this is not a true case of reflection, since the departing beam consists of secondary radiation, which results from the effect of the original beam upon atoms in the crystal. The beam of x-rays is not reflected in the sense that light is reflected from a plane mirror.

Let us now derive the mathematical relation between the distance that separates the reflecting planes of the crystal, the wave length of the x-ray, and the angle which the incident beam (or the reflected beam) makes with the surface of the crystal. A monochromatic beam of x-rays is allowed to fall upon the face of a crystal (Fig. 54). The ray A_1B_1 strikes an atom in the surface layer KK, which represents one of the planes in the crystal lattice. A secondary ray starts from B_1 and travels out, of course, in all directions. Only a part of the energy of the ray is spent in exciting a secondary ray in the surface plane. The ray penetrates

lower planes and there, also, may produce secondary rays from other atoms. Thus, we may next consider the secondary ray which originates at B_2 when an atom at this point is acted upon by the portion of ray A_2B_2 which is not reflected in passing through the first layer. Similarly, a third secondary ray originates at B_3 from the action of ray A_3B_3. The secondary rays that originate at B_1, B_2, and B_3 are very similar to the wavelets that originate at successive apertures when a beam of light falls upon a ruled diffraction grating. Now, if the distance traveled by the second ray from A_2 to C_2 is one whole wave length longer than the path of the first ray A_1C_1, and if that of the ray A_3C_3 is two wave lengths longer than A_1C_1, the waves will arrive at $C_1C_2C_3$ in the same phase. We assume, of course, that they are in phase at $A_1A_2A_3$. This means that the distance $E_1B_2D_1$ must be equal to one wave length, since this is the difference in distance between the paths of the rays $A_1B_1C_1$ and $A_2B_2C_2$. Similarly, the distance $E_2B_3D_2$ must be equal to two wave lengths, and so on.

Let us now draw the lines $B_1D_1D_2$ and $B_1E_1E_2$ perpendicular to the lines A_3B_3 and B_3C_3, respectively. These lines are also perpendicular to A_2B_2 and B_2C_2. Now, D_1B_2 and B_2E_1 are equal, and each can be expressed as $B_1B_2 \sin \theta$. Hence,

$$2B_1B_2 \sin \theta = n\lambda.$$

But $2B_1B_2$ is equal to twice the distance d between successive planes. Therefore,

$$2d \sin \theta = n\lambda.$$

If $n = 1$, we may define θ as follows:

$$\sin \theta = \frac{\lambda}{2d},$$

where $\sin \theta$ determines the direction in which the wave front $C_1C_2C_3$ will advance with respect to the crystal face. If $n = 2$, reflection will be observed when the angle has some other value. It is evident that the sine of this angle will be twice that of the first, since

$$\sin \theta_2 = \frac{2\lambda}{2d}$$

and

$$\frac{2\lambda}{2d} = 2 \sin \theta_1.$$

In the direction determined by the angle θ_2, we should expect to find, therefore, the second-order reflection of the x-ray beam.

If the incident beam consists of more than one wave length, λ_1, λ_2, λ_3, etc., each wave length will show a first-order reflection for a definite angle θ_n of the incident beam and the crystal surface. If, for example, the wave length λ is absent in the incident beam of x-rays (Fig. 54), no reflection will be noted when the angle equals θ or θ_2, as we have previously defined these angles. If the

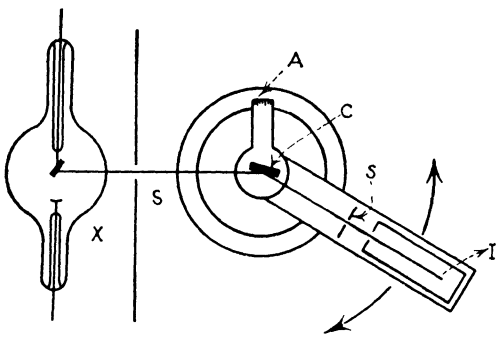

FIG. 55.—Apparatus used in the Bragg method. *X*, x-ray tube; *S*, slits; *C*, crystal; *I*, ionization chamber; and *A*, angle reading.

apparatus is adjusted, however, so that the beam falls upon the face at some other angle, let us say, θ_n, reflection of some other wave length may be observed, provided the conditions required by the equation

$$2d \sin \theta_n = n\lambda$$

are fulfilled. Any beam of x-rays can thus be spread out into a spectrum, each wave length being reflected at its characteristic angle.

Detection of Directions of Intense Reflections.—The method (Fig. 55) usually employed to find the angles at which a beam of x-rays is strongly reflected from a crystal face makes use of an ionization chamber. The beam of rays passes through two or more parallel slits made in lead plates. They then fall upon the face of the crystal which takes the place of the diffraction grating

or prism in the optical spectrometer. The ionization chamber takes the place of the telescope. The chamber rotates about the crystal so that the ionization current and the intensity of the reflected x-ray beam, which is proportional to the current, can be measured at different angles. The ionization current is then plotted against the corresponding angles (Fig. 56). The smooth part of this curve corresponds to the continuous x-ray spectrum. The maxima represent the wave lengths of the characteristic portion of the radiation. The locations of these maxima depend upon the nature of the atoms that serve as the anti-cathode in the

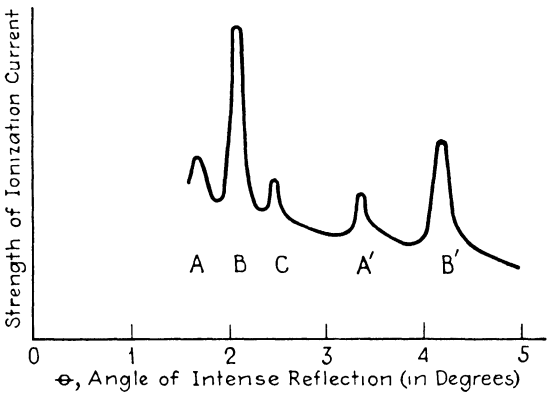

FIG. 56.—Ionization spectrum of x-rays. The smooth parts of the curve represent the continuous spectrum. Maxima A and A' correspond to the first and second orders of reflections of one wave length, and B and B' those of another wave length. C is the first order reflection of a third wave length.

x-ray tube. The sine of the angle corresponding to maximum B is twice that of the angle corresponding to B'. These represent, therefore, the first- and second-order spectra of the same wave lengths. A and A' are likewise first- and second-order spectra of radiation of another wave length.

If d is known, the wave lengths that correspond to the peaks in the ionization spectrum can be calculated. For the peak representing the intense reflection of the first order, for example,

$$\lambda = 2d \sin \theta.$$

The value of d can be determined, of course, by measuring the angle at which a known wave length is reflected. Or d can be

calculated for the planes of a crystal of known structure, such as that of sodium chloride (see page 182). The distance between the planes that are parallel to a face of a unit cube of this substance is 2.81×10^{-8} cm., or 2.81 Å. If, therefore, the wave length of a monochromatic beam of x-rays is determined from the angle at which it is intensely reflected from this series of planes in the sodium chloride crystal, the same x-ray beam may be reflected from other crystals, and the distances between their reflecting planes can be measured.

By using the same face of a crystal and, hence, a known constant value of d, for the reflection of other beams of x-rays, the

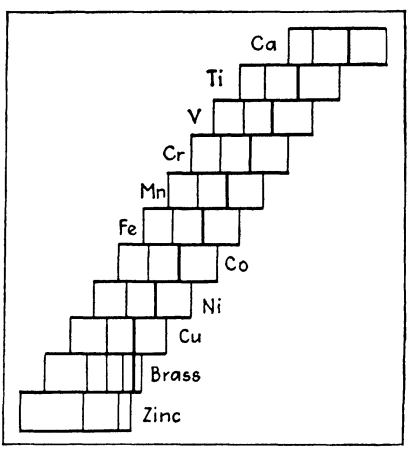

FIG. 57.—X-ray spectra of different elements, showing lines in the K series.

wave lengths present in these beams can be measured. Moseley, in 1913, determined the wave lengths of x-rays from different sources in this manner. The x-rays were produced in the x-ray tube by allowing electrons from the cathode to fall upon anticathodes made of different elements or coated with their compounds. Using the same crystal to diffract the x-rays, Moseley obtained the ionization spectra of the rays produced by different elements. The results were similar to those shown in Fig. 56 (page 167). The results obtained for different elements by using a photographic plate instead of an ionization chamber are shown in Fig. 57. In this manner, he was able to study the character of the rays produced by the elements and to note differences in

their wave lengths with variations in atomic weights and atomic numbers.

Due credit should be given to Barkla as Moseley's predecessor. Barkla, in 1905, had learned that the secondary x-rays, which result when primary rays strike different forms of matter, are not homogeneous. The hardness, or penetrating power, of these rays was shown to increase with the atomic weight and, therefore, to be characteristic of the elements emitting them. Barkla also learned that most elements emitted radiation of two widely different degrees of hardness as measured by their absorption in aluminum foils. This difference was demonstrated by gradually increasing the potential at which the primary rays were produced. To these two radiations he assigned the names K and L. Barkla's method of generating characteristic radiation differed from Moseley's in that Moseley, instead of studying secondary rays, investigated the radiation generated by the direct action of cathode rays upon the anti-cathode.

Moseley found that the x-rays produced by each element were composed of many different wave lengths. Each beam gave a continuous spectrum, corresponding to the spectrum of white light in which all the colors are represented. In addition, he found certain characteristic lines in the x-ray spectra of many of the elements. The same lines appeared in the spectra of different elements. The wave lengths of these characteristic lines, however, varied in orderly fashion as one passed in succession from element to element in the periodic table. Thus, from sodium, as the lightest element, through most of the remainder of the table, five characteristic lines appeared in the x-ray spectrum of each of the elements. Some of these lines were not discovered until later, when refined spectroscopic methods were available. These five lines were found to be grouped as two doublets and a single line. The whole group was identified with the K radiation discovered by Barkla.

The individual lines of the K series are called the α_1, α_2, β_1, β_2, and γ lines. The wave length of each of these is shifted slightly toward a shorter value with increase in the atomic weight, or the atomic number, of the elements. The repetition of these lines from element to element and the shifts in wave length are shown in Figs. 57 and 58. Moseley also observed another series

of lines for the elements from zinc to uranium. (We do not mean to say, of course, that he examined each of the elements in this list.) These lines were identified with the *L* radiation of Barkla. Refinement of the method has led to the discovery of some 15 to

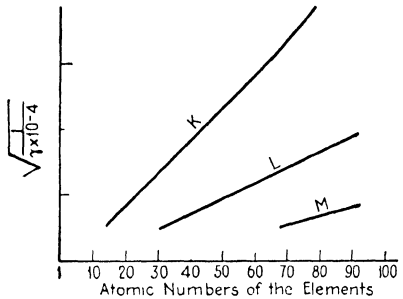

FIG. 58.—X-ray spectral lines, showing the relation between frequency and atomic number. One line in each of the three series (*K*, *L*, and *M*) is shown

20 lines belonging to this series. Each of these lines, as in the *K* series, is shifted toward the shorter wave lengths as the atomic number of the element increases. Siegbahn has discovered another series of about 20 characteristic x-ray spectral lines for the elements from dysprosium to uranium. This is called the *M* series (Fig. 58). There are indications of still other series, *N*, *O*, etc.

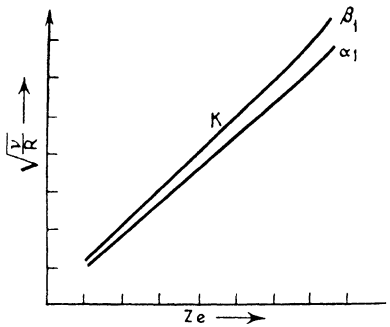

FIG. 59.—Moseley's law of high-frequency spectra.

The frequency of a given x-ray is found by dividing the velocity (in a vacuum) by the wave length:

$$\nu = \frac{c}{\lambda}.$$

More often, however, ν is taken in spectrographic work to represent $1/\lambda$, the reciprocal of the wave length, or the number of wave lengths per centimeter. Moseley found a relation that was almost linear between the square root of the frequency and the atomic numbers of the elements (Fig. 59) but not the atomic weights. The relation between the atomic numbers and the

frequencies is expressed by Moseley's law of high-frequency spectra: The square root of the frequency of any definite x-ray spectral line is a linear function of the atomic number of the element that emits the radiation. The following equation states this law in mathematical language:

$$\sqrt{\nu} = c(N - a),$$

where c and a are constants, the actual values of which depend upon the series (K, L, M, or N) to which the line with a given value of ν belongs. Since only $\sqrt{\nu}$ and N are variables, if different corresponding values of these lines are plotted, one against the other, an almost straight line (Fig. 59) is obtained.

The characteristic x-radiation of an element is thus shown to be intimately connected with the nuclear charge of the atoms of the element. It is further shown that the frequency of any one line in the characteristic x-ray spectra of several elements increases regularly with the nuclear charge. There is no periodicity in the frequencies of these characteristic lines, as there is in the chemical properties of the elements. Hence, the periodicity that occurs among the elements, and upon which the periodic table is based, does not depend in any way upon the nuclear charge (the atomic number) (see also page 45). Nor can this periodicity depend upon the number of electrons revolving around the nucleus of an electrically neutral atom, since this number must be equal in all cases to the nuclear charge. The atomic number, or nuclear charge, increases by one unit as we pass from one element to the next in the periodic table. This must mean, then, that the number of extranuclear electrons likewise increases one at a time; and there is, therefore, no evidence of periodicity. We must look for an explanation of the periodicity in chemical properties in a periodicity that occurs not in the nucleus or in the total number of extranuclear electrons but in the *arrangement* of the electrons in the outer portion of the atom. This part of the atom's structure is discussed in Chap. IX.

Atomic Numbers of Isotopes.—Isotopes are forms of the same element that have the same atomic number, the same nuclear charge, the same number of extranuclear electrons, the same chemical properties, and, hence, the same arrangement of extranuclear electrons but different masses. This means that the

nuclei of the atoms of two isotopes contain different numbers of protons and different numbers of electrons. The difference in the number of protons and nuclear electrons is the same, however, for the atoms of all isotopes of any one element; otherwise, the nuclear charges could not be the same.

Atomic Numbers and the Periodic Table.—The determination of the atomic numbers of the elements has made possible a more accurate and complete periodic table of the elements. The original Mendelyeev table was based upon atomic weight and the erroneous principle that the properties of the elements are periodic functions of their atomic weights. We have already (page 45) pointed out its defects. When the atomic numbers of all the elements are known, the actual serial order of the elements is known. The exact number of elements between hydrogen and uranium becomes definitely fixed, since hydrogen has an atomic number of 1, and uranium of 92. The gaps in the table caused by missing or unknown elements are definitely located. Furthermore, it is possible to use the x-ray spectrum method of analysis to locate and isolate missing elements. If, for example, some substance were found to give a $K\alpha_1$ line whose frequency corresponds to the atomic number 85 (Fig. 59), the presence of this element, either in the free state or combined with other elements, would be proved, and the finder would be heralded as the discoverer of a new element. This is the modern method of conducting searches for new elements. Allison and his collaborators have also developed a magnetooptic method which they use for the same purpose. By means of this method, they claim the recent discovery of element 85. Most of the elements discovered of late, however, have been found through examinations of x-ray spectra. Coster and Hevesy used this method to find element 72, which they called hafnium, in minerals containing zirconium. Hopkins used the same method to locate element 61, which is now called illinium. Berg, Noddack, and Tacke, using the same principle, discovered or gave convincing evidence of the existence of elements 43 and 75, which are now called rhenium and masurium. While, very recently, Papish of Cornell University has claimed the discovery of element 87 because of results obtained in the investigation of compounds extracted from samarskite. The discovery of element 87 was claimed by

Allison previous to the publication of Papish's results, but the latter failed to find any evidence of the element in the material in which Allison said it had been found. Many experimenters have attempted to find this element, but, until very recently, all these attempts have been in vain. It was thought that element 87 would be radioactive, since position 87 occurs in the last horizontal row of the periodic table, and all the other elements of this row are radioactive. Papish reports, however, that it is not. If it were radioactive, this property probably would have led to its discovery long ago.

Knowledge of atomic numbers has proved especially valuable in filling the gaps between cerium and tantalum, a portion of the table occupied by the rare-earth group. It had previously been impossible to say just how many elements there might be in this group. Illinium, which was mentioned above as No. 61, was the last of the rare earths to be discovered. There can be no more members of this group, since all the atomic numbers within the gap are possessed by elements that have been definitely identified.

The use of atomic numbers in determining the positions and order of the elements in the periodic table is illustrated in the case of iron, cobalt, and nickel. The chemical properties of these elements would place them in the order named, since cobalt is more like iron in chemical behavior than is nickel. According to their atomic weights, however, these elements should fall as follows:

Fe	55 84
Ni	58 68
Co	58 97

The frequencies and wave lengths of the $K\alpha_1$ line for these elements are

	ν	λ (Å)
Fe	$12\ 47 \times 10^8$	1 9323
Co	$12\ 98 \times 10^8$	1 78528
Ni	$13\ 47 \times 10^8$	1 65461

This, of course, is the order of their atomic numbers and gives their correct positions in the periodic table. In like manner, it

has been shown that the atomic numbers of argon and potassium and of tellurium and iodine are in agreement with the positions in the table that their properties indicate. Thus, the atomic weights of the elements have been replaced by atomic numbers in the periodic classification.

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CHAPTER VIII

THE STRUCTURE OF CRYSTALS

A crystal can be used to determine the wave lengths of x-rays, that are incident to a series of reflecting planes, provided that the grating space is known. By reversing the process and using a definite x-ray wave length, the spacing of different series of planes in the crystal can be measured. The method consists of finding the angles at which a constant wave length is intensely reflected by different series of planes. Each angle thus corresponds to a different value of d, provided that first-order reflections only are considered. The different values of d that are observed provide information concerning the number of different kinds of planes in the crystal and of their relations to one another.

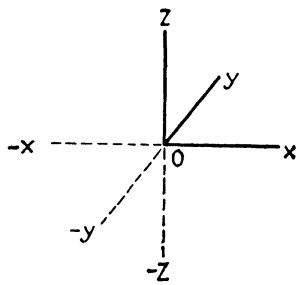

FIG. 60.—Axes x, y, and z of a cubic crystal.

The Planes of a Cubic Crystal.—For a unit cube, we can take three geometrical coordinates originating at the point O (Fig. 60). These represent three edges of the cube. If the three coordinates are extended through the point O, we obtain the system shown in the figure. Any set of planes made up of particles of a substance that crystallizes in this system can be designated by stating the number of equal parts into which each edge of the cube is divided by the set of planes. If the planes do not intercept an axis, the number for that axis is ∞, or, as it is commonly designated, 0; if the intercept is an entire edge of the unit cube, the number is 1; if the intercepts are $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, etc. of the cube's edge, the numbers are 2, 3, 4, etc. The plane ABC (Fig. 61) intercepts the axes x, y, and z at equal distances from O; this distance is equal to the edge of the cube. Hence, the ABC plane is designated by the numbers (or indices) 1 1 1. The plane $DEFB$ intercepts the x

axis at a distance from *O* that is again equal to the cube edge and that we take arbitrarily as equal to unity. This plane does not intercept the *y* and *z* axes. Hence, the plane is designated by the indices 1 0 0. The plane *GDCB* intercepts the *x* and *y* axes at distances from *O* equal to the cubic edge but does not intercept the *z* axis; hence, for this plane, the indices are 1 1 0. The indices 1 1 1, 1 0 0, and 1 1 0 designate not only the planes *ABC*, *DEFB*, *GDCB* but also all planes parallel to them. If the edges

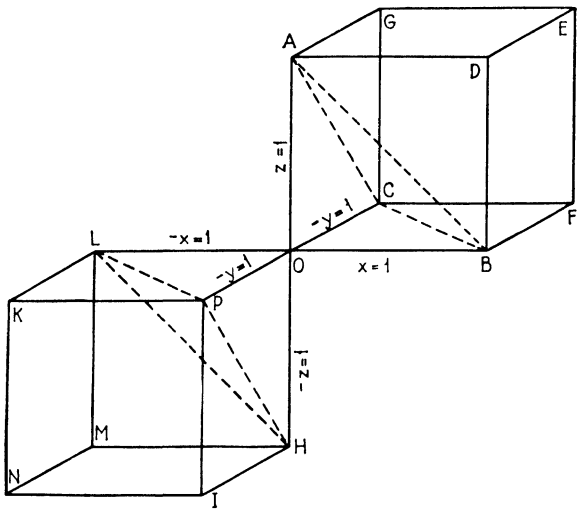

FIG. 61.—*ABC*, 1 1 1 plane; *GDCB*, 1 1 0 plane; *DEFB*, 1 0 0 plane; *LPMI*, $\bar{1}\,\bar{1}$ 0 plane; *KLMN*, $\bar{1}$ 0 0 plane; *HLP*, $\bar{1}$ 1 1 plane.

of the cube lie along $-x$, $-y$, and $-z$, as shown in the lower cubic lattice in Fig. 61, the plane *LPMI* is represented by the indices $\bar{1}\,\bar{1}$ 0, plane *KLNM* by $\bar{1}$ 0 0, and *HLP* by $\bar{1}\,\bar{1}\,\bar{1}$.

In a large crystal of a substance which crystallizes in the cubic system, such as sodium chloride, many sets of planes may be drawn to cut the edges of the unit cube. Some of these, for example, cut the edge along the *x* axis into one; some into two; and others into three, four, or even a greater number of equal divisions. Figure 51 (page 162) shows different sets of planes, all of which are perpendicular to one face of the crystal. It is obvious that the spacing for the different sets of planes is different.

The Laue Method of Crystal Analysis.—Now, if a beam consisting of many wave lengths and acting as a parallel train of waves is passed through such a crystal, certain wave lengths will strike these reflecting planes at angles that permit intense reflections. Thus, the angle at which the beam strikes the first set of planes, for which the indices are 1 1 as regards the x and

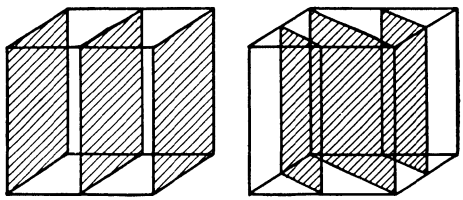

FIG. 62.—The 2 0 0 and 2 2 0 planes of a cubic crystal lattice.

z axes, may be such that one wave length λ_1 of the train will be reflected in the direction D_1. Similarly, the angles made with other planes may be such that other wave lengths λ_2, λ_3, λ_4, etc., will be reflected in other directions D_2, D_3, D_4, etc. These reflected beams strike a photographic plate, which is placed behind the crystal (Fig. 44), at different points. These are spots of the Laue photographs (page 158). A number of theoretically possible planes are shown in Figs. 62 and 63. Each set of

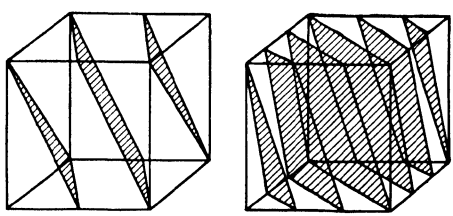

FIG. 63.—The 2 1 1 and 3 3 1 planes of the cubic crystal lattice.

these planes will reflect, provided that the incident beam contains the proper wave length which is required to satisfy the equation $n\lambda = 2d \sin \theta$. The reflections from some of the planes may not fall upon the photographic plate (or film), however, because of the angles of reflection.

Let us select the point O (Fig. 61) as the intersection of the three coordinates x, y, and z. These lines are extended through

O to give $\bar{x}$, $\bar{y}$, and $\bar{z}$. The 1 1 1 planes of the unit cube are represented by ABC. Three similar planes may be drawn:

$$ALC = \bar{1}\,1\,1$$
$$ALP = \bar{1}\,\bar{1}\,1$$
$$APB = 1\,\bar{1}\,1$$

Let us now assume that a beam of x-rays, which consists of a single wave length, falls upon a cube face of a crystal of some substance that crystallizes in that system. We may use a crystal of sodium chloride. Let us further assume that the

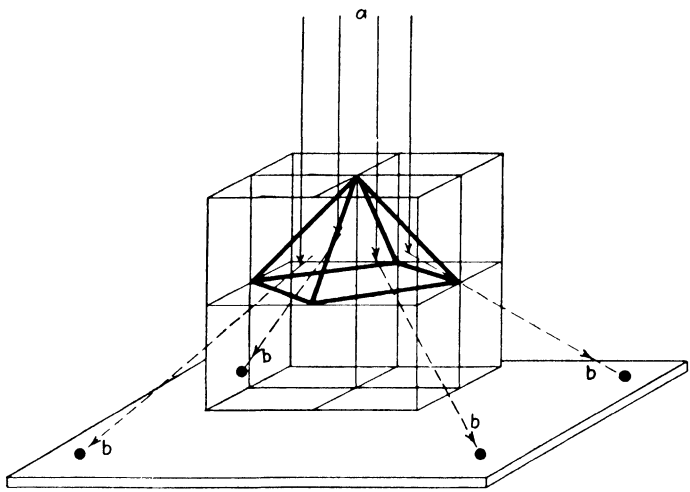

FIG. 64.—The production of Laue spots. *a*, the incident beam; *b*, four Laue spots corresponding to reflections from four planes of the 1 1 1 type: 1 1 1, 1 1 1, $\bar{1}\,\bar{1}$ 1, and 1 $\bar{1}$ 1.

incident beam is parallel to the z axis, although the results would be the same if the x or y axis were selected. From Fig. 64, it is evident that the four planes (and those parallel to them) will produce four spots on the photographic film which is used for recording, provided that the angles of reflection are such as to allow the reflections to strike the film.

Other sets of four planes in the cubic lattice will give rise to four spots each. The planes of each set differ only in the positive or negative signs of their indices. Thus, we find four spots each for the following sets of planes: 2 1 1, $\bar{2}$ 1 1, $\bar{2}\,\bar{1}$ 1, 2 $\bar{1}$ 2; 1 3 1,

$\bar{1}\,3\,1$, $\bar{1}\,\bar{3}\,1$, $1\,\bar{3}\,1$; $2\,2\,1$, $\bar{2}\,2\,1$, $\bar{2}\,\bar{2}\,1$, $2\,\bar{2}\,1$; $4\,1\,1$, $\bar{4}\,1\,1$, $\bar{4}\,\bar{1}\,1$, $4\,\bar{1}\,1$; etc. There are sets of planes in the cubic lattice, however, that produce only two spots on the film. This means that such sets consist of two members each. Thus, there are only $0\,2\,1$ and $0\,\bar{2}\,1$ planes (Fig. 65); $0\,3\,1$ and $0\,\bar{3}\,1$ planes; $2\,0\,1$ and $\bar{2}\,0\,1$

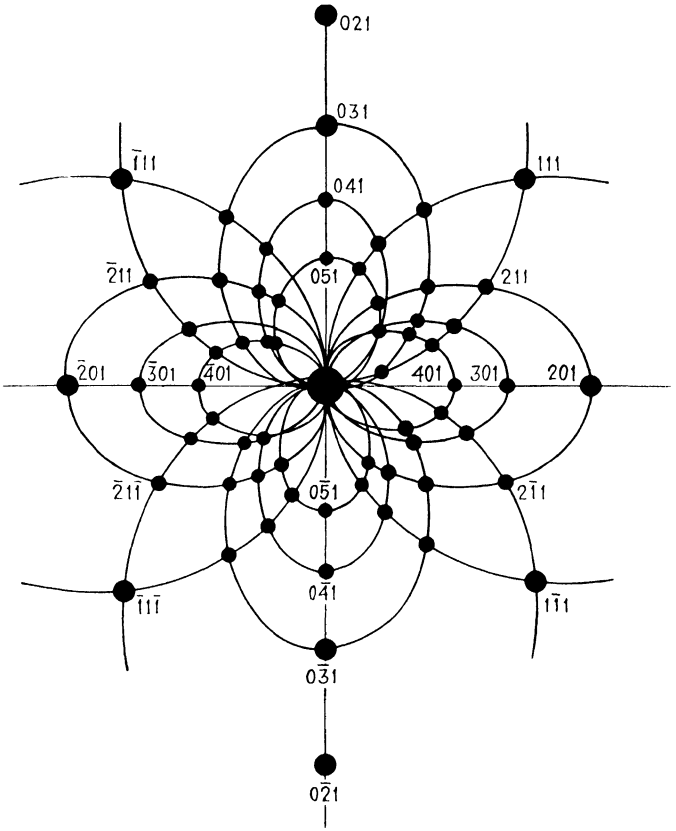

FIG. 65.—The Laue spot pattern of the sodium chloride crystal.

planes; etc. In the photograph, the spots produced by reflections from $0\,2\,1$, $0\,\bar{2}\,1$, $0\,3\,1$, $0\,\bar{3}\,1$, $0\,4\,1$, $0\,\bar{4}\,1$ planes lie in a straight line which passes through the center of the pattern; the spots corresponding to $2\,0\,1$, $\bar{2}\,0\,1$, $3\,0\,1$, $\bar{3}\,0\,1$, $4\,0\,1$, and $\bar{4}\,0\,1$ planes lie on another line which passes through the center and is at right angles to the first. It will also be noted that the spots

produced by the reflections from certain groups of planes lie on an ellipse. The planes that give rise to an elliptical arrangement of spots are those for which only the x indices vary, as in 4 3 1, 3 3 1, 2 3 1, 1 3 1, 0 3 1, $\bar{1}$ 3 1, $\bar{2}$ 3 1, $\bar{3}$ 3 1, $\bar{4}$ 3 1; or those for which only the y indices vary, as in 2 4 1, 2 3 1, 2 2 1, 2 1 1, 2 0 1, 2 $\bar{1}$ 1, 2 $\bar{2}$ 1, 2 $\bar{3}$ 1, 2 $\bar{4}$ 1. The reflections from any one group of such planes lie upon the surface of a cone, the apex of which is C (Fig. 66). The intersection of this cone with the photographic film is an ellipse, since the axis of the cone is not perpendicular to the plane of the film.

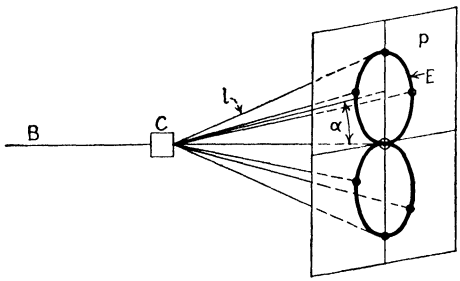

FIG. 66.—The elliptical arrangement of Laue spots. Spots on the ellipse E are made by reflections from a series of similar planes, such as 2 4 1, 2 3 1, 2 2 1, 2 0 1, 2 $\bar{1}$ 1, 2 $\bar{2}$ 1, 2 $\bar{3}$ 1, 2 $\bar{4}$ 1 (Fig. 65). These spots lie on the surface of a cone whose axis makes an angle α with the direction of the incident beam B.

The location of the spots in a Laue pattern depends upon the inclination of the planes which give rise to the reflections producing them. Since the inclination of these planes is determined by the symmetry of the crystal, it is equally true that the distribution of spots in the pattern depends upon the crystal's symmetry and the relation between the incident beam of x-rays and an axis of symmetry of the crystal. Thus far, we have described the reflections of a beam that is incident to a cube face along a fourfold axis, an edge of the unit cube. The reflections from a beam incident to a cubic crystal along a threefold axis will, of course, produce a pattern of spots different from that which we have described. For the cubic lattice, the lines joining opposite corners of the cube are threefold axes of symmetry. The Laue pattern of the reflections of a beam parallel to such an axis is shown for a crystal of sodium chloride in Fig. 67.

For x-ray beams incident to a cube face in a direction parallel to a fourfold axis, all cubic crystals reveal the same Laue pattern. Crystals possessing symmetry other than that which characterizes the cubic lattice give patterns of differently distributed spots. From these patterns the symmetry of the crystal can be deduced. The Laue method of crystal analysis does not provide, however, a means for the direct measurement of the spacings of the different planes of the crystal. It is most often employed as a check upon the results obtained by other methods.

The Bragg Method of Crystal Analysis.—We have already discussed the Bragg method of separating an incident beam of x-rays into its different wave lengths and thus obtaining an x-ray spectrum. This is the method used to determine the characteristic x-radiation of the elements (page 163).

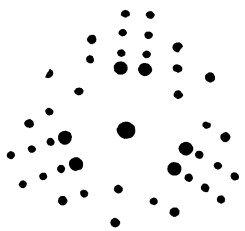

FIG. 67.—Laue pattern of a cubical crystal for which the incident rays are parallel to a three-fold axis of symmetry.

If a crystal is mounted so that it can be continuously rotated about one of its axes, and if a beam of monochromatic x-rays falls upon the crystal in a direction perpendicular to the axis about which the crystal is rotated, we have the rather simple method used by W. H. Bragg and W. L. Bragg in analyzing the structures of crystals. Various sets of planes reflect the beam of x-rays as the crystal is rotated, each set reflecting when the requirements of the equation

$$n\lambda = 2d \sin \theta$$

are fulfilled.

The reflections may be detected and the angles determined by means of a photographic plate. This is the method used by *de Broglie*. Each set of planes in the crystal may reflect the beam when the conditions are fulfilled. Since the values of d for different sets of planes are not the same, the angle θ will not be the same in all cases. Hence, the rays reflected by these planes will register at different points on the plate. It is possible to calculate the spacings of the planes and their indices from the spots produced by the reflections. In general, this method of studying the structure of crystals is not so satisfactory as that employed by the Braggs.

In the method used by the Braggs, the reflected beams are detected by means of an ionization chamber (Fig. 55), which is filled with some gas, such as methyl bromide, methylene iodide, or sulfur dioxide, which is easily ionized by the x-rays. The ionization chamber is connected to an instrument, such as an electrometer or an electroscope, that measures the flow of current (ionization current) across the chamber due to the discharge of the ions. The crystal and the chamber are rotated, the former on a rotating table C, and the latter in the arc of a circle with C as the center. The crystal and the ionization chamber are both moved to determine the required glancing angle θ for each reflection. The number of ions produced in the ionization chamber and, hence, the strength of the ionization current, is a measure of the intensity of the reflected beam.

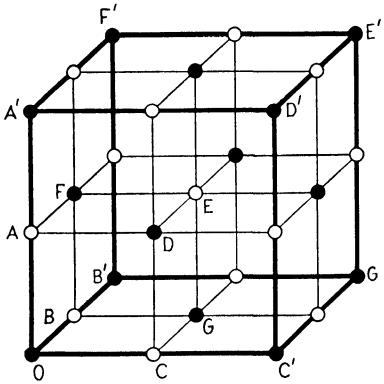

FIG. 68.—The space lattice of the sodium chloride crystal.

The Determination of d for a Set of Planes in the Sodium Chloride Crystal.—To study the structures of crystals by the Bragg method, it is necessary, first of all, to find a way of determining the wave length of a monochromatic beam of x-rays. This can be done if we use a crystal for which d, the distance between successive members of some one set of planes, is known or can be calculated. The distance d between the reflecting planes in a crystal of sodium chloride can be calculated as follows. Let us define d as the distance from one atom to the next along the edge of the cube. The crystal unit of sodium chloride (Fig. 68) is composed of eight smaller cubes; hence, it is not the smallest cube of the crystal but the smallest complete pattern of the particles of which the crystal is composed. The black spheres represent sodium ions, and the unshaded spheres chlorine ions, but the structure would be the same if these were reversed. It will be noted that the sodium and chlorine ions occupy alternate positions in the space lattice. Also, there is a sodium ion at each

of the eight corners of the cube and in the center of each face. There is a chlorine ion at the center of the cube and in the center of each edge. Probably the most important point to be noted is that the central ion is surrounded by six ions of the opposite kind in the centers of the six cube faces. In a larger crystal of sodium chloride (Fig. 69), each sodium and chlorine ion is the center of such a group, except, of course, those ions that are located in the outermost layers of the crystal. And so the crystal grows in a saturated solution of the salt; plane after plane of alternately spaced sodium and chlorine atoms are added to form new faces.

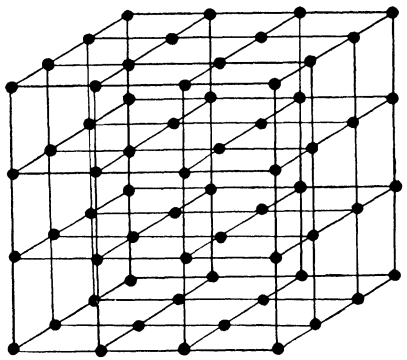

FIG. 69.—The pattern of a larger crystal of sodium chloride. This shows that a larger crystal is simply a repetition of the arrangement of ions in the space lattice or crystal unit. In this drawing the sodium and chlorine ions are not distinguished by different shading.

In the larger crystal, therefore, the atoms that compose the crystal unit do not belong entirely to this one cube. With the exception of the central atom, they are shared with the cubes that lie about the unit cube. Each of the eight sodium ions at the corners of the cube is shared by eight cubes; hence, one-eighth of each ion really belongs to each cube. Of the eight ions so located, we may say that one belongs to the crystal unit. The sodium atom in the center of each face is shared by two cubes; hence, of these six sodium ions, the equivalent of three ions can be considered as actually belonging to one cube. The cube contains, then, the equivalent of only four sodium ions. The chlorine ion at the center of the unit belongs entirely to this cube, but those in the centers of the edges are shared, each of them belonging to

four different cubes. There are 12 such chlorine ions, and the unit cube can call only one-fourth of each its own. It possesses, therefore, the equivalent of four chlorine ions.

The crystal unit is the equivalent, therefore, of four sodium and four chlorine ions or, as we are commonly accustomed to say, of four molecules of sodium chloride. It is apparent, however, that the molecule of sodium chloride has no physical meaning. The term can be used only in the chemical sense, where it expresses the chemically equivalent weights of sodium and chlorine ions which take part in a reaction. There is no particle of the composition NaCl in the crystal of sodium chloride.

Since the cube is equivalent to four sodium and four chlorine ions, its real mass is equal to four times the molecular weight of sodium chloride:

$$M = 4 \times \text{mol. wt. of NaCl} = 4 \times 58.45 = 233.80.$$

Now, four gram-molecular weights of sodium chloride contain $4 \times 6.06 \times 10^{23}$ molecules, and these have a total mass of 233.80 g. The mass of four molecules, therefore is

$$4 \times \frac{233.80}{24.24 \times 10^{23}} = 38.6 \times 10^{-23} \text{ g.}$$

We know the density of sodium chloride to be 2.16, and density is defined as mass divided by volume:

$$d = \frac{m}{v}.$$

Hence,

$$2.16 = \frac{38.6 \times 10^{-23}}{v},$$

and

$$2.16v = 38.6 \times 10^{-23},$$

or

$$v = \frac{38.6 \times 10^{-23}}{2.16} = 17.8 \times 10^{-23} = a^3 \text{ cc.},$$

since

$$v = a^3.$$

Now,

$$a = \sqrt[3]{17.8 \times 10^{-23}} = 5.63 \times 10^{-8} \text{ cm.}$$

The faces of the unit cube are, therefore, 5.63×10^{-8} cm. apart, since a is the length of the edge of the cube. But there is a plane that contains ions midway between each pair of faces; hence, d, the distance between parallel planes, is one-half of a:

$$d = \frac{a}{2} = 2.815 \times 10^{-8} \text{ cm., or } 2.815\text{Å}.^{1}$$

Thus, using the same cube face of the crystal of sodium chloride to diffract the beam, the wave length of the x-rays (we assume that the beam is monochromatic) can be determined. When this has been done, the same beam of x-rays, its wave length now being known, can be used to determine the spacing of various sets of planes in other crystals. The value of d for sodium chloride cannot be determined with very great accuracy by the method outlined above. The inaccuracy is due to errors in the determination of the density and molecular weight of sodium chloride and of Avogadro's number. For this reason, the wave lengths of x-rays are often expressed in terms of the spacing of the planes in some crystal; the above value of d for the sodium chloride is often used.

The Analysis of the Structure of the NaCl Crystal by the Bragg Method.—Let us consider the 1 1 1, 1 0 0, and 1 1 0 planes of the sodium chloride crystal and some of the possible space lattices in whose patterns this substance may crystallize. The crystal belongs to the cubic system, to which our study so far has been confined, but there are three kinds of cubic space lattices. The simple cubic lattice consists of a unit cube with an atom (or other particle) at each of the eight corners (Fig. 70). In this figure, the plane ABC is the 1 1 1, $CDFB$ is the 1 1 0, and $DEBG$ is the 1 0 0 plane to be considered, with reference to the three rectangular axes Ox, Oy, and Oz. If we call the intercept on the x axis unity for the 1 0 0 plane, then

$$d_{100} = 1,$$
$$d_{110} = \frac{1}{\sqrt{2}},$$
$$d_{111} = \frac{1}{\sqrt{3}}.$$

[1] An Ångström unit is 1×10^{-8} cm. It is the unit commonly employed in the expression of wave lengths.

These values of $d_{1\,0\,0}$, $d_{1\,1\,0}$, and $d_{1\,1\,1}$ are the lengths of the lines *OB*, *PO*, and *QO*, respectively, and can be found by simple geometrical considerations. *OP* and *PC* are equal, and the squares on *OP* and *PC* together are equal to the square on *CO*, which is 1. Let x equal the length of *PO* and *PC*, since they are equal to each other. Then

$$2x^2 = 1;\ x^2 = \frac{1}{2};$$

and

$$x = \frac{1}{\sqrt{2}} = d_{1\,1\,0}.$$

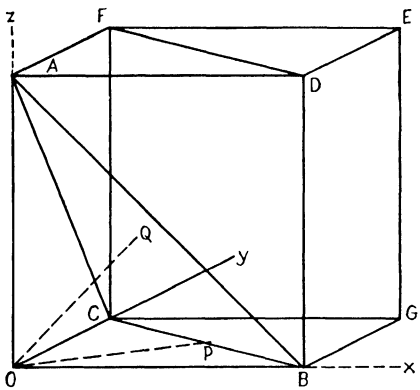

FIG. 70.—The simple cubic lattice showing 1 0 0, 1 1 0, and 1 1 1 planes. Distances between planes are represented by *OB*, the perpendicular to *BDEG* and *AFOC* at *B* and *O* for 1 0 0 planes; by *OP*, the perpendicular to *CFDB* at *P* for 1 1 0 planes; and by *OQ*, the perpendicular to *ABC* at *Q* for 1 1 1 planes.

Similarly, we can show that $d_{1\,1\,1}$ is equal to $1/\sqrt{3}$. Taking the reciprocals of the values of $d_{1\,0\,0}$, $d_{1\,1\,0}$, and $d_{1\,1\,1}$, we may write:

$$\frac{1}{d_{1\,0\,0}} : \frac{1}{d_{1\,1\,0}} : \frac{1}{d_{1\,1\,1}} = 1 : \sqrt{2} : \sqrt{3},$$

which gives the relations of the three values of d for the three sets of planes that we are considering for the simple cube.

The face-centered cubic lattice is shown in Fig. 71. Its linear dimensions (edges) are twice those of the simple cube. The 1 0 0 planes (like *DEBG*) of each of the small cubes of the space lattice contain particles. Hence, these planes have a real existence in the space lattice, and $d_{1\,0\,0}$ is 1, as for the simple

cube. The 1 1 0 planes of the small cube are real, also. Hence, $d_{1\,1\,0}$ is $1/\sqrt{2}$, as before. But it is evident that the 1 1 1 plane does not have a real existence, so far as the small cube is concerned, since it does not contain any atoms. The plane $C'B'A'$ does contain atoms, but planes of this type are twice as far apart as the 1 1 1 planes in the simple cubic lattice. The distance, $d_{1\,1\,1}$, is, therefore, twice as great as before. Hence, for the face-centered cubic lattice:

$$\frac{1}{d_{1\,0\,0}}:\frac{1}{d_{1\,1\,0}}:\frac{1}{d_{1\,1\,1}} = 1:\sqrt{2}:\frac{\sqrt{3}}{2}.$$

For the cube-centered lattice (Fig. 72), the value of $d_{1\,0\,0}$ is the same as for the simple cube. But the plane $FDBC$ contains

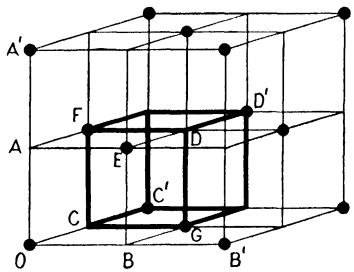

FIG. 71.

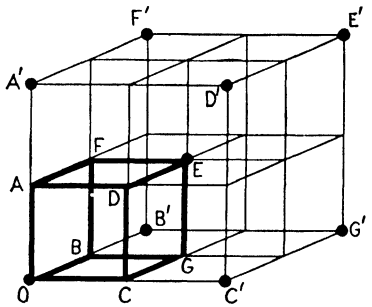

FIG. 72.

FIG. 71.—The face-centered cubic lattice. For comparison the dimensions of a simple cube are shown by the heavily shaded lines.

FIG. 72.—The cube- or body-centered cubic lattice.

no atoms, while $F'D'B'C'$ does; hence, $d_{1\,1\,0}$ is twice as great as for the simple cube. The value of $d_{1\,1\,1}$ is the same as for the simple cube, since the plane of this description is an atom-bearing plane. Hence, for the cube-centered lattice:

$$\frac{1}{d_{1\,0\,0}}:\frac{1}{d_{1\,1\,0}}:\frac{1}{d_{1\,1\,1}} = 1:\frac{1}{\sqrt{2}}:\sqrt{3}.$$

Now, for any one set of planes, reflections of different order will be obtained as the crystal is rotated so that $2d \sin \theta$ becomes successively equal to λ, 2λ, 3λ, 4λ, etc. The reflections will gradually decrease in intensity. The first-order reflections are

always the strongest. The reflections from the three sets of planes of the simple cube, the face-centered cube, and the sodium chloride crystal are plotted in Figs. 73, 74, and 75. Several lines appear for each set of planes of any of the space-lattice types; each line represents a different order of reflection of the same wave length. The relative intensities of the different orders of reflections are indicated by the lengths of the lines. The numbers 1, $\sqrt{2}$, $2\sqrt{2}$, etc., represent the relative values of the reciprocals of d for the three sets of planes and correspond to the different angles at which the different orders of reflection are obtained.

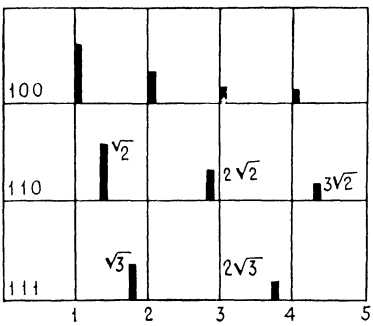

FIG. 73.—Diagram showing the relation of the intensity (vertical) of reflected x-rays to angles of reflection from planes of the simple cubic lattice. The angles for one set of planes (of a simple cubic lattice) are proportional to the spacing between parallel planes, *i.e.*, first, second, and third orders of reflection are at angles proportional to 1, 2, and 3 for 1 0 0 planes; to 2, $2\sqrt{2}$, and $3\sqrt{2}$ for 1 1 0 planes; and to $\sqrt{3}$, $2\sqrt{3}$, and $3\sqrt{3}$ for 1 1 1 planes.

One would expect any crystals belonging to the cubic system, such as those of sodium and potassium chlorides, for example, to give an x-ray pattern conforming to one of the three lattices. In the case of sylvine, KCl, for example, the spaces for the 1 0 0, 1 1 0, and 1 1 1 planes are in the ratio of $1:1/\sqrt{2}:1/\sqrt{3}$. This is the ratio that corresponds to the simple cubic lattice. But the pattern given by sodium chloride (Fig. 75) does not agree with the lines of any one of the three types of space lattices. The 1 0 0 and 1 1 0 planes of the sodium chloride space lattice correspond to those of the simple cube, but the 1 1 1 planes are those of a face-centered cubic lattice. Furthermore, the intensities of the different orders of reflection from the 1 1 1 planes do not fall off gradually, as they should. The first-order reflection is weaker, the second stronger, the third weaker, etc., than would be expected. It is also true that the spots produced on the photographic plate from the 1 1 1 planes are comparatively weak, when the ionization chamber is replaced by a plate. This variation of intensity must be explained before we can

decide upon the lattice that is to be assigned to the sodium chloride crystal.

Let us look again at the arrangement of atoms (Fig. 68) in the crystal unit of this substance. The 1 1 0 planes (*FDBC* and those parallel to it) are identical in composition; each contains both sodium and chlorine ions. Likewise, the 1 0 0 planes (*DECG* and *AFOB*) contain both kinds of ions. Hence, $d_{1\,0\,0}$ and $d_{1\,1\,0}$ are the same as for the simple cubic lattice. But the composition of the 1 1 1 planes *ABC* and those parallel to it, (*A'B'C'*, etc.) is not the same for all planes. All the ions in

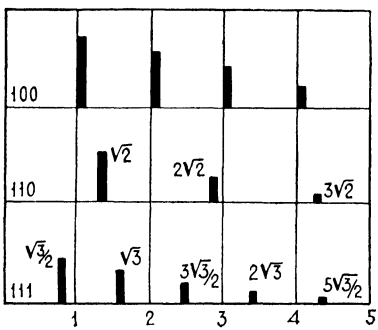

FIG. 74.—Diagram showing the relation of the intensity of x-rays reflected at different angles from planes of the face-centered cubic lattice.

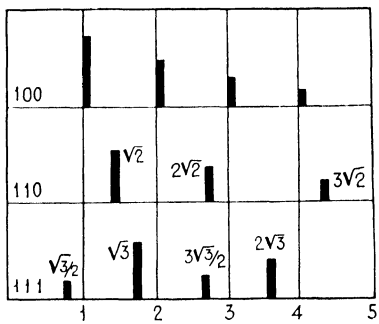

FIG. 75.—Diagram showing the relation of the intensity of x-rays reflected from different planes of the sodium chloride crystal. This diagram should be considered in comparison with the two preceding figures.

plane *ABC* are either sodium or chlorine, while those of *A'B'C'* are of the other kind. Now, $d_{1\,1\,1}$ is the distance between planes bearing the same kind, or kinds, of particles. Hence, $d_{1\,1\,1}$ for sodium chloride is twice as great as it is for the simple cubic lattice, in which all 1 1 1 planes are identical; in sodium chloride, these planes consist alternately of sodium and chlorine ions. The first order of reflection from the chlorine planes occurs when $\lambda = 2d \sin \theta$, where d is the distance between planes of chlorine ions. But there is a plane of sodium ions midway between the chlorine planes. Now, the ray from the second chlorine plane will reinforce the ray reflected from the first chlorine plane when the paths traveled by the two rays differ by one or more whole wave lengths. It is evident that the ray reflected from the plane

of sodium atoms (between the chlorine planes) travels only one-half of a wave length farther than the ray reflected from the first plane, while the ray reflected from the second chlorine plane is traveling a whole wave length farther. The ray from the sodium plane will be exactly opposite in phase to the rays from the surface of the crystal. The intensity of the reflected ray is determined, however, by the atom from which the secondary ray emanates. Since the intensity increases with the atomic weight, the ray reflected from the intervening plane of sodium ions is weaker than that reflected from the chlorine planes. Although there is interference, it is not complete, and only a somewhat weakened first-order reflection results. The second order of reflection—where $2\lambda = 2d \sin \theta$—is very intense. The ray reflected from the lower chlorine plane travels an extra distance of two whole wave lengths before overlapping the ray reflected from the upper chlorine plane. During the same time, the ray reflected from the intervening sodium plane travels one-half of the same distance, or one full wave length. All the reflected rays, therefore, will emerge in the same phase. There will be no interference but rather additional reinforcement. Hence, the second-order reflection, and all even orders of reflections, shows increased intensity, while odd orders show decreased intensity. This is the pattern that sodium chloride gives. We arrive at the conclusion, therefore, that this substance crystallizes in a modified form of the face-centered cubic lattice. Except for the fact that alternate 1 1 1 planes are composed of different kinds of ions, we might regard the lattice as that of the simple cube. Inspection of Fig. 68 will show that what we really have are two intersecting face-centered lattices. Atoms of sodium are located at the centers of the faces of one lattice, and atoms of chlorine at the centers of the faces of the other.

The Space Lattices of Other Cubic Crystals.—Sodium bromide possesses the same type of space lattice as sodium chloride. The distances between the 1 1 1 planes of the potassium chloride space lattice, however, correspond to the simple cube. Further analysis of the case, however, shows that potassium chloride crystals are similar to those of sodium chloride. Potassium and chlorine have almost the same atomic weights. For this reason, the reflections of odd order from potassium and chlorine planes

interfere almost completely. Hence, only even ordered reflections are observed for the 1 1 1 planes. If the reflections are plotted, as for sodium chloride (Fig. 75), the lines occupy the same positions as for the simple cube (Fig. 73).

Many of the elements have been found to crystallize in cubic space-lattice patterns. Silver, gold, copper, calcium, and aluminum show face-centered lattices. Sodium, chromium, potassium, lithium, iron, molybdenum and tungsten form body-centered cubic lattices. For data on the space lattices of other substances, the reader is referred to the first and second references at the end of this chapter.

The Powder Method.—Debye and Scherrer in Germany and Hull in this country have developed methods of x-ray analysis that use powdered crystalline substances, thereby doing away with the necessity of employing a more or less perfect single crystal, which is sometimes difficult or even impossible to obtain. A photographic plate is used to record the reflections. Since the substance is powdered, the conditions required for reflections from all possible sets of planes are usually fulfilled. These powder methods have enabled investigators to study the structures of many substances that crystallize imperfectly or that have always been considered amorphous. Even the structure of rubber has been determined.

The Reality of the Molecule

The results of the analyses of crystal structures have raised important questions concerning the reality of the molecule. They show that the molecule does not exist in the solid states of such substances as sodium chloride. We are led to wonder, therefore, if the molecule of such a substance ever exists. When can the molecule be said to have a real existence?

There can be no doubt about the reality of the molecule in crystals of compounds that do not conduct the electrical current when they are dissolved in water or when they are fused and that, therefore, are called nonelectrolytes. In such substances, the particles composing the various planes of the space lattices *are molecules.* The majority of organic compounds have space lattices composed of uncharged molecules. This is true, for example, of sugar. But in sodium chloride, which is typical

of salts in general, the units of the crystal are sodium and chlorine ions. There is no evidence that particles composed of one sodium and one chlorine ion exist in the crystal. Instead, each ion is surrounded by six ions of the opposite kind which lie at the centers of the six cube faces. In other words, instead of attracting and being bound to a single ion of the opposite charge, each ion is attracted equally by six ions of the opposite charge symmetrically arranged around it. The same or somewhat similar patterns of ions are found in the crystals of other salts. Thus, in a way, the entire crystal acts as a single giant molecule. When this crystal dissolves in water, for example, the solvent weakens the forces that hold the ions in the positions that they occupy in the crystal lattice. The ions in solution are more nearly independent than in the crystal. There is still reason to suppose that the forces are in operation even in the solution, although, of course, they are not strong enough to cause the different ions to take up their positions in the lattice again until some of the solvent is removed by evaporation, and the ions are thus brought closer together. There is certainly no reason for believing that the character of the forces that exist between two kinds of ions in the crystalline state should change materially when the substance dissolves. If each ion of the crystal exerts an attraction equally in six directions, or in all directions, we can scarcely assume that each ion in a solution of sodium chloride attracts a single ion of the opposite kind and, therefore, possesses attraction that operates in a single direction.

It is evident that the freedom of the ions in a solution depends upon the ability of the solvent to weaken the forces that hold the ions in the positions that they occupy in the crystal lattice. If these forces are not weakened sufficiently, the lattice arrangement is maintained, and the crystal does not dissolve. If solution does occur, the apparent degree of ionization, or fraction of the whole number of molecules which appears to be dissociated into ions, depends upon how effectively the solvent weakens these forces. All the methods in common use for the determination of the percentage of ionization of electrolytes in solution depend, in one way or another, upon the movement of the ions in the solution. It is evident that the motion of an ion in a solution in which there are millions of its own kind, as well as like numbers, or comparable

numbers, of other kinds of ions, is influenced by the attraction between the ion and others which carry the opposite kind of charge and by the repulsion that it suffers from others which carry the same kind of charge as itself. The freedom of the ion is hindered by these forces, and the ion does not behave as it would if it were in an atmosphere where there were no other charged particles. Although the solute may be 100 per cent ionized, measurements of the degree of ionization (see chapter on ionization in any textbook of general chemistry) which depend upon the assumption that all ions are free and act independently will not give this value for the percentage of the substance dissociated. Thus, sodium chloride (0.1*N*) appears to be 84 per cent ionized. Eighty-four sodium and 84 chlorine ions, if they were absolutely free and independent, would act to produce the same effects upon the properties of the solvent, by means of which the percentage of ionization is determined, as 100 ions of each kind *do* within the "resisting" environment of a solution. Eighty-four ions of each kind would carry as much electrical current, would lower the freezing point just as much and elevate the boiling point just as far as 100 ions of each kind actually do, provided that the 168 ions were free of one another's influences. Because the ions are not free, and because the ionic forces mentioned above do exist within the solution, the degree of ionization of a solute in a solution may appear to be only 84 per cent, whereas in reality no molecules at all exist.

The best evidence of the reality of the molecules of many substances is obtained when the substances are studied in the gaseous state. We are convinced of the validity of Avogadro's hypothesis, which states that equal volumes of all substances in their gaseous states contain an equal number of molecules, or ultimate particles, when the volumes are measured at the same temperature and pressure. The weight of 22.4 l. (measured at 0° and 760 mm.) of any pure gaseous compound is the molecular weight of the substance as compared with the molecular weight of oxygen. Now, if this weight compares exactly with the molecular formula of the compound, this is good evidence that the ultimate particles that make up this volume are particles each of which has the formula assigned to the molecule of the compound. If this condition is fulfilled, the particles are not the individual atoms, or

ions, as in the crystal of sodium chloride. They are complete and neutral particles, corresponding to what, in the case of sodium chloride, would be molecules of sodium chloride.

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CHAPTER IX

THE STRUCTURE OF THE ATOM

THE OCTET THEORY

The nuclear theory of the atom, introduced, developed, and experimentally substantiated by Rutherford, is the basis of all modern theories of atomic structure. The fact that the nucleus is positively charged necessitates that the neutral atom contain a number of electrons, outside the nucleus, equal to the number of units of positive charge on the nucleus. The arrangement of these external electrons, or at least the arrangement of some of them, determines the chemical properties of the atom. We have already learned (page 171) that these properties are not determined by the nuclear charge or by the total number of external electrons. The arrangement of the electrons about the nucleus in a manner that will account for the valence of the element and for other properties of the atom, such as the emission of its spectrum, is a problem that has called forth several solutions and has led to several theories of atomic structure. This problem has without doubt been the most interesting and captivating subject of scientific investigation of the present century. While none of these theories is entirely acceptable, they are worth while as stepping stones to the ultimate solution of the problem.

The theory of the atom with which we are to deal in this chapter is now largely of historical interest. It represents an attempt to explain the structure of the atom from almost purely chemical considerations and without much regard for the mechanics of the system. This theory, however, has been responsible for much of the interest that has been taken in the structure of the atom from the chemical point of view. For this reason, it is a subject of considerable significance in our present discussion.

Introduction to the Octet Theory.—In 1904, Sir J. J. Thomson proposed the theory (see page 145) of the positive sphere of

electricity to explain the structure of the atom. The positive charge was supposed to be uniformly distributed throughout the spherical volume of the atom, while the electrons were arranged in stable groups of concentric rings within the sphere of positive charge. Thomson determined the probable number of electrons for each of the concentric rings and attempted to correlate this information with the valences of different elements and with the periodic table. Abegg, in the same year, had called attention to the importance of the number eight in the consideration of the valences of the elements and the positions that they occupy in the periodic table. Since eight seemed to be the maximum valence of an element, Abegg regarded this as the maximum number of electrons that an atom could accommodate on its points or on that part of its structure that was exposed to combination with other atoms.

Helmholtz, in 1881, suggested that the number of units of valence possessed by an atom is equal to the number of units of charge associated with the atom. Twenty years later, Nernst extended this view to mean that uncombined atoms are electrically neutral and that the charges on combined atoms are produced by exchanges of negative and positive charges between the atoms. Lodge, in 1902, added the idea that negative charges alone are transferred during chemical reactions. The atom losing electrons by the transfer was said to acquire a positive charge. The gain of electrons by the other atom was assumed to result in a negative charge for this atom. Lodge also suggested that the electrons in one atom might be the means of union with another atom without any actual transfer's occurring or before one occurs. Stark, in 1908 and later in 1915, interpreted this idea to mean that electrons may belong to the structures of two atoms simultaneously. Each electron shared by atoms in this manner was regarded as a valence bond. In 1915, Parson suggested that two shared electrons form one bond. He designated such a pair of electrons as a "magneton."

In 1916, Kossel and G. N. Lewis independently suggested many important principles which have served as the basis for later theories of the atom's structure and chemical action. Both Kossel and Lewis employed the idea that atoms acquire positive valence by losing electrons and negative valence by gaining them.

Kossel accepted the dynamic model of the atom, which had been proposed by Bohr (page 236), while Lewis based his considerations upon a static model, which has been called, upon many occasions, the "static" atom. Lewis further assumed that atoms may share electrons; he thus explained the difference between electrolytes and nonelectrolytes. If electrons are actually transferred from one atom to another, that atom that gives up electrons to the other acquires a positive charge, while the atom that gains one or more additional electrons becomes negatively charged. In this way, Kossel and Lewis explained the charge and, hence, the valence of atoms in substances, such as sodium chloride, hydrogen chloride, etc. The idea of the shared electron accounts for the structure of molecules of substances such as H_2, CH_4, and H_2O. In these substances, electrons belong to both atoms, and no charge results from the combination.

Lewis later modified his original concepts in accordance with the principles of atomic mechanics which were then thought acceptable. In 1919, Langmuir employed the original assumptions of Kossel and Lewis in developing a somewhat modified explanation of atomic structure and valence and extended the theory to cover all the elements of the periodic table. Langmuir's theory was intended only to explain the valences of the elements and their action in forming molecules. The theory will not stand the test of physical stability; it was not intended that it should. What merit it has rests only upon its use in explaining the chemical properties of the different elements. Because Langmuir, and Lewis before him, sometimes showed models of atoms in the form of cubes with electrons at their eight corners, the theory has sometimes been called the "cubic," or, more often, the "octet," theory of the atom. Although this idea has lost most of its original significance, the conception of the octet has survived. An idea based upon a principle as fundamental as Abegg's rule of maximum valence is not easily discarded.

The Langmuir Theory

This theory, like all others, is concerned only with the arrangement of the electrons about the nucleus. No attempt is made to explain the arrangement of protons and electrons within the nucleus. The number of electrons that are to be placed in their

proper positions in the extranuclear structure is equal to the atomic number of the element. Practically all theories agree in dividing these electrons into stable groups, each group requiring a definite number of electrons for maximum stability and located at a definite distance from the nucleus.

Stable Electron Groups.—In deciding upon the grouping of the electrons, Langmuir made use of a mathematical equation derived by Rydberg:

$$N = 2(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 \cdots).$$

This equation states that the atomic numbers N of the rare gases of the atmosphere are, respectively:

$$\begin{aligned}
\text{Helium} &= 1 \times 1^2 = 2. \\
\text{Neon} &= 2 \times (1^2 + 2^2) = 10. \\
\text{Argon} &= 2 \times (1^2 + 2^2 + 2^2) = 18. \\
\text{Krypton} &= 2 \times (1^2 + 2^2 + 2^2 + 3^2) = 36. \\
\text{Xenon} &= 2 \times (1^2 + 2^2 + 2^2 + 3^2 + 3^2) = 54. \\
\text{Radon} &= 2 \times (1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2) = 86.
\end{aligned}$$

The Rydberg equation suggested to Langmuir that the first group of electrons is complete in helium and, hence, can contain only two electrons. The rare gases are inert chemically and have zero valence. In terms of the theories of Kossel and Lewis, this means that their atoms exhibit no tendency to gain or to lose electrons. Hence, the atoms of these elements represent the most stable configurations of electrons. Langmuir reasoned, therefore, that in the case of each rare gas, some one group of electrons has acquired a sufficient number of members completely to fill the group. When an additional electron is added, as in the element that follows a rare gas in the periodic table, it must occupy the first position of a new group. Upon this basis of reasoning, the second electron group is filled, evidently, in the neon atom and can contain, therefore, a maximum of 8 electrons. The remaining 2 electrons of the neon atom lie, of course, in the completed first group, as in the helium atom. The third group can hold 8 electrons, also, while the fourth and fifth can contain 18 each, and the sixth can accommodate a maximum of 32 electrons. Atoms lying between two of the inert gases in the periodic table tend to gain or lose a sufficient number of electrons so that

they may attain the structure of the nearest stable element. They build up to the structure of the next inert gas by acquiring electrons, or they revert to the structure of the inert gas next below them by losing electrons. Thus, lithium (atomic number, three) contains only one electron in the second group, while fluorine contains seven. The lithium atom becomes a lithium ion, Li^+, by losing its one electron and reverting to the stable configuration of helium. The fluorine atom, on the other hand, tends to acquire one electron, thus attaining the stable state of the neon atom and becoming a fluorine ion F^-. The likeness of F^- and Ne and of Li^+ and He is a matter of exteriors only. The nuclei of the fluorine and the neon atoms are not the same. Furthermore, one atom (F^-) is electrically charged, while the other (Ne°) is neutral. There are other atoms in the periodic table whose neutral structures may exhibit certain degrees of stability and to which the structures of other atoms may change in their effort to attain stability, but none is so stable as the inert gases.

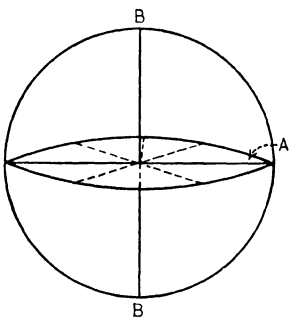

FIG. 76.—Langmuir's arrangement of electrons about the nucleus. The arrangement is symmetrical with respect to the polar axis *BB*, the equatorial plane *A*, and four planes that are normal to the equatorial plane, contain the polar axis, and make angles of 45 deg. with one another.

Shells and Cells.—The various groups of electrons are placed in concentric shells with the nucleus of the atom at the center. Each shell is divided into cells, all of which are of equal volume within a given shell. Since the respective shells can accommodate, respectively, 2, 8, 18, and 32 electrons, Langmuir thought that the effective radii of the shells are in the ratio of 1, 2, 3, 4. The effective surfaces of the shells, therefore, are in the ratio of 1^2, 2^2, 3^2, 4^2. Hence, if the surface of the first shell can hold two electrons, the second can hold four times, the third nine times, and the fourth sixteen times as many electrons as the first.

Within a shell, the electrons are arranged in cells and symmetrically placed with respect to (1) an equatorial plane; (2) a polar axis perpendicular to this plane and passing through its

center; and (3) four planes perpendicular to the equatorial plane and making angles of 45 deg. with one another.

The first shell (Fig. 77) consists of two cells, each of which is a hemisphere. Each of these cells is capable of holding one electron. The two electrons of this shell are on opposite sides of the equatorial plane and at equal distances from it in the direction of the polar axis. This shell contains one electron in the hydrogen atom and two in helium. The helium atom is stable; hence, the first shell is complete. Since the number 1^2 occurs but once in

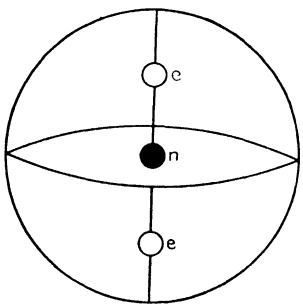

FIG. 77.—The first shell. This shell contains two cells, one above and one below the equatorial plane. Each cell contains one electron (e).

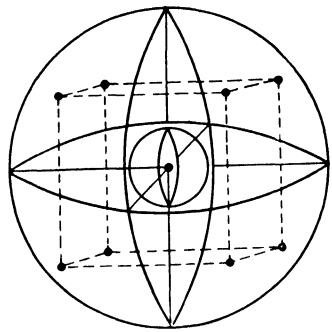

FIG. 78.—The second shell. This shell contains eight cells. In the neon atom each cell contains one electron, and the eight electrons are arranged at the corners of a cube.

the Rydberg equation, it appears unlikely that these cells ever contain more than one electron each.

The Second Shell.—The second shell (Fig. 78) contains eight cells. In the lithium atom, only one of the cells of this shell contains an electron. In the succeeding elements (Be, B, C, N, O, F, Ne), the second shell contains two, three, four, five, six, seven, and eight electrons, respectively. In neon, each cell contains an electron, and the arrangement is again one of great stability. The Rydberg equation $N = 2(1^2 + 2^2 + \cdots)$ shows that these eight electrons occur in two groups of four each. This means that there are four electrons in each hemisphere. Each group of four is arranged symmetrically with respect to the four planes that cut the equatorial plane and make angles of

45 deg. with one another. This arrangement gives eight electrons at the corners of a cube (Fig. 78).

The first elements of this series do not contain sufficient numbers of electrons for stable configurations; hence, there is a tendency to lose electrons and revert to the stable structure of the helium atom with its completed first shell. Thus, the ions Li^{+} and Be^{+2} are formed. Theoretically, it should also be possible to have ions of B^{+3}, C^{+4}, N^{+5}, O^{+6}, and F^{+7}, and these elements sometimes do appear to exhibit such valences as in H_3BO_3, H_2CO_3, HNO_3, etc. None of these elements, however, is ever found as simple cations in solutions of their compounds. The ions B^{+3}, C^{+4}, N^{+5}, O^{+6} are unknown. In fact, very few cations (positively charged ions) with valences greater than four are known. Stannic ion, Sn^{+4}, is one of the few quadrivalent ions. And although pentavalent ions, such as As^{+5} and Sb^{+5}, do exist, they are never found in great numbers in aqueous solutions or in the fused states of their compounds. Even in stannic chloride, $SnCl_4$, which does not conduct the current in the pure form, the tin atom probably carries no charge. This means, therefore, that the atoms of tin are bound to atoms of chlorine by shared electrons. When dissolved in water, however, stannic chloride liberates Sn^{+4} ions, a fact that indicates that the solvent causes a radical change in the character of the combination of tin and chlorine. The valence that depends upon shared electrons is changed by the effect of the solvent to a valence that depends upon the transfer of electrons from tin to chlorine atoms. The usual valences which most atoms acquire by losing electrons to other atoms appear to be one, two, or three, depending upon the number of electrons in the outer shell of the atom. Even when the outermost shell contains more than three electrons, a greater number is seldom transferred from the atom to another. This is probably due, in large part, to the fact that, whereas the first electron can be removed from the neutral atom with ease, additional electrons are increasingly difficult to remove, because the negatively charged electrons have to be separated from an already positively charged body. The electrostatic attraction makes the separation increasingly difficult as more electrons are removed. When four electrons have been separated from the atom, the positive charge is so great that a fifth

electron can scarcely be removed by the ordinary forces involved in chemical reactions.

The last half of the elements of this series (carbon to fluorine) tend to acquire a sufficient number of electrons to attain the stable arrangement of the neon atom. Thus, fluorine has a negative valence of one, NaF; oxygen two, H_2O; nitrogen three, NH_3; carbon four, CH_4. Here again, however, oxygen, nitrogen, and carbon never appear as the ions O^{-2}, N^{-3}, and C^{-4}, respectively. It appears that simple anions (negatively charged atoms) seldom possess a valence higher than two (Cl^-, S^{-2}, etc.). This is probably due to the fact that an atom that has acquired one or two electrons, thus becoming negatively charged, repels (electrostatically) additional electrons more strongly than it attracts them to complete an electron group. The positive valences of carbon, nitrogen, and other elements that occur near the end of each series (just before an inert gas) and the negative valences of elements that precede an inert gas by more than two places in the periodic table cannot be explained, therefore, upon the basis of a loss or gain of electrons, as in the cases of lithium and fluorine. The valences of the elements that occur somewhere near the middle of each series often result from the sharing of electrons between atoms rather than the actual transfer of electrons from one atom to another. Such atoms are not charged, and their ions are not formed in their combinations with other atoms. We shall later discuss in more detail (page 211) the compounds produced by the combinations of atoms that share electrons with each other.

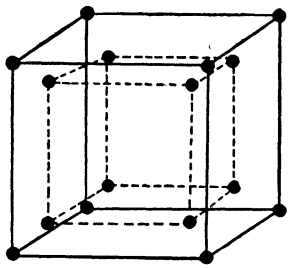

FIG. 79.—The two octets of the second shell.

The Rydberg formula contains the number 2^2 twice: $N = 2(1^2 + 2^2 + 2^2 + -)$. This indicates that, besides the first group of eight electrons in the second shell, there is another group of eight. This makes two electrons in each cell in the finally completed second shell. Langmuir assumed that no cell could contain two electrons, however, until each cell contained one. The second electron in each cell is slightly farther removed from

the nucleus than the first and is lined up radially with the first electron in the cell and with the atomic nucleus. In the atom of argon, the second cube of the second shell is complete. This second cube fits closely upon the first (Fig. 79).

The tendency of electrons to pair together, as shown in the close association of the electrons at the corners of the two cubes of the second shell, means that there is undoubtedly an attraction between two electrons, despite the electrostatic repulsion which necessarily exists because of their like charges. This attraction is caused, according to Lewis, by the magnetic fields of the electrons. As each electron rotates about a point, which we assume to be the corner of a cube, in agreement with the theory that we are now discussing, a magnetic field is produced by the circular movement of the charged particle, in much the same manner as a current of electricity produces a magnetic field when it passes through a coil of wire. If, now, two electrons rotate in the proper manner, their magnetic fields will cause them to be drawn together in such a way as to reduce their mutual magnetic moments.

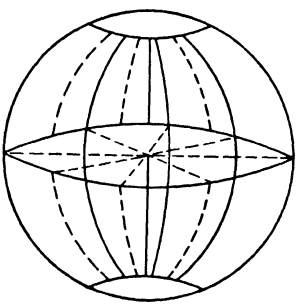

FIG. 80.—The third shell.

The elements of the second series resemble the corresponding elements of the first:

First series	Li	Be	B	C	N	O	F	Ne
Second series	Na	Mg	Al	Si	P	S	Cl	Ar
Maximum valence	+1	2	3	4	5	6	7	0
	−1			4	3	2	1	0

The valences of the elements in the second series can be explained in the same manner as those of the first series.

The Third Shell.—Beginning with potassium, electrons must go into the third shell, which contains 18 cells. This shell with its cells is shown in Fig. 80. Each hemisphere contains nine cells, one of which is located about the end of the polar axis. The first eight electrons to go into cells of this shell take positions

immediately overlying the electrons of the second shell. It is assumed that these electrons are attracted and held by the electrons below them through their respective magnetic fields, which produce an attraction that is stronger than the electrostatic repulsion of the electrons for one another. The first elements of this series resemble the corresponding elements of the first and second series. Thus, potassium is like lithium and sodium, and calcium closely resembles beryllium and magnesium. But none of the first eight elements of this series form simple anions corresponding to F^-, Cl^-, and S^{-2}. The reason for this is not hard to find, since these elements of the first half of the third series are not followed by an inert gas. Hence, there is no tendency on the part of any of the atoms of these elements to acquire electrons, except, probably, by sharing electrons with other atoms. Vanadium, chromium, manganese, iron, nickel, and cobalt form positive ions whose valences are two and three. Unlike nitrogen, oxygen, and chlorine they do not possess negative valences. Langmuir explains these valences by attempting to show that, whereas two or three electrons can be removed from atoms of these elements, it is probably very difficult to remove a greater number. The energy required to remove additional electrons from atoms already possessing two or three units of positive charge is not provided by the ordinary reactions that occur between atoms and that result in the transfer of electrons from one atom to another. The energy required to remove electrons from one atom is supplied by the liberation of energy when electrons combine with atoms of chlorine or of similar elements. Langmuir thinks that the energy liberated when a single electron combines with an atom of chlorine is not sufficient to pull the electron off the atom of the electropositive element (*e.g.*, chromium) and at the same time separate this atom from others of its kind, a thing that, of course, must be done if an independent ion of the element is formed. The energy liberated, when two or three electrons combine with as many atoms of chlorine, is sufficient to remove this number of electrons from a chromium atom, for example, and to separate this atom from others. As more electrons are removed and the chromium atom becomes more strongly charged, a greater quantity of energy is required to pull off an additional electron. Hence,

Cr^{+4}, and similar ions of the other neighboring elements, cannot be formed. In short, the chlorine atom cannot bring about the transfer of a fourth electron, since the energy liberated when the electron combines with the chlorine atom is smaller than the energy required to separate the electron from the atom of chromium.

In the atom of iron there are eight electrons in the third shell. These are arranged at the corners of a cube which immediately overlies the cubes of the second shell. In the next element, cobalt, the ninth electron goes to one of the polar cells; in the tenth, nickel, the additional electron goes into the other polar cell. This gives the structure that Langmuir called α nickel. The number of electrons has now grown until electrostatic repulsion between electrons has reached considerable proportions and is equal to, or slightly stronger than, the magnetic attraction that causes the first electrons of the third shell to line up with those below them. Hence, the eight electrons that form a cube in α nickel may move through an angle of 45 deg. so that they will be as far away as possible from the electrons below them. The two electrons in the cells of the polar axis remain as they were in α nickel. In this way, a structure of considerable stability results. This is called β nickel. The next succeeding elements tend to lose electrons and revert to this form, which is the most stable electronic arrangement between argon and krypton. Thus, copper has a valence of one; zinc, two; etc. In this respect, the last eight elements of this series resemble the elements of the first and second series; bromine is like fluorine and chlorine; selenium is like sulfur and oxygen; arsenic is like phosphorus and nitrogen. Toward the end of the series, the tendency is to gain electrons, and the atoms attain the stable structure of the inert gas krypton. In the krypton atom, each of the 18 cells contains one electron.

The fourth series, rubidium to xenon, is much the same as the third. Corresponding to β nickel we find β palladium in the middle of the series, and the valences of the succeeding elements are explained in the same manner as those of the elements from copper to krypton.

The Fourth Shell.—When xenon is reached, each cell of the third shell contains two electrons; hence, this shell is now com-

pletely filled. The additional electron of the next element, caesium, must go into a cell of the fourth shell, which contains 32 cells in all (Fig. 81). The first few elements of this series tend to revert to xenon and have valences, therefore, that are identical with the valences of the corresponding elements in each of the other series. Beginning with cerium, there is a group of elements, 14 in all, which very closely resemble one another, and each of which has a valence of three. These are the rare earths (page 41). These elements resemble one another for the same reason, according to Langmuir, that certain elements in the smaller groups (*e.g.*, vanadium, chromium, manganese, iron, nickel, and cobalt) of other series resemble one another.

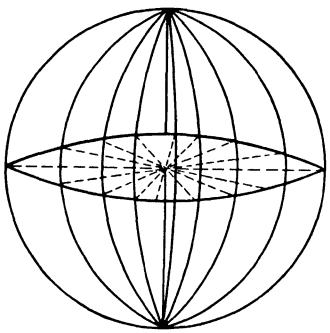

FIG. 81.—The fourth shell.

The 14 electrons first added to the cells of the fourth shell may lie in cells directly above electrons in the shell below; they may also shift their positions in such a way that the 18 empty cells of the fourth shell will lie directly above the electrons of the third shell. The fourteenth element of this series is erbium. The structure of the atom of erbium, in which empty cells lie directly above electrons of the third shell, is called β erbium. Langmuir calls the atom in which the 14 electrons are lined up with the electrons below them α erbium. The former represents a structure of some stability, less stable than the structure of an atom of an inert gas, even less stable than an atom of β nickel, but stable enough to cause succeeding elements to tend to revert to it. The eighteenth element is hafnium, and this definitely closes the rare earth group. This is the last element in which the electrons of the fourth shell can line up with those below. The elements between erbium and hafnium can exist in either α or β forms. Of these, β erbium is most stable. The elements following hafnium have valences that indicate their tendency to revert to the structure of β erbium. Thus, tantalum has a valence of five, and tungsten of six. The electrons added for the atoms of the elements between erbium and osmium, eight in all, probably

go into previously empty cells, so situated that the eight electrons form a cube which lies directly over the cubes of the second shell. In iridium and platinum, the two additional electrons go to the ends of the polar axis, just as they do in cobalt and nickel of the third shell. A β platinum structure is therefore possible, since there are now eight empty cells. In the β form of platinum, these eight empty cells lie immediately over the eight electrons that form the outer cube of the second shell. The succeeding elements gold, mercury, thallium, and lead tend to revert to β platinum and possess valences of one, two, three, and four, respectively. Other valences of these elements, such as three for gold and two for lead, are not satisfactorily explained by the theory. The same is true for the valences of other elements. Missing element 85 should have a valence of negative one, since it immediately precedes an inert gas. The known elements of the latter part of this group, however, seldom have the negative valences that we might expect them to have, such as polonium minus two, bismuth minus three, and lead minus four, as compared to other elements which are similarly located with respect to inert gases.

The last 6 elements of the periodic table represent the beginning of a second series of 32 elements and, in terms of Langmuir's theory, the beginning of the outer group of 32 electrons in the fourth shell. The one electron of the atom of element 87, the two of radium, etc., go into cells of the fourth shell which already contain one electron each. The grouping of electrons in the last element, uranium, might be expected, therefore, to be 2-8-8-18-18-32-6.

If this series were completed, we should expect to find another rare earth group, of which the last elements would correspond to the elements of the erbium-hafnium group and would exist in α and β forms; another transitional group like osmium, iridium, and platinum; then a group of elements exhibiting positive valences of one, two, three, and four; followed by another group resembling bismuth, polonium, and No. 85; and finally another inert gas. Among the first six elements of this series, however, there is no indication of even the beginning of a group that can be compared to the rare earth group. With the sixth element, this series ends, not because the shell is filled but

because we know no other members of the series. It seems that uranium is the most complex atomic structure that can exist under the present conditions of our planet. That more complex atoms can exist under other conditions is possible but is only a conjecture.

The Magnetic Properties of the Elements.—In support of the idea that the first electrons that enter a shell tend to lie directly above those in the shell below and are held in position by magnetic forces, Langmuir claimed that only those elements where electrons are so arranged, according to his theory, are paramagnetic. A substance is said to be *paramagnetic* when it is attracted by the pole of a magnet and when small particles of the substance tend to line up along the lines of force in the magnetic field. *Diamagnetic* substances, as opposed to paramagnetic, are repelled by a magnetic pole. Thus iron, cobalt, and nickel are the most strongly paramagnetic of all elements. Argon is diamagnetic, potassium is slightly paramagnetic, and this property increases in strength from calcium to the iron-cobalt-nickel group. Beyond cobalt, there is an abrupt change to elements that are diamagnetic. Cupric salts, however, show feeble paramagnetism, while cuprous compounds do not. For this reason, copper is thought to resemble iron, cobalt, and nickel when it shows divalence. Cuprous ion, on the other hand, has the same structure as β nickel because of the loss of one electron.

In the second long series, paramagnetism increases gradually up to palladium, where it attains its maximum value in this series and then drops to a negative value (diamagnetism) in silver, which corresponds to copper. Similarly, the rare earths of the the third long series are also found to be paramagnetic, although much less so than cobalt or palladium.

In every case, paramagnetism gives way to diamagnetism at exactly the same point in the periodic table where alpha forms of the atoms change into beta forms. Langmuir saw, therefore, some evidence in support of his ideas of magnetic influences within the atom in the agreement of the paramagnetic properties of the elements and the structures of their atoms as predicted by his theory of atomic structure.

Electrovalence and Covalence.—Langmuir recognized two kinds of valence. One of these is found in such compounds as

sodium chloride, where the two parts of the molecule[1] are actually charged by the transfer of one or more electrons (one in the case of sodium chloride) from one atom to the other. Only electrons in the outermost group or shell of the atom are transferred, and upon entering the atom which accepts them they enter its outermost shell. The attractive force in such compounds is the electrostatic attraction that exists between particles of the opposite kinds of charge. This type of valence is called *electrovalence*, and compounds formed by it are said to be electrovalent. Sometimes they are called polar compounds. The positive and negative charges of the molecules are not centered at the same point within the molecule. The difference in the location of these centers results in the production of what we may term positive and negative *poles*. The term *polar* properly should not be used to describe electrovalent compounds, since, in many cases, at least, the existence of the molecule is extremely doubtful. There is no *particle*, therefore, consisting of two poles. Furthermore, there are certainly some substances that are slightly polar in the sense in which this term is used; yet these are not greatly ionized, if ionized at all (page 191).

Other examples of electrovalent compounds include the salts, such as $Li^{+}Cl^{-}$, $Ca^{+2}Cl_2^{-}$, $Al^{+3}Cl_3^{-}$ (at least in solutions), $Fe^{+3}Cl_3^{-}$, $K^{+}NO_3^{-}$, $NH_4^{+}Cl^{-}$, $Na_2^{+}SO_4^{-2}$, etc; strong acids, such as $H^{+}Cl^{-}$, $H^{+}NO_3^{-}$, $H_2^{+}SO_4^{-2}$ etc., which act as electrovalent compounds at least in aqueous solution; and strong bases, such as $Na^{+}OH^{-}$ and $K^{+}OH^{-}$.

There is another class of compounds which are not electrovalent in character. These do not form ions in solution, and they show no evidence of consisting of positively and negatively charged parts. We may name as examples of these substances H_2, CH_4, CO_2, CCl_4, NO, and SO_2. Langmuir believes that electrons are shared by the atoms composing these compounds. This is called *covalence*.

Let us consider the covalence of the atoms in a molecule of hydrogen. As two hydrogen atoms approach, the nucleus of

[1] In view of our present knowledge of the structure of the crystal of sodium chloride, we should, perhaps, refrain from the use of the term molecule and speak, rather, of the sodium and chlorine ions of sodium chloride (p. 182).

one atom attracts the electron of the other as well as its own. Finally, the electrons are pulled out of their normal positions and lie between the two nuclei. This results in the formation of a bond which holds the two atoms together. The bond between the two atoms of hydrogen consists of a pair of shared

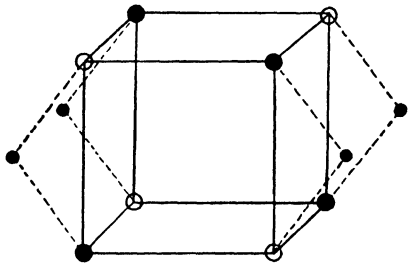

FIG. 82.—The methane molecule.

electrons. Each hydrogen atom shares its electron with the other; hence, no charge results, since there is no transfer of electrons from one atom to the other. In the molecule of methane, CH_4, the carbon atom shares four pairs of electrons with hydrogen (Fig. 82). The carbon atom completes its cube, or octet, of electrons, but there is no charge on any part of the molecule.

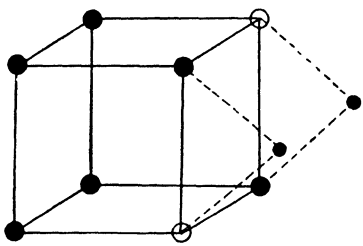

FIG. 83.—The water molecule.

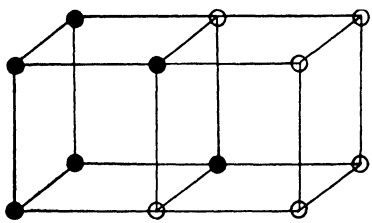

FIG. 84.—The oxygen molecule.

The oxygen atom possesses six electrons in the outermost shell. If it shares a pair of electrons with each of two hydrogen atoms, it completes its octet and forms a molecule of water (Fig. 83). The oxygen atom can also complete its octet by sharing two pairs of electrons with another oxygen atom, forming a molecule (Fig. 84). The structure of ozone, O_3, can also be

explained by the sharing of pairs of electrons by three oxygen atoms (Fig. 85). Carbon dioxide's structure is shown in Fig. 86.

The nitrogen atom in the ammonium ion, NH_4^+, is thought to complete its octet by sharing four pairs of electrons with hydrogen (Fig. 87). For a neutral condition of the group NH_4,

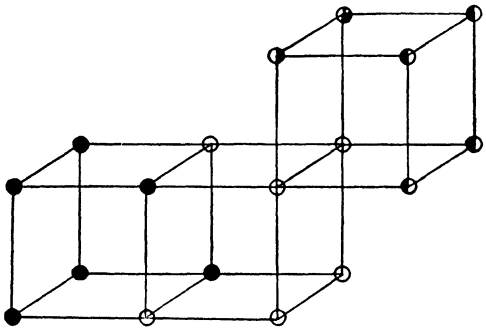

FIG. 85.—The ozone molecule.

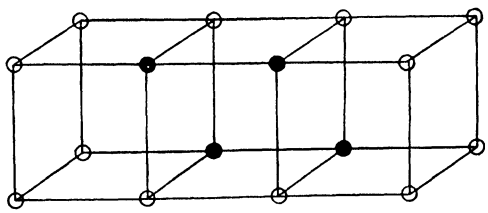

FIG. 86.— The carbon dioxide molecule.

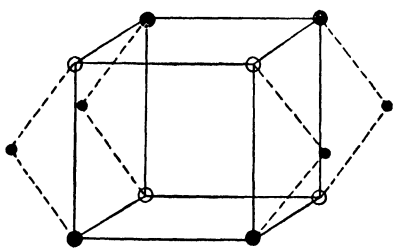

FIG. 87.—The ammonium ion.

nine electrons would be required, one for each hydrogen atom and five for nitrogen. But there is a single octet of electrons. Hence, the NH_4 group is positively charged. The ninth electron is transferred to some electronegative atom, such as an atom of chlorine. Thus is produced electrovalent ammonium chloride,

$NH_4^+Cl^-$, in which the ammonium ion acts as Na^+ and K^+ in their corresponding salts.

Other molecular models, all based upon Langmuir's theory, are shown in Fig. 88.

In closing this account of the "static" atom, we wish to remind the reader that it is not intended that the model of the atom which has been drawn in this chapter should be accepted as showing what an atom really looks like. Nor should we regard molecules as collections of cubes. The chemist is concerned primarily with an explanation of the atom's structure that will portray satisfactorily the action of the atom in chemical reactions. A successful explanation from the chemical point of view must

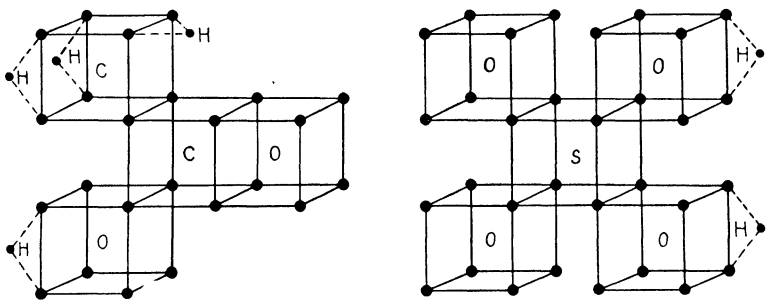

FIG. 88.—Diagrams of molecules of acetic acid (left) and sulfuric acid (right).

account for the valence, or valences, of the atom and the structures and properties of the molecules that it forms. It is evident to any chemist that there are distinct differences between molecules of hydrogen, H_2, and the molecules of hydrogen chloride, HCl. Carbon tetrachloride, CCl_4, and chloroform, $CHCl_3$, are not much like sodium chloride, NaCl, and cupric chloride, $CuCl_2$. There must be some good reason why tin can have a valence of four while copper cannot and why manganese can have a valence of seven in such compounds as potassium permanganate, $KMnO_4$, but never exists as a cation, in solution, with a greater valence than three. Water, HOH, and alcohol, C_2H_5OH, are somewhat alike and yet are widely different in some respects. All such facts as these must be explained upon the basis of atomic and molecular structures.

As we stated in the opening paragraphs, Langmuir's theory should be judged only upon its ability to furnish an explanation

of the properties, particularly the valences, of the elements. The theory did this better than anything that the older concepts of the atom could offer. On the other hand, it must be admitted that the model of the atom that the theory gives us is a physical impossibility. It is not conceivable that an atom so constructed would possess the physical stability required for its existence. It must be remembered, however, that Langmuir's theory preceded any extensive development of atomic mechanics. We can regard it only as a qualitative treatment of atomic structure and one that, at present, offers little but historical interest.

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CHAPTER X

RADIATION

Transmission of Energy.—Energy can be transmitted from one place to another in at least three ways. One means of transmission requires a mechanical appliance of some kind—a belt, a pipe, a wire, or a rod. In an engine, the energy that is generated by the expansion of steam or by the explosive action of a mixture of gas and air in cylinders is transmitted to the drive wheels by the piston rods. In the old-fashioned threshing "rig," energy is transmitted from the engine to the grain separator by means of a belt. Electrical energy is transmitted from the generator to our homes by the flow of an electric current through a wire. Energy stored in water behind a dam can be transmitted through a pipe, which leads the water to a lower level, where a turbine converts the energy into a mechanical form.

But energy can also be transmitted through space without the aid of any mechanical carrying devices. Particles ejected from a position where energy is stored, as in a cartridge in the barrel of a rifle or in the nucleus of an atom of radium, can traverse space and impart energy to objects upon which they fall. The object struck may be given kinetic energy if its inertia is not too great; it may absorb the energy and become warmer; or it may radiate the energy again, as in the emission of light by a body that has been heated to incandescence and in the production of x-rays when atoms are struck by electrons.

But light and x-rays are also forms of energy. These are seemingly transmitted through space from one place to another without the help of belts and flying particles. How, then, is light transmitted?

Newton's Corpuscular Theory of Light.—In 1675, Newton announced a theory of the nature of light and, several years later, reiterated his ideas in his treatise of "Opticks." Newton believed that light consists of corpuscles emitted by luminous

bodies and traveling with greater and greater speed until finally the force that moves them is equaled by the resistance of the "aetherial" medium through which they pass. They then move with a constant velocity as long as the resistance of the medium remains unchanged. The aetherial medium consists of a substance somewhat like air but rarer and more elastic.

This theory of light held the field for more than one hundred years. Attempts were made to explain many of the properties of light, such as reflection, refraction, and prismatic dispersion by modifications of the properties of light corpuscles.

The Wave Theory of Light.—In 1690, Huygens suggested a wave theory of light. He proposed the idea that light is a wave motion somewhat like sound in character. The proposal was not generally accepted at the time, however, and the corpuscular theory continued to dominate the situation. In the early part of the nineteenth century, a modified wave theory was very successfully employed in explaining the diffraction, interference, and polarization of light. Young and Fresnel are largely responsible for the development of the theory during this period. Later, about the middle of the century, Foucault further strengthened the theory by proving that light travels more slowly in water than in air, as the wave theory predicted. Maxwell and Hertz, at a still later period, finally established the *electromagnetic* character of light waves. During the latter part of the nineteenth century and also in the early years of the twentieth, no one seriously doubted the reality of light waves. All the facts appeared to verify them, while the corpuscular theory was left without the support of experimental evidence. The problem, however, was not yet solved. The first quarter of the present century was to bring forth an entirely new array of facts with which the wave theory does not agree in all respects. These facts tend to support, in a certain measure, modified forms of the earlier ideas of the corpuscular nature of radiation. The purpose of this chapter is to present, first, the wave theory and, second, the new or so-called quantum theory.

Waves.—Everyone has observed the waves that spread out in circles of ever increasing diameter when an object is dropped into a large body of water. Let us consider water waves, since they are very similar to light waves in certain respects. When a

stone, for example, is dropped into water, the water directly beneath the stone is displaced. This means that the water is pushed above the surface all around the stone. This gives the first wave crest. Eventually, the water forming this crest must fall. The water in the hollow where the stone struck must rise. But neither comes to rest at the original water level. Owing to the inertia of the moving mass, the falling water passes below the original level, and the water in the hollow simultaneously rises above it. Thus is formed a wave crest, where first there was a hollow, and there is now a hollow in the place of the first crest. As the water that formed the first crest falls below the original water level, that immediately outside is forced upward into a new crest. This crest in falling produces still

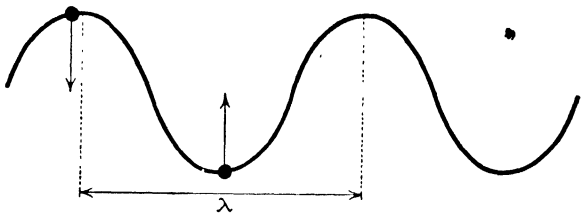

FIG. 89.

another crest farther out from the center of the disturbance, while in its own place a trough, or hollow, is formed. Thus, a series of crests and troughs spreads out over the surface of the water. The height of the crests and the depth of the troughs gradually decrease with each new wave produced. If the disturbance is regularly repeated by a series of stones dropped into the same place, one after the other and at equal time intervals, the series of waves will be maintained. Each stone pushes up a new crest around it to take the place of the crest belonging to the original wave.

The water of a crest in falling pushes up into a new crest not only the water outside but also the water inside. Thus, a piece of timber or a boat on the surface of the water does not move in a longitudinal direction; it moves only up and down along with the molecules of water as they are pushed up into a crest and then fall into a trough (Fig. 89).

In any series of waves (sometimes called a wave train) originating at a common point of disturbance, the molecules of water in one wave are matched by particles in the next wave which are in exactly similar positions at any one moment and which move in the same direction, up or down, at the same time. Such particles are said to be in the same phase of the wave; thus, particles of water at the very tops of successive wave crests are in the same phase. The distance between two particles that are in the same phase and lie in successive waves is called a *wave length* and is usually represented by *lambda* (λ). The velocity in a longitudinal direction divided by lambda gives the frequency *nu* (ν) or, in other words, the number of waves per second.

Waves like those that we have just described are called transverse waves, since the particles move in a direction transverse to the general direction of the wave's advance.

Evidence That Supports the Wave Theory of Light.—We cannot here consider all the evidence that supports the wave theory of light, but there are a few considerations of the subject which appear of fundamental importance for our study of the nature of light and similar forms of radiation. Much of the work that led to the establishment of the wave theory is credited to Young and Fresnel. The latter furnished explanations for many of the phenomena of light. The former performed one series of experiments in particular that exerted a powerful influence in favor of the wave theory. This work had to do with the diffraction of light (see also page 155). A beam of light passing through a slit A next passes through openings B and C between adjacent lines in a grating, which is a glass plate upon which lines are very closely drawn (Fig. 90). The apertures B and C are located at equal distances from A. Alternate light and dark areas appear on the screen beyond the grating. This is called *diffraction*. The wave trains are diffracted around the edges of the apertures B and C. From each slit as a center, new wave trains start out between the grating and the screen. These may be compared to the water waves that are produced when two stones are simultaneously dropped close together into water. But unlike the latter, of course, the light waves are spherical. The series of waves that start from the slits in the grating overlap. At a certain angle from the line OX, which is drawn perpendicularly to BC at B or C, the

wave train starting from *C* will coincide with the wave train starting from *B*; the two will be in the same phase. This means, simply, that the wave train starting from *C* must travel farther in arriving at the point *E* on the screen *SC* than does the wave train starting from *B* and that the extra distance is a whole wave length. Hence, a bright area appears on the screen at *E* while *D* represents darkness. The exact direction of this intensified or reinforced beam depends evidently upon the distance between

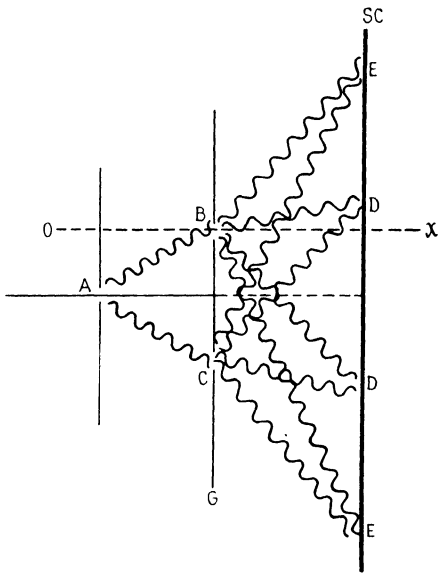

FIG. 90.—Diffraction of light. The points at *E* are illuminated regions on the screen because waves from *B* and *C* meet at these points in the same phase and mutually reinforce each other. At *D* the waves starting from *B* and *C* meet in exactly opposite phases and destructively interfere with each other.

the slits *B* and *C*. At points on the screen beyond *EE*, other bright areas also appear because a train of waves starting from *C*, for example, reinforces the train starting from *B*, when the extra distance which the former must travel in arriving at the point *F*, where the two trains coincide, is two whole wave lengths. Still others appear at farther points beyond *EE*. The dark areas are caused by the interference of the two overlapping wave trains. The crests of one series of waves must coincide with crests of the other to produce reinforcement. If crests and

troughs coincide, interference results in the formation of dark areas on the screen.

The phenomenon of diffraction is thus seen to be satisfactorily explained by the wave theory of light, but it provides a serious stumbling block for the corpuscular theory.

Although it was thought at first that light waves might be like sound waves, they were later proved to be transverse. Sound waves start from some center of disturbance, such as a vibrating tuning fork, and spread out spherically from the center. They consist of alternate spherical shells of compressed and rarefied particles. There is no up-and-down movement in a direction perpendicular to the path of the wave, as in transverse water waves. Instead, the particles move longitudinally in the same direction as the path of the sound wave. The discovery that light could be polarized established the transverse character of light waves. If light is passed into a crystal of tourmaline, for example, in the direction of one of the principal axes of the crystal, only light waves that move transversely in a certain plane are

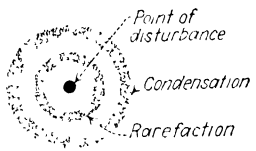

FIG. 91.— Sound wave showing alternate condensation and rarefaction.

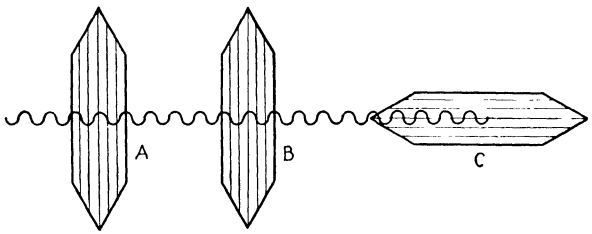

FIG. 92.—Polarization of light. Only transverse vibrations in one plane pass through *B* in which crystal planes are parallel to the planes of *A*. These vibrations are stopped by *C*.

allowed to pass through. The light that passes through must vibrate in a plane parallel to certain planes of atoms in the crystal. This light which emerges from the crystal is said to be *polarized*. If the beam of polarized light which emerges from one tourmaline crystal is passed into another in which the atomic planes lie at right angles to the planes of the first crystal, it is found that all of the light is absorbed. The light waves vibrating in a plane

that permits them to pass through the first crystal are stopped because of the failure of this one set of waves to get through the second crystal. It is evident that if light waves were longitudinal —of the same character as sound—polarization of light would be impossible. If they were longitudinal, one wave train would have as much chance of passing through the crystal as another. Only transverse waves which lie in planes that are not parallel to the planes of a crystal would be prevented from passing through.

The Electromagnetic Character of Light.—Clerk Maxwell and Hertz are responsible for establishing the electromagnetic theory of the origin of light. It was found that electromagnetic waves (Hertzian waves) are produced when an electrical discharge occurs between two charged points. When a Leyden jar is discharged, or when a discharge occurs between the points of an induction coil, the discharge is oscillatory. It first passes in one direction and then in the other. This oscillatory discharge produces electromagnetic waves in the surrounding medium. These spread out spherically in all directions. By such waves as these, energy is transmitted through space from a radio transmitting station to the receiver, which is perhaps thousands of miles away. Hertz proved that electromagnetic waves have the same characteristics as light. They travel with the same velocity; they suffer interference; and they are reflected and diffracted in the same manner. These discoveries appeared to establish the electromagnetic character of light.

In accordance with this view of the nature of light, its origin was later associated with the oscillations of electrons within atoms. X-rays (page 152) and other forms of radiation were thought to have a similar origin.

The Ether as the Medium of Light Transmission.—But what of the medium through which these waves are transmitted? Water waves are propagated in water, sound waves in air or in another equally material medium, but light and other electromagnetic waves pass through interstellar space and through artificially produced vacuums where, seemingly, there is nothing but empty space. To think of light as a wave motion is to think of it as a periodic vibration. But there is nothing to vibrate in a vacuum. To provide just such a medium for the propagation

of light waves as water gives for water waves, the "luminiferous ether" was postulated. This "ether" was thought to fill all space, regardless of the presence or absence of matter. Space was no longer considered empty; it was filled with ether. Definite properties, such as the elasticity of ordinary forms of matter, were ascribed to ether, and it came to be regarded almost as a reality. It has no real existence, however, and experiments, of which there have been many, to determine its existence have all resulted in failure. It must be regarded purely as a convenient creation of the imagination. It can endure, even as fiction, only as long as the theory of light which called it into being endures.

The Quantum Theory of Radiation

Resting upon so uncertain a medium of propagation as the ether, the wave theory of light naturally became the object of suspicion. A great deal of evidence was gradually produced to show that the theory did not adequately explain many of the facts concerned with the origin and effects of radiation. Just what some of these facts are we shall shortly see.

A new theory arose to take controversy with the wave theory. The new point of view represents, in a way, a revival of the corpuscular theory of Newton. It treats energy in much the same manner as the atomic theory deals with matter. We are led to believe, with certain reservations, that energy is atomic in character; it exists in definite quantities, called quanta, or their multiples, as matter exists in collections of atoms or molecules. When radiated through space, it is transmitted not continuously, as the older, classical wave theory demanded, but discontinuously; not as waves but as quanta or, to use the more common term at present, as *photons*.

Although the quantum theory cannot be regarded as the final solution of the problem of radiation, it is certainly one of the important milestones along the road toward that final solution. Since the theory is intimately related to the Bohr theory of atomic structure, which we are shortly to consider, we shall now investigate some of the evidence upon which it is based. This evidence reveals some of the outstanding failures of the wave theory and, at the same time, shows why a new theory was necessary. Our primary interest, however, goes further than

this. Any satisfactory explanation of the structure of the atom must adequately account for the radiation of energy by the atom, vibrating as a whole or as a system containing one or more vibrators. If we turn the matter around, it is equally true that any sound theory of the nature of radiation must throw some light upon the structure of the atom which is the source of that radiation.

Black-body Radiation.—The quantum theory was introduced by Max Planck (Berlin) in 1900. Previously, energy was thought to be emitted and absorbed by the gradual and continuous action of the atoms and molecules of radiating bodies. Planck's divergence from this point of view was extremely radical. He assumed that the action of a radiator of energy is not continuous but is intermittent and that radiation occurs in quanta of definite magnitudes. Planck saw no reason to regard his theory as conflicting with the views of Maxwell. He was concerned only with the emission of corpuscular radiation. This idea did not imply, necessarily, that radiation after emission could not be propagated through space as a wave motion. The idea that propagation is also a corpuscular phenomenon was arrived at later, when the action of radiation upon bodies was considered. This effect will be discussed in the section dealing with the photo-electric emission of electrons. Planck developed the theory to explain radiation from a black body. Such a body is one that absorbs all radiation, whatever the wave length, that happens to fall upon it yet emits radiation the wave length of which is determined by the temperature of the body. Let us think of such radiation as that which might be found inside a vessel whose walls are at a definite temperature but within which there are no atoms or molecules. In explaining the radiation from a body of this kind, Planck was forced to the conclusion that the classical theory does not account for the distribution of the radiant

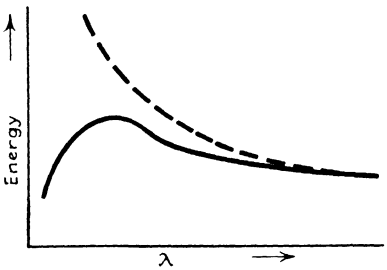

FIG. 93.—Black-body radiation. The dotted line represents the distribution of energy among different wave lengths according to the classical theory. The lower curve represents the observed distribution of energy.

energy among the different observed wave lengths. The classical theory predicted that most of the energy would be in the form of the shortest wave lengths. Measurements of the intensities, however, showed that this was not true experimentally (Fig. 93). Certain wave lengths which were neither the shortest nor the longest possessed most of the energy. Planck concluded that black-body radiation could be explained if the elementary oscillators producing the radiation did not radiate continuously but accumulated energy until a certain amount was present and then allowed definite quantities to be radiated, or discharged, at a time. The quantity of energy radiated in this manner is expressed as $nh\nu$, where n is an integer, ν is the frequency of the radiation, and h is an universal constant named after Planck.

The conclusion that Planck arrived at can be shown by the following line of reasoning concerning the character of the radiation emitted by a heated body: The classical theory required that the color of light emitted by the vibrations of the different oscillators of a system should not be related in any way to the temperature. Regardless of how much heat is imparted to the system, the color of the emitted light should not change. Only the intensity should vary with the quantity of heat added. Now, of course, the color of a body does change when the body is heated. A high temperature must be attained before the body emits blue light, which has a relatively high frequency. Planck explained this by the assumption that only at high temperatures do the vibrating parts of the atoms of the body possess sufficient energy to radiate quanta corresponding to the frequency of blue light. At lower temperatures, the energy of the vibrators may be sufficient to emit radiation quanta correspondingly to lower frequencies. This means that the quanta of energy $nh\nu$ radiated from a body at a low temperature have relatively smaller values, since ν is smaller than for the radiation from a body at a higher temperature.

The constant h is called the *elementary quantum of action*, since the constant represents the product of energy and time, a product that in mechanics is called action. The value of h is 6.55×10^{-27} erg per second.

The Photoelectric Effect.—When exposed to certain kinds of radiation, different forms of matter emit electrons. Thus, the

feeble light of a candle falling upon the surface of sodium or potassium causes the emission of electrons. Other metals act in a similar manner when subjected to radiation of greater frequency such as ultraviolet light. X-rays and gamma rays are sufficiently powerful to cause the emission of electrons from all forms of matter.

Electrons liberated by the action of radiant energy are called *photoelectrons*. The maximum velocity attained by these elec-

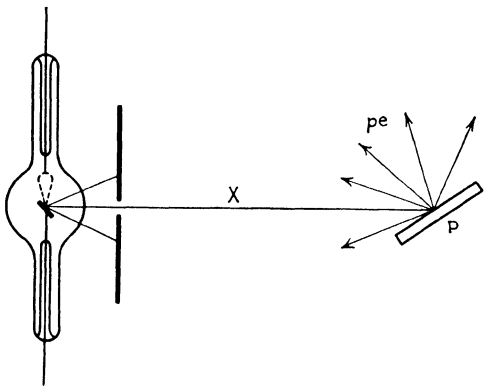

FIG. 94.—The production of photoelectrons. *X*, the x-ray beam; *P*, the plate of metal; and *pe*, the photoelectrons released from the metal.

trons has been found to vary directly with the frequency of the radiation that liberates them. The intensity of the radiation has nothing to do with the velocity that the electrons attain. A very weak beam of light, for example, can liberate electrons that travel with a very high velocity, provided that the frequency of the radiation is high, while a low frequency of light, however intense, does not liberate high-speed electrons.

The maximum energy E of the emitted electrons is expressed as

$$E = h\nu - K,$$

where K is the amount of energy required to separate the electron from the atom, ν is the frequency, and h is the elementary quantum of action. In the case of x-rays, the kinetic energy of the electron is so much greater than the energy required to remove an electron from the atom that K may be neglected.

X-rays are produced by bombarding the anti-cathode of the x-ray tube with rapidly moving electrons. As an electron strikes

the target, it spends a certain quantity of energy in producing an x-ray of a certain frequency. This means that each electron liberates an energy quantum equal to $h\nu$ (Planck's constant times the frequency of the x-ray produced). To produce an x-ray of a definite frequency, an electron must strike the anti-cathode with a definite maximum momentum. Hence, the electron must attain a definite maximum velocity. The velocity of the electron depends, in turn, upon the potential at which the tube operates. As the potential between the terminals of the tube is increased, x-rays of greater and greater frequencies are emitted.

According to the wave theory, x-rays produced at the anti-cathode travel out, as does light from a luminous body, into space as a sphere of ever increasing diameter. When they fall upon another object, such as the surface of another metal, they cause electrons to be emitted again. The number of electrons that are liberated from the second object will depend upon the number of quanta of energy that strike the surface of the object and are absorbed. And, strange as it may seem, the maximum velocity of the liberated electrons is the same as that of the electrons that produced the x-rays. Now, if the x-ray is propagated through space as a wave motion, the facts just described are very difficult to explain. On the basis of the wave theory, these results would be just as impossible as the following hypothetical action of water waves: Let us imagine that a cask is thrown into the middle of a large lake. This cask takes the place of the electron in the x-ray tube. It strikes the water, just as the electron strikes the anti-cathode of the tube. A train of water waves travel out from the point of disturbance in all directions over the lake; the water waves correspond to the x-rays. Finally, the waves reach a distant part of the lake, where another cask, exactly like the first, is floating; this corresponds to the second electron. The cask is suddenly shot out of the water into the air, reaching a height equal to that from which the first cask was dropped.[1] This happening, of course, is purely imaginary. It cannot occur, because the energy imparted to the water medium, when the first cask is dropped, cannot be imparted in its entirety to another cask floating at a point far removed from the first.

[1] A. H. Compton, *Sigma Xi Quart.*, March, 1929, and *J. Chem. Ed.*, **7**, 2769, 1930, has given a more interesting version of this same illustration.

The energy is dissipated in all directions around the center of disturbance, and only a small fraction ever reaches the second cask. But just as this is impossible, so is it impossible to impart all of the energy that an electron liberates in producing an x-ray to another electron, if the x-ray is to be regarded as a wave motion somewhat like the water wave.

The phenomena connected with photoelectrons certainly do not place the classical wave theory of light in a very favorable position. On the other hand, they furnish one of the most convincing arguments in favor of the quantum theory. According to the wave theory, the energy of the x-ray becomes less and less intense as the intensity is measured farther and farther from the source. When the wave strikes an electron of an atom far removed from this source, only a small part of the energy, which is now dissipated over the surface of a large sphere, would be available to dislodge the electron from the atom. Certainly, it could not impart to the electron an amount of energy sufficient to give it a velocity exactly equal to the velocity of the electron that produced the x-ray. Yet, this is just what does happen. It is much more satisfactory to think of energy as appearing in definite quanta at the time of its liberation and also at the time of its absorption. If this be true, then, of course, the maximum quantum that can be absorbed is the same as the maximum quantum which is liberated. The evidence is overwhelmingly in favor of the "corpuscular" theory.

Specific Heats at Low Temperatures.—Certain facts relating to the specific heats of different elements at low temperatures were explained by Einstein upon the basis of the quantum postulate. The satisfactory character of such explanations offers further substantiation of this theory.

The specific heats of some solid elements, such as diamond (carbon), diminish very rapidly with decreasing temperatures. The change is very pronounced for variations at low temperatures such as that of liquid air. Other elements, of which lead may be cited as an example, do not exhibit these pronounced decreases in specific heat. Now, the specific heat of a substance is defined as the quantity of heat (number of calories) required to raise the temperature of one gram of the substance one degree (Centigrade). The heat added to an atom produces an increase in the vibration

rate of the atom about some fixed position in the solid. Newtonian, or classical, mechanics would lead one to conclude that all atoms should require equal amounts of energy to increase their temperature by an equal number of degrees. This, however, is not the case, as has been pointed out for diamond and lead. Einstein offered the following explanation for this difference: Let us assume that the motion of an atom about its fixed position in the solid is quantized. This means that if an atom vibrates at all, it must have associated with it a quantity of energy corresponding to a quantum for which there is a perfectly definite frequency. Now, if such a quantum of energy is not available, the atom will not absorb energy and, therefore, will not vibrate. Let us assume that the frequency of vibration for the carbon atoms of diamond is very large, while the frequency for lead atoms is small. Now, the quanta corresponding to the large frequencies are probably not available in large numbers at low temperatures. Hence, when diamond at a low temperature comes into contact with a body which is warmer, its atoms take up, relatively, far less heat than atoms of lead. This is because there are far fewer quanta which atoms of diamond can absorb, since these quanta are relatively very large. Thus, we find further support for the quantum conception in an entirely different source.

Perhaps a still more convincing source of evidence for the quantum theory is found in the study of the spectra of the elements. The wave theory can explain spectra no better than it can explain photoelectrons and black-body radiation. Yet, we must remember that the wave theory does offer a satisfactory explanation of many of the properties of radiation, such as diffraction, reflection, refraction, and polarization. For this reason, we must not discard the older theory too quickly. It is still capable of great service and has many features that recommend it.

Optical Spectra

Kinds of Radiation.—White light consists of all the colors of light, violet, indigo, blue, green, yellow, orange, and red. If a beam of white light is allowed to pass through a prism (Fig. 95), the rays of different colors, or wave lengths, are refracted.

Refraction is the bending of the path of the ray due to the change in velocity when the ray leaves one medium and enters another, as, for example, when it passes from air into the glass prism. Light of long wave length (red) is refracted only slightly, while the other colors (shorter wave lengths) are bent more strongly, violet being refracted most of all. When these rays, now separated because of their different degrees of refraction, emerge from the prism into the air again, they suffer a second refraction because of a second change in velocity. Upon striking a screen, the different colors will be arranged in the order of their wave lengths, with light of the longest wave lengths

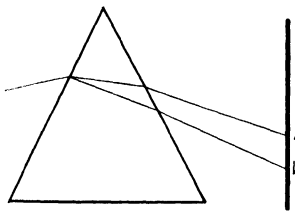

FIG. 95.—The dispersion of light by a prism.

above. The composite white beam has been dispersed, and a spectrum has been produced.

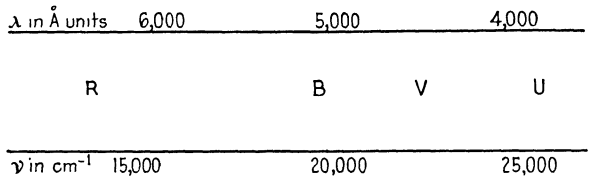

FIG. 96.—The optical spectrum. Showing the approximate ranges of the wave lengths and frequencies of the red (*R*), blue (*B*), violet (*V*), and ultraviolet (*U*) portions of the spectrum

Beyond the red of the visible spectrum lies a region called the infrared. This region consists of relatively long wave lengths.

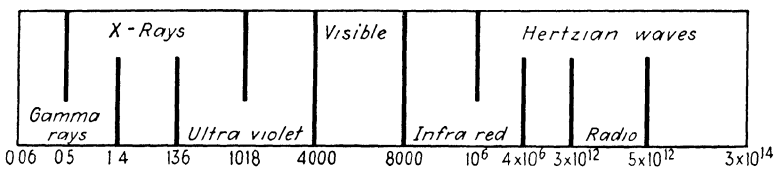

FIG. 97.—The complete electromagnetic spectrum. The scale refers to wave lengths measured in Ångström units.

Infra radiation produces a rise in temperature and increased molecular motion, when absorbed by forms of matter. Such rays belong to the group of so-called heat rays. Beyond the

violet, there is a region of very short wave lengths called the ultraviolet. Neither of these regions of waves affects the eye; they are not visible. Each consists of a long series of wave lengths. Hertzian waves have still longer wave lengths than those of the infrared region. X-rays, gamma rays, and cosmic rays lie in a

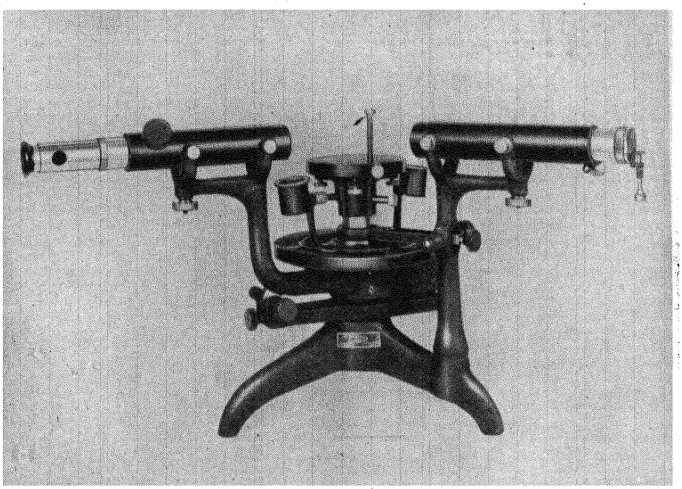

FIG. 98.—A spectroscope. (*Courtesy of the Gaertner Scientific Corporation.*)

region of very short wave lengths, beyond the ultraviolet. The ranges of the wave lengths for the different regions of the complete electromagnetic spectrum are shown in Fig. 97.

The Spectroscope.—The spectroscope is an instrument for analyzing a beam of light into its various wave lengths by means

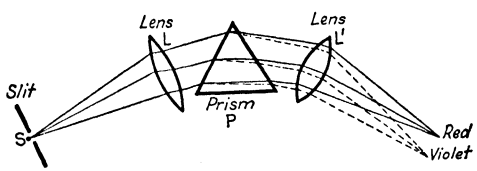

FIG. 99.—Diagram of prismatic spectroscope.

of a prism or a diffraction grating (page 155). In the prism type of instrument (Fig. 99), the beam of light that is to be analyzed enters through a small perpendicular slit S and passes through a lens L which is so located that its principal focus is at S. This

lens produces parallel rays of light which fall upon the prism P. Because of differences in the refraction of the wave lengths that compose each bundle of rays, these parallel rays are broken up into their various wave lengths. The various bundles of rays pass through different thicknesses of the prism and are refracted to different extents. Those that pass through the top of the prism are bent less than those that pass through the bottom. After leaving the prism and entering the air, the rays pass through a second lens L'. Here the rays of the same wave length from the different bundles of rays are brought to a common focus. The various wave lengths are thus spread out to form a series of spectral lines, each wave length producing a line. The lines of the spectrum are really images of the slit, which is usually narrow and straight; hence, we speak of the lines of the spectrum. If the spectrum passes through a camera and falls upon a photographic plate or film, a picture of it can be obtained. With the camera attachment, the instrument becomes a spectrograph.

Kinds of Spectra.—*Emission spectra* are produced by light emitted from luminous bodies, such as the filament of an electric light or an incandescent solid of any kind. When the luminous substances are gases, only certain wave lengths are emitted, and the spectra of light from such sources consist of only certain lines, or colors. Since different lines are found in the spectra of different gases, spectrum analysis can be used to detect the constituents of a given gaseous mixture. Each element produces characteristic lines. Substances that are naturally gases under ordinary conditions, such as hydrogen and helium, form spectra when they are made to glow. Other substances which are not gaseous at ordinary temperatures can be volatilized, as in a flame. Thus, barium chloride volatilizes, when placed in a flame. The salt is ionized. The incandescent barium particles then emit their characteristic radiations, and the spectrum of the light from the flame shows the characteristic lines of barium.

So far, we have spoken only of spectra that consist of relatively widely separated and distinct lines. *Band spectra* consist of various bands, each band consisting, in turn, of a great many lines crowded closely together. The different lines in a band become apparent only when a spectroscope, or spectrograph, of great precision and dispersing power is used. Band spectra are

due to light that is emitted by vibrations of molecules, while spectra are associated with light of atomic origin. In this book, line spectra are discussed at some length, since theories of atomic structure are largely dependent upon such lines of evidence. The limitations of our treatment prevent us from entering upon the consideration of band, or molecular, spectra at this time. References concerning this topic are listed at the end of this chapter.

If light from a given source is passed through an absorbing medium before it is allowed to enter the prism, certain wave lengths are absorbed, while others are not. Red glass, or a solution containing some red salt, absorbs all wave lengths except those that lie in the region of red light. Luminous gases absorb the same wave lengths of light as those that they emit when they are made to glow. If a beam of white light is passed through any of the media that absorb only certain wave lengths of light, the spectrum reveals the wave lengths which are removed as dark lines against the background of the otherwise complete spectrum. Such a spectrum is called an *absorption spectrum* and can be used for the analysis of "unknown" substances in the same manner as an emission spectrum. Absorption spectra of many substances can be obtained with less difficulty than emission spectra, because of the ease with which their solutions can be prepared. In many cases, it would be very difficult, or impossible, to raise the temperature of the substance to the point where an emission spectrum could be obtained.

The lines that appear in the spectrum of light emitted from a given source depend to some extent upon the manner in which the body is made luminous. Thus, a body heated in a flame shows characteristic lines. Many more are found in the light of a body exposed to the action and high temperature of an electric arc or spark. For the production of *arc spectra*, the substance to be examined is usually placed on the positive carbon electrode of the arc. To obtain *spark spectra*, the terminals of an induction coil are made of the substance to be studied, or the terminals are coated with the substance. For the examination of a gas, glass tubes containing the gas under greatly reduced pressure are used. These tubes have two electrodes, or terminals, sealed through the glass and attached

to the terminals of the secondary of an induction coil. When so connected, a bright discharge, the color of which depends upon the contents of the tube, passes between the terminals.

The wave lengths of light emitted by a heated body depend upon the temperature of the body (page 223). As the temperature is gradually increased, infrared heat rays are first emitted. The body becomes luminous at about 600°; it is red hot and emits red light. As the temperature continues to rise, the body finally becomes incandescent, or white hot; it emits all the wave lengths of white light. The color of a heated object is thus a measure of its temperature. In this way, something can be told concerning the temperature of the sun and of the stars. The most intense sunlight lies in the region of yellow and green light; hence, the sun is comparatively cool, for the hottest stars emit most of their light as wave lengths of the blue region of the visible spectrum.

The Hydrogen Spectrum.—The spectra of almost all of the elements contain so many lines that their unraveling is an almost impossible task. The spectrum of hydrogen is comparatively simple; hence, most of the applications of spectral data to the problem of atomic structure have been made from the spectrum of this element.

The spectroscope reveals three bright lines in the spectrum of the light emitted by luminous hydrogen. These lines lie in the red, blue, and violet, respectively. These are all that are visible; but when the camera is substituted for the eyepiece of the spectroscope, and the spectrum is photographed on plates that have been sensitized by organic dyes so that they are readily affected by infrared and by ultraviolet light, many other lines are observed. The lines of the complete hydrogen spectrum lie in four distinct series, or groups. In the region of visible light and extending into the range of the longest ultraviolet wave lengths, there is a certain group of lines called the Balmer series. This series is named after Balmer, who discovered the relations of these lines to one another. The first 20 lines of the series can be observed in the emission spectrum which is obtained by the discharge of electricity in Geissler tubes, which contain hydrogen under greatly reduced pressure. Some 13 other lines can be observed in the spectrum of the light from nebulae. Still others can be observed in absorption spectra. In 1885, Balmer found that

the frequency (velocity/wave length) of any line in this series can be calculated by means of the following equation:

$$\nu = \frac{4c}{A}\left(\frac{1}{4} - \frac{1}{n^2}\right),$$

where ν is the frequency or wave number, which is far more often used; n is a whole number (3, 4, 5, 6, etc.); and $4c/A$ is a constant, c being the velocity of light.

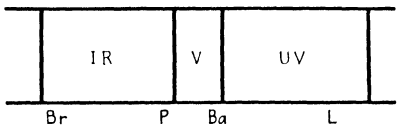

FIG. 100.—The spectrum of hydrogen; showing the approximate locations of the Lyman (*L*), Balmer (*Ba*), Paschen (*P*), and Brackett (*Br*) series of lines.

The wave number is usually employed to designate a spectral line instead of the frequency, since the latter is always an inconveniently large number. The former is defined as the number of waves in a wave front which is 1 cm. long.

A few years after Balmer's discovery, when more spectral data had accumulated, Rydberg found that the following equation was applicable to the Balmer series of the hydrogen spectrum

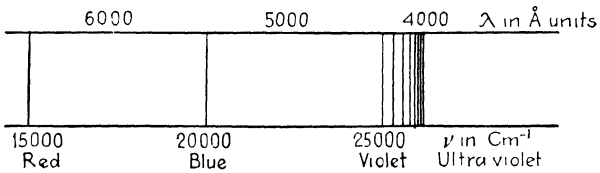

FIG. 101.—The Balmer series of lines in the spectrum of hydrogen.

and, with certain modifications, to lines in the spectra of other elements, particularly that of ionized helium:

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

where R takes the place of $4c/A$ in Balmer's original equation.

After the beginning of the twentieth century, three other series of lines were discovered in the hydrogen spectrum: the Lyman series in the ultraviolet, the Paschen series in the infrared, and the Brackett series among the lowest infrared wave lengths. Natu-

rally, an effort was made to apply Rydberg's equation to each of these series. The results were entirely satisfactory:

$$\text{Lyman,} \quad \nu = R\left(\frac{1}{1} - \frac{1}{n^2}\right).$$

$$\text{Paschen,} \quad \nu = R\left(\frac{1}{9} - \frac{1}{n^2}\right).$$

$$\text{Brackett,} \quad \nu = R\left(\frac{1}{16} - \frac{1}{n^2}\right).$$

Now, $1/1 = 1/1^2$; $1/4 = 1/2^2$; $1/9 = 1/3^2$; and $1/16 = 1/4^2$. Hence, we write an equation that will apply to the frequency of any line in any of the four series:

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

where n_1 is 1, 2, 3, or 4, for the Lyman, Balmer, Paschen, and Brackett series, respectively; and n_2 is a whole number greater than n_1 by at least 1. Thus, if n_1 is 3, n_2 can be 4 or any number larger than 4, which, if substituted in the equation, will give the wave length of some line in the Paschen series. R is the Rydberg constant, 3.291×10^{15} (vibrations per second), or 109,677 cm.$^{-1}$ (wave number).

The frequency, or wave number, of any line in the hydrogen spectrum is thus shown to be the difference between two quantities. One of these quantities is the same for all the members of any series. Since it defines the maximum frequency for the series, it is called a *limit.* The second quantity is called a *term.* The term is characteristic for each line of a given series. It will be noted, however, that the limit of one series is a term of another. Thus, the limit of the Balmer series is a term of the Lyman series. Considering the spectrum, as a whole, therefore, there is no essential difference between limits and terms. For this reason, we may regard the lines of the hydrogen spectrum as represented by the differences between two members of a sequence of terms which have the values R/n^2, where n is an integer of a sequence beginning 1, 2, 3, etc.

Probably the most important information revealed by the discovery of the relations between the spectral lines of hydrogen is the fact that these lines are in no way comparable to the rela-

tions between a fundamental and its harmonic vibrations. In other words, the frequency of the light emitted by an electron bears no relation to the "fundamental" frequency of the revolution of the electron in an orbit.

Although the Rydberg equation was developed from empirical considerations of spectroscopic data, the fact that it applies to all the lines of the hydrogen spectrum furnished excellent reason for believing that some physical basis exists for the explanation of the different frequencies of this spectrum. It should be possible to relate the spectrum of the element to the structure of the atoms of the element. This was what Niels Bohr attempted in developing the theory of atomic structure which we shall consider in the next chapter.

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CHAPTER XI

THE BOHR THEORY OF ATOMIC STRUCTURE AND THE ORIGIN OF SPECTRAL LINES

Introduction.—Realizing that the ultimately acceptable picture of the atom must be one that displays it as a physically stable model, chemists have attempted to find, first, a theory of atomic structure that was acceptable to the greatest number of physicists and then to modify this theory to meet the needs of chemistry. The Bohr theory, until recently at least, has served this purpose in a fairly satisfactory manner. We are not to regard the Bohr theory as entirely acceptable. In fact, recent methods of treating the problem of the atom's structure have left only a remnant of the original theory, and Bohr's model of the atom has lost most of its semblance of reality. It is true, however, that in many respects the fundamental principles of the Bohr theory still serve as a satisfactory basis for the considerations of chemistry. Matrix and wave mechanics, which are discussed later, have not destroyed the force of Bohr's fundamental concepts of energy levels and quantized electron orbits. In the main, the newer treatments are concerned with methods of calculating and formulating the different energy states of the atom and leave us free, if we choose, to think of electrons rotating in orbits about the nucleus. Furthermore, without a knowledge of the Bohr atom, these newer concepts and methods of calculation would be unintelligible to most of us. Hence, let us see how the Bohr theory was developed and how it explains the structure of the atom.

Fundamental Assumptions.—Bohr assumed that electrons rotate about the nucleus in much the same manner as the planets rotate about the sun. An atom, then, is somewhat like a solar system, the atomic nucleus corresponding to the sun, the electrons to the planets. Let us confine our study for the present to the simplest atomic system, the hydrogen atom, in which a single planetary electron rotates about the nucleus, or atomic sun.

There is a defect in the description of the atom as a planetary system that must be corrected. According to all previously accepted notions of electricity, an electron must act as a radiator of energy when it moves in a circular or elliptical path. Electromagnetic waves are sent out into space, when either the speed or direction of the electron is changed. When moving in an orbit, the direction of the electron is changing continuously. In this respect, an electron moving through space in a circular path acts in the same manner as a current of electricity which flows through a coil of wire. In fact, a current is nothing more or less than a stream of electrons flowing through the conductor. Now, a current of electricity flowing through a wire coil generates a magnetic field which is the seat of energy. This field extends from the coil to infinity and is renewed as long as the current flows. It appears, therefore, that the current, or the electron, is a source of energy. In accordance with the principle of conservation of energy, the current, or electron, must lose energy as long as it moves. This loss of energy is impossible, however, as long as the electron rotates in a definite orbit and thus maintains its position at a definite distance from the nucleus. As long as the electron does this, it must possess an equally definite quantity of energy.

The electron's energy is both kinetic and potential in character. Its potential energy depends upon the distance that separates it from the nucleus, just as the potential energy of a book lying upon a table depends, in part, upon the distance through which the book may fall from the table to the floor. The kinetic energy of the electron depends upon its velocity and its mass, which, of course, is constant for small velocities. The velocity determines the radius of the orbit of rotation, since the velocity determines the centrifugal force of the electron which prevents it from falling into the nucleus in response to the attraction, or the centripetal force, exerted by the nucleus upon the electron. Any loss of energy necessitates a change in the orbit of the electron's rotation; the electron rotates in an orbit of smaller radius. If energy were gradually lost by radiation, the electron would move in an orbit of gradually diminishing radius, until it finally "fell into" the nucleus or at least approached it very closely. We cannot say how far an electron might be able to penetrate the

nucleus, since we know very little concerning the forces that exist there or concerning the arrangement of the protons and electrons within the nucleus.

Since it appears, however, that electron orbits, if they exist, are capable of maintaining a more or less permanent existence and that the electron moves in an orbit indefinitely, unless forced out of it by some external force, Bohr concluded that *electrons can rotate in certain orbits without radiating energy.* This was a bold assumption, revolutionary in character, and destined to create a bitter controversy between the adherents of the new theory and those who preferred to cling to the old ideas of radiation.

If Bohr's assumption is accepted, then it necessarily follows that the atom, when acting as a radiator of energy, does not radiate continuously. Radiation occurs only when the electron moves from one orbit, where it possesses a definite quantity of energy, to another, where it possesses another quantity of energy which is just as definite as the first but smaller. Likewise, energy is absorbed when an electron moves to orbits that are farther removed from the nucleus. Here, again, the energy involved in the change in the position of the electron must be a very definite quantity, representing the difference between the values of the energy that the electron possesses in the two orbits. Because electrons do not radiate when moving in "certain" orbits, these are commonly called *stationary* orbits and sometimes *quantized* orbits, because of the definite quantities of energy that the electron possesses while it rotates in them. The various states of the atom, *e.g.*, of hydrogen, in which the electron rotates in any one of its different stationary orbits are called the stationary states of the atom.

The evidence upon which Bohr's theory was based consisted of observations of the spectrum of the radiation emitted by the hydrogen atom. We turn next, therefore, to Bohr's explanation of the origin of the lines of this spectrum and to the model of the hydrogen atom, which is based upon this evidence.

Bohr's Theory of the Hydrogen Atom.—Basing his ideas upon the nuclear theory of atomic structure, Bohr pictured the hydrogen atom as a system consisting of a single electron which rotates about a single proton as the nucleus. If this electron radiates energy continuously, because of the orbital path in which it

moves, it should eventually fall into the nucleus (page 237), and the spectrum of the radiant energy that is emitted should be continuous. All wave lengths should be observed, at least all wave lengths within certain limits. But instead, we find only the definite lines of the Balmer, Lyman, Paschen, and Brackett series; the spectrum is discontinuous.

Bohr assumed, therefore, that it must be possible for the electron of the hydrogen atom to rotate in certain orbits without radiating energy. These are the stationary orbits to which we

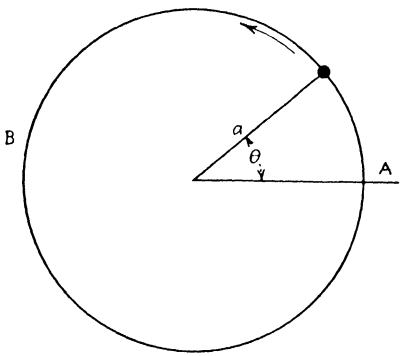

FIG. 102.—Angular and linear velocities. Linear velocity is considered along the path AB. Angular velocity depends upon the rate at which the angle θ varies. Linear velocity (v) = angular velocity (ω) $\times$ a. Angular momentum = mass (m) $\times$ a^2 $\times$ ω = mva.

have already referred (page 238). When the electron revolves in one of these, the atom is in a stationary state—stationary with respect to its energy content. Energy is emitted as radiation only when the electron moves from one orbit to another, where it possesses less energy than when moving in the first orbit.

The energy that the electron possesses in any one orbit depends upon the distance of the electron from the nucleus and upon its velocity, which varies with the orbit of rotation. Bohr's fundamental assumption states that the electron rotates in the stationary orbit nearest the nucleus in the *normal* state of the hydrogen atom. For this normal stationary state, the *angular momentum* of the electron multiplied by 2π is equal to the elementary quantum of action h. Angular momentum is defined as the product of the velocity of the electron in its orbit, its mass, and the radius of the orbit:

$$\text{Angular momentum} = mva.$$

Hence,

$$h = 2\pi mva.$$

There are, however, many other orbits in which the electron can revolve without loss of energy as long as it remains in any one of them. Each of these orbits corresponds to a stationary state of the atom. For each of these, the product $2\pi mva_n$ is a multiple of the elementary quantum

$$nh = 2\pi mva_n,$$

in which n is called the quantum number of the orbit. Thus, we speak of the one-quantum, two-quantum, three-quantum, and n-quantum orbits of the electron and of the corresponding energy states of the hydrogen atom.

Bohr attempted to calculate the radius of the orbit and the corresponding energy for a state of quantum number n, *i.e.*, of an arbitrarily selected state. Let us say that the charge on the nucleus of the atom is Z. For the hydrogen atom Z, of course, is unity, since the nucleus is a single proton. Let us designate the velocity of the electron in its orbit as v, its mass as m, and the radius of the orbit as a_n. Let us now determine the energy that the electron possesses when it revolves in the orbit of the n-quantum state.

The electron possesses both potential and kinetic energy. Its potential energy can be calculated by applying Coulomb's law, which states the relation of the attraction of two unlike charges, their magnitudes, and the distance that separates them. The following equation, therefore, defines the potential energy E_P of an electron rotating in an orbit of radius a_n about a nucleus of charge Ze

$$E_P = P - \frac{Ze \times e}{a_n} \tag{1}$$

where P is the maximum potential energy of the electron when it lies in some reference state which, let us say, is at an infinite distance from the nucleus. At any finite distance a_n from the nucleus, the potential energy will be less than P by an amount equal to $Ze \times \frac{e}{a_n}$. When a is the radius of the first quantum

orbit, $Ze \times \frac{e}{a}$ has its maximum value, and $P - Ze \times \frac{e}{a}$ is smaller than for any other quantum state of the atom. Hence, the potential energy associated with the one-quantum orbit of the electron is the smallest amount of energy of any of the possible stationary states of the atom.

The kinetic energy of the electron revolving in the nth-quantum orbit is equal to the product of one-half its mass and the square of its velocity:

$$E_K = \tfrac{1}{2}mv^2. \tag{2}$$

For a body moving in a circular path, two equal but opposing forces must act to keep the body in position. For the electron, this means that the attraction of the nucleus must be balanced by the centrifugal force of the revolving electron. If we designate the radius of the *nth* orbit as a_n and the velocity of the electron in this orbit as v, we may express the attraction of the nucleus for the electron by Coulomb's law, as Ze^2/a_n^2. The centrifugal force of the electron is equal to mv^2/a_n. Since these are equal,

$$\frac{mv^2}{a_n} = \frac{Ze^2}{a_n^2},$$

or

$$mv^2a_n^2 = Ze^2a_n,$$

and dividing through by a,

$$mv^2a_n = Ze^2. \tag{3}$$

We now introduce the quantum condition. We have assumed (page 239) that the product $2\pi mva_n$ is a multiple of the elementary quantum of action h:

$$2\pi mva_n = nh,$$

or

$$mva_n = \frac{nh}{2\pi}, \tag{4}$$

Square Eq. (4) and divide by Eq. (3):

$$m^2v^2a_n^2 = \frac{n^2h^2}{4\pi^2},$$

$$\frac{m^2v^2a_n^2}{mv^2a_n} = \frac{n^2h^2}{4\pi^2Ze^2} \qquad \text{or} \qquad ma_n = \frac{n^2h^2}{4\pi^2Ze^2}.$$

We can now determine the value of a_n in terms of n, h, Ze^2, and m:

$$a_n = \frac{n^2h^2}{4\pi^2Ze^2m}. \tag{5}$$

Now, let us determine the value of v, the orbital velocity, by dividing Eq. (3) by Eq. (4):

$$\frac{mv^2a_n}{mva_n} = \frac{Ze^2 2\pi}{nh}$$

$$v = \frac{Ze^2 2\pi}{nh}. \tag{6}$$

Equations (5) and (6) show that the radius of the nth-quantum orbit is *directly* proportional to n^2, the quantum number, and that the velocity is *inversely* proportional to the same number.

From Eq. (3), we find that

$$\frac{Ze^2}{a_n} = mv^2 \tag{7}$$

and from Eq. (1) that

$$E_P = P - \frac{Ze^2}{a_n}.$$

Substituting the value of Ze^2/a_n from Eq. (7) in Eq. (1):

$$E_P = P - mv^2. \tag{8}$$

The kinetic energy of the electron is defined by Eq. (2). The total energy E_T can be defined as

$$E_T = E_K + E_P.$$

Substituting the value of E_K from Eq. (2) and that of E_P from Eq. (8), we obtain the following value of E_T:

$$E_T = \tfrac{1}{2}mv^2 + (P - mv^2),$$

or, by removing parentheses,

$$E_T = P - \tfrac{1}{2}mv^2. \tag{9}$$

Squaring Eq. (6), which expresses the value of v,

$$v^2 = \frac{Z^2e^4 4\pi^2}{n^2h^2}.$$

Substituting this value of v^2 in Eq. (9):

$$E_T = P - \frac{1}{2}m\frac{Z^2e^4 4\pi^2}{n^2h^2},$$

or

$$E_T = P - \frac{Z^2e^4 2\pi^2 m}{n^2h^2}. \qquad (10)$$

Since P is a constant, as are also Z, e, π, m, and h, it is evident that the energy of the nth-quantum orbit depends upon the value of n, the quantum number of the orbit. The larger the value of n the smaller is the number that is subtracted from P to determine E_T. Hence, the total energy of the electron is greatest in the orbit that has the largest quantum number.

The Origin of Spectral Lines.—According to Bohr's theory of the atom, energy is radiated when an electron moves from an orbit of quantum number n to an orbit of quantum number n', where n' is less than n. Energy is absorbed if the electron moves in the opposite direction—from the n'th to the nth orbit, for example. Since the electron possesses definite and different quantities of energy in two orbits, *viz.*, E_n and $E_{n'}$, it is evident that a perfectly definite quantity of energy is radiated, or absorbed, for any change of the electron from one quantum orbit to another. The quantity of energy E_R so radiated (let us assume $n > n'$) can be expressed as the difference between E_n and $E_{n'}$:

$$E_R = E_n - E_{n'}. \qquad (11)$$

Substituting the values of E_n and $E_{n'}$, as determined by Eq. (9), in Eq. (11):

$$E_R = \left(P - \frac{2\pi^2Z^2e^4m}{n^2h^2}\right) - \left(P - \frac{2\pi^2Z^2e^4m}{n'^2h^2}\right). \qquad (12)$$

The energy E_R will be radiated (according to the assumptions of the quantum theory) at a certain frequency ν, which is defined by the equation

$$E_R = h\nu$$ (see page 223).

The frequency of the radiation depends, therefore, upon the values of n and n'. Substituting the value $h\nu$ for E_R in Eq. (12),

$$h\nu = \left(P - \frac{2\pi^2 Z^2 e^4 m}{n^2 h^2}\right) - \left(P - \frac{2\pi^2 Z^2 e^4 m}{n'^2 h^2}\right). \tag{13}$$

Simplifying and dividing Eq. (13) by h:

$$\nu = P - \frac{2\pi^2 Z^2 e^4 m}{n^2 h^3} - P + \frac{2\pi^2 Z^2 e^4 m}{n'^2 h^3}.$$

Canceling $+P$ and $-P$,

$$\nu = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^3} + \frac{2\pi^2 Z^2 e^4 m}{n'^2 h^3}. \tag{14}$$

Equation (14) may also be written as follows:

$$\nu = \frac{2\pi^2 Z^2 e^4 m}{h^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \tag{15}$$

Let us now compare Bohr's equation (15) with Rydberg's equation (page 233). The latter has been written as

$$\nu = R\left(\frac{1}{4} - \frac{1}{m^2}\right)$$

and the more general equation which fits all four series of lines in the hydrogen spectrum is

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

If

$$R = \frac{2\pi^2 Z^2 e^4 m}{h^3},$$

then Rydberg's equation for the frequency of any line in the hydrogen spectrum and Bohr's equation (15) are identical. For a given frequency ν, $1/n'^2$ and $1/n^2$ are known from the theory. Let us say that the value of ν under consideration is the frequency of the radiation that is emitted when the electron moves from the third quantum orbit to the second. This will give, theoretically, the line of smallest frequency in the Balmer series. Now,

$$\frac{1}{n^2} = \frac{1}{3^2}$$

and

$$\frac{1}{n'^2} = \frac{1}{2^2}.$$

All the other terms in the fraction $\frac{2\pi^2 Z^2 e^4 m}{h^3}$ are constant; the number Z of units of positive charge is unity for hydrogen, h and π always have the same values, and the charge e and the mass m of the electron are, of course, constant if we neglect the effect of velocity upon mass (page 94). It is, therefore, possible to calculate the value of R from both Bohr's equation (15) and the Rydberg equation. That both values are the same is a remarkable substantiation of Bohr's theory.

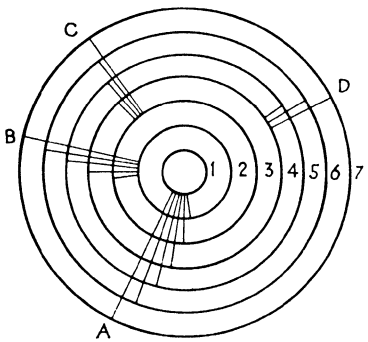

FIG. 103.—Origin of lines of the hydrogen spectrum. *A*, Lyman series; *B*, Balmer series; *C*, Paschen series; and *D*, Brackett series.

Bohr's explanation of the various lines in the four series of the hydrogen spectrum is illustrated in Fig. 103. Shifts of electrons from different quantum orbits to the first quantum orbit give the Lyman lines; shifts to the second quantum orbit give Balmer lines; to the third, Paschen lines; and to the fourth, Brackett lines. Upon the basis of this theory of radiation, it is possible to explain why lines in the Balmer series that cannot be observed in the light from luminous hydrogen can be observed in the light from nebulae. In nebulae, matter is less dense, and atoms are not so much compressed as on the earth. In this rare atmosphere, the electron of the hydrogen atom can occupy orbits of greater quantum numbers than it can be made to take in atoms in the laboratory. Hence, more shifts to the second quantum orbit are possible. Since electrons move into this orbit from orbits farther away from the nucleus, correspondingly greater quantities of energy are liberated. Energy is radiated, in other words, at higher frequencies, since $E_R = h\nu$.

The lines of an absorption spectrum are produced by the absorption of light of definite frequencies. The energy absorbed

E_A is equal to some value of $h\nu$ and is used to move the electron from a smaller to a larger quantum orbit. The process is just the reverse, therefore, of that which gives the lines of the emission spectrum.

The original Bohr theory which we have just described dealt with the hydrogen atom as if the nucleus were stationary. Later, Bohr treated the electron and the nucleus as revolving about a common center and derived the following formula to take the place of Eq. (15) (page 244):

$$\nu = \frac{R}{1 + \frac{m}{M}}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right).$$

Where M is the mass of the nucleus. This method of treatment permitted a more exact correlation between the theory and the lines observed in the spectrum of ionized helium. It also gave an explanation of certain otherwise unexplained differences between the frequencies of lines in some of the helium series and lines in the Balmer series of hydrogen.

In addition to its explanation of the spectrum of hydrogen, the Bohr theory has been successfully applied to the spectrum of ionized helium. In forming a helium ion, the atom loses an electron; hence, the helium ion resembles the hydrogen atom in having a single electron revolving about the nucleus. The nuclear charge of the helium ion is $2e$; hence, in Eq. (15), Z^2 becomes equal to 4, and

$$\nu = 4\frac{2\pi^2 e^4 m}{h^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$$
$$= 4R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right).$$

The emission and absorption spectra of the elements, other than hydrogen and ionized helium, are so complex that as yet they have not been completely analyzed. Each spectrum shows series of lines much like the series observed in the spectrum of hydrogen. Close approximations to the relations of the lines in these series and of the series themselves can sometimes be expressed by equations similar to that proposed by Rydberg. But these equations are by no means so simple or so exact as

Rydberg's equation for the spectral series of hydrogen. We are very much interested, however, in any information that will throw light upon the distribution of electrons in the region of the atom around the nucleus. That is the all-important question toward whose answer all the material that we are now presenting is directed. Although our knowledge of atomic spectra is not so complete as we might desire, we shall find that it is a rich source of information concerning atomic structure.

X-ray Spectra.—In Chap. V, we spoke of lines in the K, L, M, and N series of the x-ray spectra of the elements. We can now offer an explanation of these lines and the source of the rays. The K lines are produced by shifts of electrons from the second-, third-, fourth-, and higher-quantum orbits to the first; the L lines, by shifts to the second; and the M lines, by shifts to the third orbit from orbits of larger quantum numbers. The K, L, M, and N series of the x-ray spectrum correspond, therefore, to the four series of lines in the spectrum of hydrogen. The frequencies of the x-rays are greater, however, than the frequencies of the radiation emitted by hydrogen atoms, since Z and consequently R is greater for an atom that emits an x-ray than the corresponding value for the hydrogen atom. We are speaking as if the Rydberg equation were applicable to the lines of the spectra of all the elements, which of course is not true. To be applicable to x-rays, the equation would have to be greatly modified in order to account for the series of lines that are observed, for the combinations of terms in different series, for the multiplicity of individual terms, etc., as in the case of arc spectra.

Because the quantum orbit represents a definite energy state of the atom, or a definite energy value of the electron, we speak of the different quantum orbits as the energy levels of the atom. Thus, we often use the terms K, L, and M levels. Now, Kossel, in 1914, showed that a line in any of the series of lines in the x-ray spectrum of an element is produced only when an electron has been removed from the orbit in which it normally revolves to a position beyond the ordinary limits of the atom, *i.e.*, to the periphery of the atom. Thus, it appears that each level can normally hold a certain number of electrons, since an electron from the outside cannot fall into one of the inner levels until an electron

has been removed from that level. This principle at once led to further efforts to determine the number of electrons that each level is capable of holding and, later, to many modifications of Bohr's theory. All of these ideas have been very helpful in forming a satisfactory theory of the structure of the composite atom and an explanation of the atom's chemical behavior.

An x-ray is produced when a high-speed electron collides with an atom of the anti-cathode in the x-ray tube. If the energy that the electron possesses is sufficient to cause an electron in the atom that is struck to move from its normal quantum orbit (energy level) to one not completely filled, the opportunity is opened for an electron to drop into the position vacated by the expelled electron. Thus, there is generated an x-ray quantum, $h\nu$, the frequency of which depends upon the energy liberated, which, in turn, depends upon the level from which the electron comes and the level into which it falls. The energy of the electron in the x-ray tube is determined by its velocity, which depends, in turn, upon the difference of potential (voltage) at which the tube is operated. When the potential is low, the relatively slow electrons may not possess sufficient energy to remove electrons from any of the K, L, M, or N energy levels of the atom, and no x-rays are produced. As the potential is increased, the energy of the bombarding electrons becomes greater. X-rays of relatively low frequencies are produced at first. Finally, with a sufficiently high potential, the complete x-ray spectrum can be produced.

In addition to the lines of the K, L, M, and N series, the x-ray spectrum of every element shows a continuous distribution of radiation over a wide range of wave lengths. This continuous portion of the spectrum does not vary, except in intensity, with the character of the anti-cathode.

Modifications of the Bohr Theory and Its Extension to Atomic Systems Other Than Hydrogen.—In 1915, Sommerfeld modified the atomic model of Bohr by adding elliptical orbits. The system of mechanics upon which the Bohr theory is based predicts that an electron executing periodic motion around a nucleus should move in elliptical orbits of which the circular orbit is merely a special case. By considerations based upon the quantum theory, Sommerfeld showed that the major axis of the

elliptical orbit is equal to the radius of the circular orbit for the same energy state. For each value of the major axis, however, there are n values of the minor axis, where n is the principal quantum number of the energy level.

Sommerfeld treated the motion of the electron in an elliptical orbit as a problem involving two degrees of freedom. The position of an electron in such an orbit can be described with respect to (1) the radial distance of the particle from the focus of the ellipse (the nucleus lies in this focus) and (2) the azimuthal angle made by this radius and the major axis of the orbit (Fig. 104). Two quantum numbers therefore may be used to represent the two degrees of freedom. These are called the radial and azimuthal quantum numbers and are represented by the letters r and k, respectively. The total energy of the electron in an orbit is represented by the total quantum number n, which is equal to the sum of r and k. In a circular orbit, the radial distance is constant; and hence, the radial quantum number is zero, a condition which means that for such orbits the problem involves only one degree of freedom. Hence, the energy for circular orbits is represented by the azimuthal quantum number alone, or $n = k$. For any definite value of n, the number of different types of elliptical orbits evidently depends upon the number of ways of obtaining the sum of r and k, provided that these have integral values. Thus, if $r = 0$ and $n = 1$, there can be only one value of k, since $r + k = n$. When $n = 1$, no elliptical orbit is possible. When $n = 2$, there may be one circular orbit and $1(n - 1) = 1$ elliptical orbit, since the value of $n = 2$ can be the sum only of $k = 2$ and $r = 0$, or $k = 1$ and $r = 1$. When $n = 3$, there may be one circular orbit and two kinds of elliptical orbits, corresponding to $k = 2$, $r = 1$, and $k = 1$, $r = 2$. The total number of types of orbits for any value of n is thus equal to n. Of this number, one type is always circular, and $n - 1$ are elliptical.

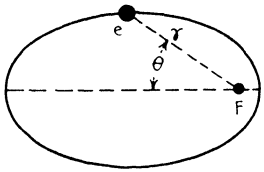

FIG. 104.—The azimuthal angle. F, focus of ellipse; e, electron; θ, azimuthal angle.

To summarize the modifications introduced by Sommerfeld, we may say that two quantum numbers must be used to define

a quantum orbit. These are the principal, or total, quantum number n and a subordinate number k, which is usually called the azimuthal quantum number. The former represents the sum of k and r, the radial number. Instead of indicating the different states of the atom as 1, 2, 3, or 4 quantum states.

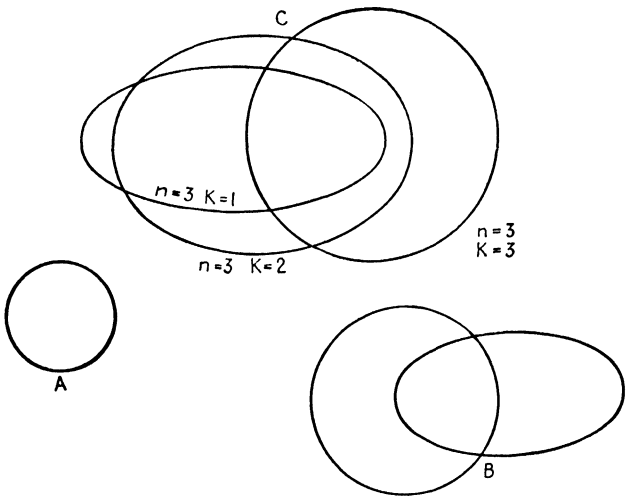

FIG. 105.—Hydrogen orbits. *A*, first energy state (normal state); *B*, second energy state (first excited state); *C*, third energy state (second excited state).

Sommerfeld's method provides a much greater variety of energy levels:

$$1_1 - 2_1 2_2 - 3_1 3_2 3_3 - 4_1 4_2 4_3 4_4 - 5_1 5_2 5_3 5_4 5_5.$$

The Precession of Elliptical Orbits around the Nucleus.—An electron that rotates around the nucleus of its atom in an elliptical orbit does not travel with uniform velocity. During one part of the rotation, it approaches the nucleus; and during the other part, it moves away from it. As it approaches the attracting center, its velocity increases; and as it moves away, its velocity decreases. These changes in velocity are of considerable magnitude and must produce accompanying changes in the mass of the particle. The effect of this change in mass upon the character of the orbit in which the electron rotates must now be considered. Owing to the increase in mass, the electrostatic attraction arising from the nucleus is not able to hold the heavier

electron in the path of the lighter one—the path of the electron before its mass was increased. As a result, the electron moves farther out from the nucleus into a path that lies outside the regular orbit. In other words, increase in mass is accompanied by an increase in the radius of the orbit. Hence, as the electron approaches perihelion, its path lies farther and farther out of the course of the normal orbit. When the electron has passed around the nucleus, the velocity begins to decrease. The mass now also decreases, and the lighter electron is drawn into an orbit of smaller radius. This means that the aphelion of the ellipse must occupy a new position with each rotation. (The aphelion of the ellipse is opposite the perihelion.) The orbit of the electron, therefore, does not follow a closed ellipse. The perihelion moves around the nucleus in the direction of the electron's motion. The aphelion of the ellipse also moves around the nucleus in a circle the radius of which is equal to the distance between the aphelion and the nucleus. The radius of the circle describing the rotation of the perihelion is equal to the distance between the perihelion and the nucleus, which acts, of course, as one focus of the ellipse. This movement of the perihelion of the electron's orbit is much like the precession of the perihelion of the elliptical orbit of the planet Mercury in our solar system. In both cases, the rotation of the perihelion of the orbit is slow as compared with the rotation of the body in the orbit.

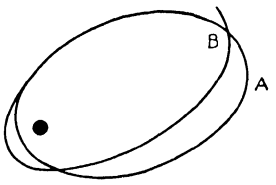

FIG. 106.

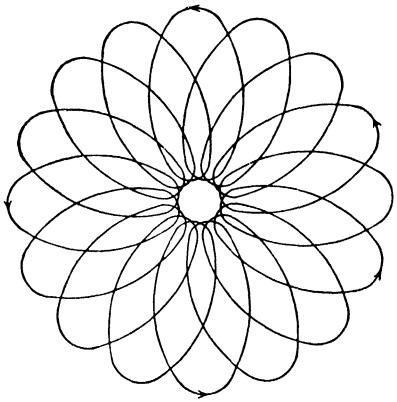

FIG. 107.

FIG. 106.—Effect of variable mass upon the elliptic orbit of an electron. *A*, closed ellipse for invariable mass; *B*, precessing ellipse resulting from variation in mass

FIG. 107.—The precession of an elliptic orbit about the nucleus.

Just as Bohr assumed that the electron revolves in quantized circular orbits, for which the product $2\pi mva$ is equal to the elementary quantum of action h or to some multiple of it, Sommerfeld assumed that the rotation of the perihelion of the elliptical orbit is also quantized. Only elliptical orbits of certain degrees of eccentricity are possible. These must fulfill the quantum conditions for the rotation of the perihelion just as the stationary electronic orbits must fulfill similar conditions. Superimposing this second quantum condition upon the quantized motion of the electron in the ellipse makes necessary the correction that the azimuthal quantum number k expresses. Roughly approximated, the principal and azimuthal quantum numbers are in the same ratio as the major and minor axes of the ellipse.

In accordance with the principles of classical mechanics, it was thought at first that the energy of an electron was dependent only upon the principal quantum number. An electron revolving in the 2_2 orbit, for example, was thought to possess the same quantity of energy as one revolving in a 2_1 orbit. This could be true only if the motion of an electron in an elliptical orbit was not influenced by other electrons within the atom or by external electrical and magnetic fields. Nor does this supposition take into account the relation between the velocity of the electron, which must be different in the various kinds of elliptical orbits, and the mass of the electron, which must be considered as changing with the velocity.

So-called perturbations resulting from variations in the electron's mass are represented by variations in the values of the secondary quantum number k. As a result, the different energy states corresponding to a definite value of n differ from one another and should permit transitions of electrons which give rise to slightly different spectral lines. Instead of a single line, which one would expect if only one transition from a given quantum state n were possible, a group of lines which lie close together may appear. It is said, in this case, that the lines are resolved. This means that the lines of even the hydrogen spectrum should be resolved. Sommerfeld predicted that this should be the case, and his prediction has been fully confirmed. In the case of hydrogen, however, the resolution of the lines is so slight that the measurement and even the observation of the

closely related lines is extremely difficult even under the most favorable conditions. Better results are obtained in observing the resolution of lines in the spectrum of helium.

The number of transitions between the n and the n' levels of an atom should be equal to $n \times n'$. The number of possible transitions is decreased, however, by the application of the selection principle, which limits transitions to those in which the azimuthal quantum numbers of the levels involved, k and k', differ

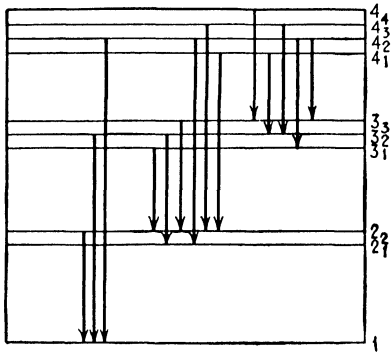

FIG. 108.—Four energy levels and possible transitions in accordance with the selection principle.

by unity. There can be, then, only one shift to the first level from any other quantum state. Similarly, there can be three shifts to the second, five to the third, and so on. According to the same principle of selection, transitions between circular orbits occur only when the principal quantum numbers differ by unity. Hence, only the first lines of the different (theoretical) series are produced by such transitions. Other lines are produced by transitions involving elliptical orbits. The Lyman series of hydrogen, for example, is produced by transitions to the first quantum state. Only one transition from each higher state is possible. In confirmation of this view, it is interesting to note that all of the lines of the Lyman series are single, a condition that is not true of the other series.

ATOMIC SPECTRA

Bohr's model of the hydrogen atom was designed to explain the origin of the lines in the hydrogen spectrum, each line of which was assumed to correspond to a frequency resulting from

the transition of an electron from one energy level to another. We should expect to find somewhat similar relationships between the spectra of other elements and their atomic structures. And as in the case of hydrogen, we may anticipate that a definite frequency will correspond to a transition between two energy states of the atom. A study of the frequencies that can be observed and their relations should provide, therefore, some information concerning the number and character of the different energy levels of the atom.

The spectra of all the elements have many features in common, although some are much more complex than others. What we shall say in this chapter deals primarily with the spectra of the alkali metals and other elements of the first and second groups of the periodic system. The spectra of these elements are considerably easier to analyze and to study than those of atoms containing more than one or two electrons in the valence group. For the most part, the alkali metals may be considered as two component systems—the nucleus with the electrons which lie near it acting as one component, and the outermost electron which rotates about the core acting as the other. A single electron therefore serves as the source of the radiation. This is called the optical electron. The problem is thus greatly simplified, since the transitions of one electron between different levels of the atom are assumed to be responsible for variations of the stationary energy states E_{n_1} and E_{n_2} of the atom as these are defined in the Bohr equation:

$$h\nu = E_{n_2} - E_{n_1}.$$

It is because the alkali metals contain single electrons in the outermost level that we have selected the spectra of these elements for our present purposes.

The remainder of the atom including the nucleus and all the other electrons acts as a complex nucleus and is generally called the core. The optical electron moves in orbits that lie far outside the core. These orbits may be circular, as Bohr originally assumed, or some of them may be elliptical. In fact, the elliptical orbit is the one that would be expected generally. If we assume that the electron in the outermost level of an atom rotates in an elliptical orbit, this electron is far removed from the core

during the greater part of its period of rotation (Fig. 105). In the case that we are describing (*e.g.*, sodium), the atom acts therefore very much as the simple hydrogen atom with its simple nucleus and its single electron. So far as our assumption is valid, the entire core of the sodium atom acts as a unit positive charge.

The energy of the electron in its different quantized orbits and the corresponding energy states of the atom can be calculated by means of the equations already derived (page 243) for the atom of hydrogen. The justification of our assumption that the sodium atom may be regarded in the same manner as the hydrogen atom must rest upon the success with which it explains the spectra of the elements. We cannot hope that this success will be complete in every sense.

It is evident that the core of the atom cannot act under all conditions as a single unit of positive charge located at a point. Instead, the core is a complex system consisting of a positively charged nucleus and several extranuclear electrons revolving around it. Through this complicated electrical system, the electron must move during a part of its revolution, provided that its orbit is an ellipse which has a moderate or a high degree of eccentricity. If the orbit is circular, our assumption concerning the hydrogen-like character of the atom holds very well, since the optical electron at all times rotates around the core and at no time penetrates it. Let us consider further the case of the elliptical orbit. When the electron is in the outer portions of its orbit, it is acted upon by a positively charged nucleus whose charge is "screened" by the other electrons; hence, the core acts as a unit charge. As the electron penetrates the atom, however, it enters a region where there is little or no screening effect. The entire nuclear charge, consisting, perhaps, of 50 or 60 units, acts upon it. During its penetration of the core, we cannot assume that the same law governs the behavior of the electron in this field as governs it when it is acted upon by an [redacted]arying point charge. Thus, the inverse-square law cannot [redacted]plied to an electron moving through a field that contains [redacted]bits of other electrons, without taking into account vari[redacted]s in the character of the electrical field through which it moves. The effect of this divergence from the inverse-square law, upon which Bohr's equation for the energy of the electron

in a given orbit is based, causes slight differences in the quantities of energy possessed by the electron in slightly different orbits. In addition to the effect of a changing electrical field upon the energy of the electron, we must also take into account the possible variation in the mass of the electron with changes in its velocity as predicted by the relativity theory. Now, if the electron moves around the nucleus in an elliptical orbit, changes in its velocity are to be expected, since it approaches the nucleus during one-half of the revolution and moves away from it during the other half. If the mass varies with the velocity—and the facts indicate that it does—any change in the mass of the electron accompanying such changes in velocity should affect the energy of the electron which rotates in an elliptical orbit. This effect should be different for elliptical orbits of different eccentricities. Let us now examine the spectral data which show that such modifications of the energy levels of an atom exist.

Spectral Series.—At least four series of lines can be recognized in most atomic spectra. At one time, the four series were given the names sharp, principal, diffuse, and fundamental. These names have now lost their original significance, and, instead, the initials *S*, *P*, *D*, and *F* are often used in referring to the series. These series are distinguished by differences in the appearance and intensity of the lines that compose them; by the fact that a magnetic field causes the same shift of all the lines belonging to one series; and by other means.

The following equations show the relations of the lines in each of the series and also the relations that exist between the four series themselves. Each line is designated as the difference between two quantities, one of which is the same for all the lines of a given series and the other of which is a variable. The former is called the limit of the series, and each value of the latter constitutes a term.

$$(P) \quad \nu = R\left(\frac{1}{(1+s)^2} - \frac{1}{(m+p)^2}\right); \; m = 2, 3, \cdots$$

$$(S) \quad \nu = R\left(\frac{1}{(2+p)^2} - \frac{1}{(m+s)^2}\right); \; m = 2, 3, \cdots$$

$$(D) \quad \nu = R\left(\frac{1}{(2+p)^2} - \frac{1}{(m+d)^2}\right); \; m = 3, 4, \cdots$$

$$(F) \quad \nu = R\left(\frac{1}{(3+d)^2} - \frac{1}{(m+f)^2}\right); \; m = 4, 5, \cdots$$

In the preceding equations, the terms s, p, d, and f represent the value of α in the general equation $A - \frac{R}{(n+\alpha)^2}$, in which A is the limiting frequency (or wave number) of the series, R is Rydberg's constant, n is an integer, and α is a fraction that has approximately the same value for all the lines of one series. The quantity A designates the limit of the series and corresponds to a value of $m = \infty$.

It appears, therefore, that the value of ν for any line in the spectrum of any element is equal to the difference between two quantities, as in the case of the hydrogen spectrum.

A Comparison of the Spectral Series of Hydrogen and the Other Elements.—The complete hydrogen spectrum is represented by a single set of terms, *i.e.*, the terms of a single sequence (page 234). Thus, each term has the form R/n^2, where n is an integer and all the possible values of n are numbers of one sequence. In most atomic spectra, however, four sequences of terms are recognized, one for each of the four series. Thus, an individual term is represented by the following expression: $R/(n+\alpha)^2$, in which n represents a number in the sequence which begins with 1 for the S series, 2 for the P series, 3 for the D series, and 4 for the F series. This expression applies to arc spectra. Slight modifications are necessary when it is applied to spark spectra. In this discussion and in that which follows, we refer generally to the former.

The S, P, D, and F series are not entirely unrelated, however, as shown by the fact that the limits of the S and D series are the same, $R/(2+p)^2$. It will be noted, also, that the difference between this limit [$m = 2$ in $R/(m+p)^2$] and the limit of the P series [$R/(1+s)^2$] is the frequency of the first line of the P series. Other similar relations will be observed. For example, the constant term $R/(3+d)^2$ of the F series is the first variable term of the D series.

Lines are observed in the spectra of many elements that do not belong to any of the four series or to any other. Ritz has shown that such lines can be represented as the difference between two variable terms of different series. Thus, a line might appear, for

example, that represents a frequency corresponding to the difference between a term in the S series in which $m = 4$ and a term in the P series for which $m = 5$. This explanation of the origin of these lines is based upon the Ritz combination principle. Theoretically, the difference between any terms in one series and any term in another series should correspond to an observed frequency. In practice, however, terms of one series never appear to combine with those of any but neighboring series. Thus, a term of the P series may combine with terms of only the S and D series. This restriction of the combination of terms is the basis of the so-called selection principles.

The Interpretation of Spectral Data

If we accept the model of the atom proposed by Bohr and his explanation of radiation, the lines of the spectrum are related undoubtedly to the manner in which electrons are distributed about the nucleus. If these lines were single, or if they formed definite and simple series, they might be accounted for by assuming that electron transitions occur between a few definite kinds of quantized orbits. This condition would call for relatively few energy states of the atom. But the complexity of spectral lines and series shows that this is not the case. The fundamental principle of Bohr, however, may be retained. We may still think of the relatively few energy states of the atom. It becomes necessary, in addition, to think of most of these energy states as consisting of a number of substates which differ slightly from one another. In short, it is necessary to assume that an electron, instead of revolving around the nucleus in one stationary orbit of quantum number n, may revolve in any one of perhaps several orbits which differ only slightly in character. The same quantum number n may be used to describe the energy of the electron in any of these closely related orbits. Additional quantum numbers will have to be added, however, to show the slight variations in the energy states. These numbers must be added in some way to the values of n, the principal quantum number, and may be called subordinate numbers. Sommerfeld has supplied the physical interpretation of at least one such subordinate number by introducing the idea of elliptical orbits and azimuthal quan-

tum numbers to designate the quantized precession of the orbit about the nucleus.

Let us consider the origin of the spectral lines which form the four series in the spectra of the alkali metals. In order to simplify the problem, the frequencies of the lines in the different series are generally represented as follows:

$$(P)\quad \nu = 1s - mp.$$
$$(S)\quad \nu = 2p - ms.$$
$$(D)\quad \nu = 2p - md.$$
$$(F)\quad \nu = 3d - mf.$$

Each frequency represents the difference between two terms, and each term corresponds to a definite energy level of the atom. These different levels may be understood more easily if we represent them by the following diagram, which also shows the transitions between levels that result in the production of the observed frequencies.

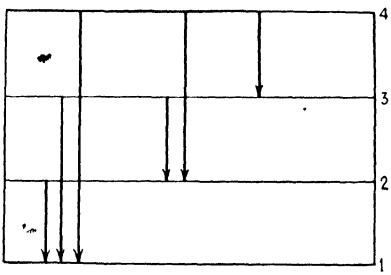

FIG. 109.—Energy levels of the hydrogen atom. This diagram is in accordance with the first and most simple form of the Bohr theory.

In explaining the origin of the lines in the four series of the hydrogen spectrum, one set of energy levels is sufficient (Fig. 109). In explaining the spectra of the alkali metals, however, several sets of levels must be used. Instead of simple first, second, third, and fourth energy levels, each of these is replaced by a set of S, P, D, and F levels, each of which is represented by the same value of n but different values of the subordinate quantum number. The diagram (Fig. 110) explains why the constant term of the S and D series is $R/(2 + p)^2$ and why the term $R/(3 + d)^2$ of the D series is the limit of the F series.

The Multiplet Structure of Spectra.—The spectra of most of the elements reveal a complicated multiplicity of lines. Sometimes single lines occur, but the lines are double in the spectra of the alkali metals; and in the more complex spectra of other elements, not only doublets but triplets and multiples of even higher order occur. In the spectrum of manganese, for example,

there are multiples consisting of eight lines. By multiplicity we mean that what was considered at first as a single line has been shown upon more complete resolution of the spectrum to consist of a number of closely related lines. Since the multiplicity of the lines of a spectrum must depend upon a corresponding multiplicity of the individual terms, let us consider the latter as a simpler problem with which to deal.

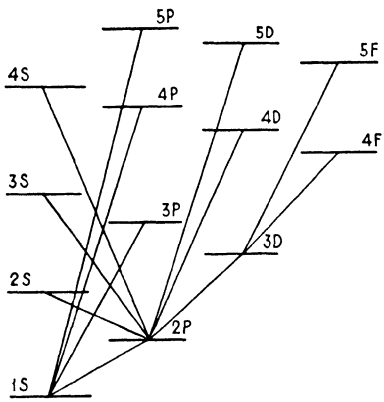

FIG. 110.—Energy levels of an alkali metal, and transitions of valence electron which produce lines in the spectrum.

For S levels, $l = 0$ For D levels, $l = 2$
P levels, $l = 1$ F levels, $l = 3$.

The multiplicity of the terms of the four series is not always the same. It appears that the multiplicity of the S series never exceeds one, while for the P, D, and F series it may be no greater than three, five, and seven, respectively. Because of the complexity of atomic spectra, as revealed by this multiplet structure, it is evident that neither the single quantum-number system of the original Bohr theory nor the two quantum numbers proposed later will suffice to account for all the possible energy states of the atom. The lines of a multiplet group can be explained as due to electron transitions involving energy states that are almost but not quite identical. The use of two quantum numbers will explain how it is possible to have more than one transition from a fourth to a third level, but it cannot show why each of the lines thus accounted for should, when resolved more completely, be found to consist of several lines. It becomes necessary, therefore, to introduce one or more additional quantum numbers to provide the means of representing the greater number of modifications of energy levels.

The spectra of the elements are classified according to systems. Systems are singlet, doublet, triplet, quadruplet, etc., depending upon the multiplicity of the terms of the four series of lines. The singlet system is made up of series of single lines. In a doublet system, all the terms of the S series are single, and those of the

other series are double. All the series of the triplet system are composed of triple terms, except the *S* series, which again is single. It has also been shown that groups of lines occur that represent combinations of terms of very great complexity. These groups include quartets, quintets, sextets, septets, octets, and are known generally as multiplets. All the lines of a single multiplet are characterized by the same value of n.

Owing to the multiplicity of the terms in different series and to the fact that terms in one series may combine with terms in another, it is evident that frequencies representing a great many combinations may result. Let us consider, for example, the different combinations that are possible between a *P* and a *D* term in a triplet system. Both terms are triple. Theoretically, each component of the triple *P* term can combine with each component of the triple *D* term. This would result in nine different spectral lines. Actually, only six lines are observed. It is necessary, therefore, to introduce another phase of the selection principles to cover restrictions in these combinations. Let us assign a number that will represent the type of the term—*S*, *P*, *D*, *F*. In a general case, this number is represented by the letter k. It always has the value of 1 for an *S*-series term, 2 for a *P*, 3 for a *D*, and 4 for a term of the *F* series. Let us next assign a number to the term that represents its order in the series, *i.e.*, its serial number. This is represented in the general case by the letter n. The multiplicity of the term is indicated by the letter r, which is written before and slightly above the value of k. This number (r) shows whether the term is double, triple, quadruple, etc. Now, to represent the combination of a single component of a multiple term, it is necessary to add as a suffix of k another number, which in the general case is represented by the letter j. In general, therefore, a term is denoted by the following combination of symbols: $n^r k_j$. Thus, the numbers of a triple *P* term of a triplet system are indicated as follows:

$$n^3 2_0;\ n^3 2_1;\ \text{and}\ n^3 2_2.$$

Likewise, the members of a triple *D* term are

$$n^3 3_1;\ n^3 3_2;\ \text{and}\ n^3 3_3.$$

The selection principle that governs the combinations occurring between multiple terms of different series, such as those that we have just described, may be stated as follows: Only those combinations of terms whose suffix numbers (values of j) differ by 0 or ± 1 ever occur. Thus, for the triple P and D terms of the foregoing illustration, the following combinations are possible:

$$n^3 2_0 \text{ and } n^3 3_1$$
$$n^3 2_1 \text{ and } n^3 3_1$$
$$n^3 2_1 \text{ and } n^3 3_2$$
$$n^3 2_2 \text{ and } n^3 3_1$$
$$n^3 2_2 \text{ and } n^3 3_2$$
$$n^3 2_2 \text{ and } n^3 3_3$$

Three of the theoretically possible combinations are prohibited by this rule. This restriction accounts for the appearance of only six of the nine lines that are theoretically possible. As a further restriction upon the possible combinations, it has been shown that the difference in the values of r must be 0 or 2.

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CHAPTER XII

DISTRIBUTION OF ELECTRONS ABOUT THE NUCLEUS

Many sources of information must be investigated to determine the number of electrons that normally revolve in each of the different kinds of orbits in different atoms. The most valuable source of such information, perhaps, consists of spectral data such as we considered in the preceding chapter and which we shall further treat in this chapter. Other sources also deal with physical measurements, such as ionization potentials. Others depend upon the chemical properties of the elements.

Evidence Supplied by Chemical Properties

The electrons that lie in the outermost portion of the atom, *i.e.*, its outermost group of orbits, are undoubtedly of the greatest importance in determining the chemical and many of the physical properties of the atom. These are the electrons that are most easily separated from the remainder of the atom. They are also in a position in which they are more strongly acted upon by forces originating in other atoms than the electrons that lie in quantum levels nearer the nucleus. The valence of an element is thought to depend upon the number of electrons in the outermost level, and these are called the valence electrons of the atom. It may be well, therefore, to review the changes that occur in the valences of the elements as we pass from the lighter to the heavier members of the periodic system.

A general examination of the periodic table reveals that the most extraordinary feature of the classification is a periodicity of properties and particularly of valence. This periodicity must correspond to the recurrence of some structural feature in the atoms of those elements which are so closely related in properties. It appears that some structural unit, which we may now call the electron, is added one at a time until some portion of the structure is completed. Another portion is

then started; hence, the structure of the outermost level of the atom is repeated at more or less regular intervals in the list of the elements. Since the valence depends upon the number of electrons in the outermost level of the atom, it is logical to conclude that the periodicity means that elements possessing the same valence consist of atoms containing the same number of valence electrons. Furthermore, the periodic table is divided into several series of elements. We find one series of 2 elements (H and He), two series of 8 elements each, two series of 18 each, and one series of 32. The length of each of these series must be related in some way to the number of electrons that can be accommodated in the corresponding classes of quantum orbits—first, second, third, etc.

Let us now proceed to the study of the structures of the atoms of the different elements, starting with hydrogen. As we come to structures of increased complexity and to elements that display valences that cannot be explained by the simple assumptions and principles of the original Bohr theory, we shall find it necessary to discuss modifications, other than those that have already been presented, to cover these cases. Whatever modifications of the theory may be made, however, and whatever explanations may be offered, the basis upon which the explanations are founded is the fundamental concept of the quantized electron orbit of the Bohr atom. In the end, it may be necessary to discard many of the concepts usually associated with this theory and to abandon all or almost all of the modifications of the theory that have been proposed, but the quantized orbit appears to have come to stay.

The single electron in the normal state of the hydrogen atom occupies a circular orbit 1_1. A second electron is present in the helium atom, and every indication points to the fact that both of the electrons normally lie in the first (K) level and revolve in 1_1 orbits. This level appears to be completed, however, by these two electrons, and only two electrons are found in the K level of any of the succeeding elements.

A third electron is added in the atom of lithium. This must lie in another level. If it were placed in the first, the repulsion of the two electrons already present would not permit it to remain there. Spectroscopic and chemical observations show that the

third electron revolves in a 2_1 orbit. This electron is easily removed from the atom. If lithium atoms in the vapor state are acted upon by a potential difference which is sufficient to remove an electron from its normal position to a place outside the atom, positively charged ions of lithium are formed. Only 5 volts is required to accomplish this change, although 25 is required to ionize helium. The single, easily separated electron accounts for the valence of lithium (+1) and explains why no other valence is possible. As we pass through the periodic table from the inert gases to the next heaviest elements, there is always a similar change in ionization potential (page 273). The potential increases up to an inert gas, there reaches a maximum, and then suddenly and sharply drops off with the next element. It appears, therefore, that in each inert gas the outermost group of electrons is stable and represents a completed portion of the atom's structure. Each of the alkali metals follows an inert element. We may conclude, therefore, that in each of these an electron goes into an orbit of a quantum group which previously contained no electrons.

The atomic numbers of the inert gases have been shown by Rydberg (page 198) to be represented by the equation

$$N = 2(1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 \cdots)$$

This equation indicates that the K level contains two electrons (2×1^2). In the atoms of the elements between helium and neon, electrons go into the second, or L, level, where they revolve in 2_1 and 2_2 orbits. Neon is a stable element which exhibits no tendency to liberate, acquire, or even share electrons. Since neon is the eighth element after helium, it is logical to conclude that the second level is completed by eight electrons.

The elements from sodium to argon resemble very closely those of the preceding series lithium to neon. Beginning with potassium, which follows argon in the periodic table, there is a series of 18 elements the last of which is krypton. The first few elements of this long series are similar to those in the preceding series lithium to neon and sodium to argon. Thus, potassium resembles lithium and sodium in possessing a single electron in the outermost quantum group of its atoms. The difference in the three atoms is in the quantum group to which the valence

electron belongs; this is the second for lithium, the third for sodium, and the fourth for potassium. Similarly, calcium, like beryllium and magnesium, has two electrons in the valence level; and so on. But the eighth element does not resemble neon and argon. The latter are inert, while this eighth element is iron, a relatively active metal. The ninth and tenth elements (cobalt and nickel) are very closely related to iron. Then comes another series of elements (copper to krypton) the valences of which range from one for copper to seven (or negative one) for bromine and zero, of course, for krypton.

The next series (rubidium to xenon) is practically a repetition of the potassium-krypton series. A triad of elements (ruthenium, rhodium, and palladium) occurs in the center of the series. These elements correspond to the iron-cobalt-nickel triad of the first long series.

The next and last series is much larger than any other; it consists of 32 members—cesium to radon. The first few elements resemble the first members of the other series. Cesium is like sodium, potassium, lithium, and rubidium; barium is like beryllium, magnesium, calcium, and strontium. But from lanthanum to lutecium there are 14 trivalent elements. These are called the rare earths and are so closely related in a chemical way that their separation is very difficult. Next comes a group of elements, beginning with hafnium, which resemble the elements of groups 4, 5, 6, and 7 of the earlier series. Thus, tungsten, W, resembles chromium, Cr. Then comes another triad (osmium, iridium, platinum) resembling the triads in group eight of the other long series. Finally, there is a group of eight elements (gold to radon) which resemble, in some ways at least, the last eight elements of each of the preceding series.

From the above considerations of the periodic groups of the elements and their valences, the following conclusions concerning the structures of the atoms of the different elements may be drawn.

1. The properties of the elements that immediately precede or immediately follow an inert gas are closely related to those of the elements that occupy corresponding positions in the table before or after another inert gas. The structures of the atoms of these elements must have certain features in common. Disre-

garding hydrogen and helium, the structures of the elements of the first series are produced by successive additions of electrons, one at a time, until a group of eight results in the neon atom. A similar group of eight electrons is built up in the second series.

2. The number of electrons in the outermost group of quantum orbits is the same for elements that possess the same valence. The variable valences of some atoms, however, indicate that (1) electrons in certain orbits of the next lower quantum group may be involved in chemical reactions or (2) that the number of electrons in an outermost group may vary (usually by one) when another group within the atom is only partially filled.

3. The arrangement of electrons in the various quantum groups of the inert gases is shown in the following table:

Atomic No.	Element	Quantum group					
		1	2	3	4	5	6
2	Helium	2					
10	Neon	2	8				
18	Argon	2	8	8			
36	Krypton	2	8	18	8		
54	Xenon	2	8	18	18	8	
86	Radon	2	8	18	32	18	8

4. The maximum number of electrons in any level is $2n^2$, n being the principal quantum number. This number of electrons provides maximum stability, but groups of 8 and 18 are comparatively stable in the higher levels.

5. The number of electrons in the outermost group never exceeds eight. As soon as this number is reached, the next few electrons go into the next higher group. This results in the formation of atoms of elements that possess positive valences of one, two, or three. The negative valences of elements are determined by the number of electrons required to complete the group of eight in the outermost level. After two or three electrons have been added in an outermost group (in the longer series of elements), further additions go into inner groups provided that any of these are incomplete. This explana-

tion accounts for the fact that the elements in the middle of the long series have the same valences, although they are members of different periodic groups. When the inner groups are complete, the outermost group is then built up to eight. Additions to the next higher quantum group then begin, and the general structural scheme is repeated.

6. Argon possesses a group of eight electrons. These lie in the third quantum group, which is not complete until it contains 18 electrons. After argon (2–8–8), the first two or three electrons may go into the fourth-quantum group; thus, the structure of the potassium atom is 2–8–8–1, and that of calcium is 2–8–8–2. Further additions then go to complete the third group. Thus, we may assume that the structure of the iron atom is 2–8–14–2; cobalt, 2–8–15–2; nickel, 2–8–17–2; and zinc, 2–8–18–2. These structures account for the divalences of these elements. Univalent copper may have the structure 2–8–18–1. Trivalent iron may be 2–8–**18**–3, etc. As soon as the third group contains 18 electrons, the fourth group then takes further additions until it contains 8 electrons in krypton, 2–8–18–8. The structural arrangement in the next series of elements is largely a repetition of the arrangement in the series from potassium to krypton. After the addition of three electrons in cerium (2–8–18–8–3), the group of 8 electrons in the fourth level grows until it contains 18, as in gold (2–8–18–18–1) and mercury (2–8–18–18–2). Although the fourth group is not complete until it contains 32 electrons, the electrons that are next added go into the fifth group until this contains 8 in xenon (2–8–18–18–8). The basis of this argument is that these elements immediately precede an inert gas and, therefore, should have the same numbers of electrons in their outermost group as the elements in the corresponding positions of the first series.

In the next long series (cesium to radon), the first few electrons go into the sixth-quantum group. The fourth group is then completed; this requires 14 electrons, since 18 have already been added, and the group can hold 32 in all. After the completion of the fourth level, the fifth then expands from 8 to 18. The next electrons complete the group of 8 in the sixth group. The last element in the series—radon—has the structure 2–8–18–32–18–8.

7. The electrons in any quantum group (except the first) do not revolve in exactly the same kinds of orbits. The eight electrons of the second level, for example, revolve in two kinds of orbits—2_1 and 2_2. It should be possible, therefore, to divide the electrons of all groups (except the first) into various subdivisions, the number of subdivisions being equal to the number of kinds of orbits for that group. We shall also find that it is possible to divide further some of the subdivisions into smaller groups. Such subdivisions are indicated not only by chemical properties but also by spectral data (page 275). From a chemical point of view, they are consistent with the different valences of certain elements. These relations may be observed in Table X (page 286).

Let us now continue with the presentation of other evidence concerning the divisions of the different electron groups.

Evidence Supplied by the Photoelectric Effect

The energies of different electrons in an atom being known, it is not difficult to determine the groups or energy levels to which these electrons belong. Such information can also be secured by observations of the photoelectrical emission of electrons from atoms. X-rays of very high frequency cause electrons to be emitted from all the energy levels of the atom. Each x-ray quantum may liberate an electron, provided that it is of sufficient magnitude, *i.e.*, it exceeds a definite limiting value. If the x-rays have the same wave length (if the beam is monochromatic), each electron emitted as the result of the absorption of a quantum of energy should possess the same quantity of energy, provided that no energy were required to separate the electrons from the atoms. But the liberated electrons come from different energy levels; hence, they are differently bound to the nucleus. Hence, different amounts of energy will be required to liberate different electrons. The energies, therefore, of the liberated electrons will not be the same. The energy of any one electron will be equal to that of the quantum that liberated it minus the quantity of energy used in the separation from the atom. Thus, the electrons from a large number of atoms of the same kind will fall into a number of groups, the members of each group possessing the same residual

energies and coming, therefore, from the same energy level of the atom. These groups may be distinguished by passing them through a magnetic field, where electrons possessing different amounts of energy are deflected to different extents by the action of the field. From the extent of the deflections, it is possible to calculate the energies of the electrons of the different groups. From these values and from the energy of the x-ray quantum, it is possible to calculate the energies of the electrons in the different levels.

Evidence Supplied by the Critical Potentials of the Elements

Information concerning the distribution of electrons within the atom can also be obtained from the *ionization potentials* of the elements. These are determined by bombarding atoms of the element with electrons. As the potential through which the bombarding electron falls is gradually increased, a voltage is eventually attained for which the bombarding electron causes the expulsion of an electron from the bombarded atom and leaves behind a positive ion. The lowest potential that accomplishes the removal of the electron from the atom is called the ionizing potential. The ionizing potentials of some of the elements are shown in Fig. 112.

Determination of Critical Potentials.—Let us assume that the atom under consideration is "hydrogen-like"; *i.e.*, it consists of a single electron rotating about a nucleus (or a nucleus with other revolving electrons which do not change their states). Now, the ionizing potential of an atom is the potential that corresponds to the energy required to remove the electron from its normal position in the atom to a position entirely beyond the atom. If the atom is bombarded by electrons whose velocity, and hence energy, is known, the energy required to ionize the atom can be calculated. This energy is equal to Ve, where V is the potential (volts) that accelerates the bombarding electron and e is the electron's charge expressed as coulombs.

$$(V) \text{ volts} \times (e) \text{ coulombs} \times 10^7 = \text{ergs}.$$

As the potential increases, it finally reaches a value where it corresponds to a sufficient quantity of energy to eject the electron

from the atom. Thus, the ionizing potential for hydrogen can be calculated as follows. According to Bohr's theoretical relation between the energy of the atom and the quantum state n:

$$E_n = -\frac{Rch}{n^2},$$

where R has its usual value 109,737 cm.$^{-1}$, h is Planck's constant (6.55×10^{-27}), and n for the normal state of the hydrogen atom is unity. This equation is derived by substituting the value of R (page 244) in the equation for the energy of a stationary atomic state. For an explanation of the negative sign, see page 240. Hence, substituting Ve for E_n,

$$Ve = -\frac{Rch}{1^2}.$$

Now, using the known values of R, c (the velocity of light), h, and e, we find that

$$V = 13.54 \text{ volts.}$$

It is also possible to calculate the potential at which the electron is removed from its normal, or lowest, quantum orbit to the next highest. This transition produces what is called the first *excited state* of the atom. The potential required to produce the excited state is called a resonance potential. It can be calculated by means of expressions like the following, which shows the energy change accompanying a transition from the first to the second quantum orbit of the hydrogen atom:

$$V_r e = \frac{Rch}{1^2} - \frac{Rch}{2^2}.$$

From known values of e, R, c, and h, we can show that

$$V_r = 10.16 \text{ volts,}$$

where V_r is the resonance potential.

In a similar manner, such potentials can be calculated for transitions of an electron from the normal quantum orbit to any other orbit of the excited atom. And, of course, it is also possible to apply the same general method to the determination of the resonance potentials of elements other than hydrogen.

This information is of considerable value in defining the different energy states of an atom.

Measurement of Resonance and Ionization Potentials.—Many experiments aimed at the determination of resonance and ionization potentials have been made. To give an idea of how the results are obtained and interpreted, we shall describe one of these. This is the method used by Franck and Hertz, whose apparatus is sketched in Fig. 111. Electrons come off the heated filament F. Under the influence of the potential V_1, these electrons move toward the plate P, which is attached to the galvanometer G. A small potential V_2 is applied between the screen S and P. The space between F and S contains atoms of the element to be studied. The voltage V_1 is varied in small amounts, beginning at zero, and is measured by the galvanometer. At first, when the voltage V_1 is small, the electrons from F collide with atoms of the substance in the space FS without losing any energy. Hence, they pass through the screen and strike the plate, and the galvanometer registers the passage of a current. But when V_1 becomes sufficiently great, the collisions result in a transfer of energy from the electrons to the atoms with which they collide. Hence, the electrons may not have sufficient energy left to permit them to pass through the screen and strike P, since they are opposed by the potential $V_2(V_2 < V_1)$, which operates upon them in the opposite direction. Consequently, the galvanometer will show the passage of less current with the first transfer of energy from electrons to the atoms of the substance in the space through which they pass. When this first decrease in the current happens, of course, we can assume that the first resonance potential has been reached.

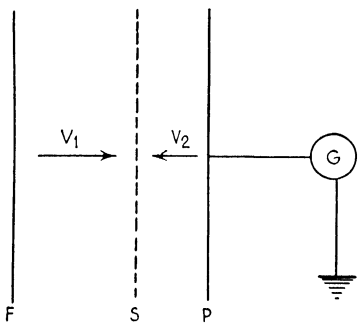


FIG. 111.—Franck and Hertz's method of determining ionization and resonance potentials.

If the energy is increased by the application of a higher voltage, more electrons will again reach P, and the reading of the galvanometer will show the passage of more current once again. Then,

suddenly the reading of the instrument will drop, when the energy of the bombarding electrons becomes sufficiently great to raise the struck atoms to their second excited states. When the ionization current is plotted against volts, the alternate increases and decreases in the amount of current that flows through the space FS and between S and P become apparent. The voltage corresponding to the difference between two adjacent maxima is taken as a resonance potential.

Ionization Potentials and the Periodic Table.—The first member of each of the periodic series (the alkalis) has a low ionization potential (Fig. 112). Within a given group (vertical), this potential decreases as the atomic weight and atomic number

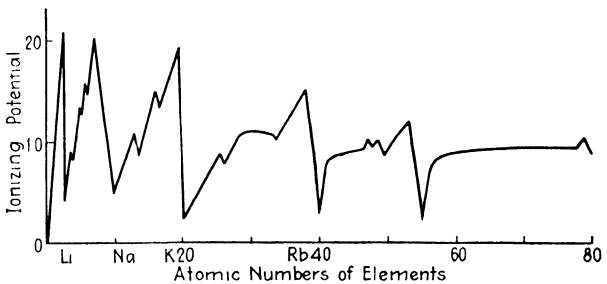


FIG. 112.—Ionization potentials of the elements.

increase. Thus, the ionization potential of lithium is 5.37 volts; sodium, 5.12; potassium, 4.32; and cesium, 3.88. The same kind of change is noted in other groups. This means, of course, that the heavier atoms of each group are more easily ionized. This prediction is in keeping with the chemical properties of the elements. Cesium, for example, is more easily ionized and is, therefore, more strongly electropositive[1] than any of the other metals of its group.

Within a given series, let us say the series sodium to argon, the ionization potential increases from one element to the next. Thus, in this series, sodium has the lowest and argon the highest ionization potential. The inert gas of each series has the highest ionization potential of the series. For the next element, which is an alkali of the succeeding series, the potential drops back to a value slightly lower than that of the preceding alkali metal. In

[1] Cesium exhibits a stronger tendency to lose one electron per atom than the other alkali metals; it is a more active metal than the others.

the long series, the changes of potential are less sudden and more irregular. From scandium to germanium in the first long series, the total change in ionization potential is only about one volt; this change in potential is scattered over some 12 elements. Similarly, the ionization potentials of the rare earths of the third long series differ only slightly.

Knowing the minimum potential that is required to give an electron sufficient energy to expel another electron from a given atom, or kind of atom, it is possible to calculate the energy of the bombarding electron. This quantity is a measure of the energy required to remove the expelled electron from its normal state to a place outside the atom. The relation between the applied potential V_1 and the kinetic energy of the electron is given by the equation

$$V_1 e = \frac{mv^2}{2},$$

where e is the electron's charge, m is its mass, v is its velocity, and V_1 is the potential.

It is also possible to move electrons from one quantum state within the atom to another. Such transitions produce the excited states of the atom, which we have previously discussed (page 271). As the potential of the bombarding electrons is increased, the energy becomes sufficiently great to raise the atom to successively higher excited energy states. Finally, the energy becomes great enough to ionize the atom by the complete removal of an electron. Up to certain voltages, the bombarding electrons are without effect. The collisions of such electrons with atoms are elastic, which means that they occur without any transfer of energy.

There are, of course, many resonance potentials for each kind of atom, corresponding to the production of the different excited states. For most atoms, there are also several ionization potentials, since the atoms contain several electrons bound by different amounts of energy and requiring the expenditure of correspondingly different amounts of energy to liberate them. Through studies of the resonance and ionization potentials, it is possible to arrive at rather definite conclusions concerning the various energy levels of any one kind of atom. It is also possible to

determine the number of such levels for one kind of atom and to compare their values with the values of the corresponding levels in other atoms.

Evidence Supplied by Optical Spectral Data

The distribution of electrons about the nucleus of an atom may be determined with a fair degree of success by considerations that depend largely upon the data of optical spectroscopy. The distribution pattern thus arrived at is the same as that proposed originally by Bohr and is in accordance with the circular and elliptical orbit scheme of his atomic model. Electrons are, therefore, distributed among orbits to which two quantum numbers (n and k) are assigned. Let us assume that the electrons are added, one at a time, and that each electron goes into a particular type of orbit. The orbit to which an electron is assigned, therefore, must in addition to being a possible or stationary orbit, be one that previously has been vacant. Bohr also assumed that each electron goes into the orbit that will cause the atomic system as a whole to possess its minimum energy state. This is assumed to be the state of maximum stability. Let us, then, see what conclusions may be reached upon this basis concerning the positions occupied by the different electrons of various kinds of atoms.

Since the hydrogen atom has a single electron, there is no reason, in the case of the unexcited state, for assigning the electron to any but the orbit corresponding to the lowest possible level. This is the circular orbit 1_1. We speak here, of course, only of the normal state of the hydrogen atom. Optical spectra, and other lines of evidence, indicate that both electrons of the normal helium atom also occupy 1_1 orbits. In lithium, however, there can be no doubt that the third electron occupies a different kind of orbit from the other two. The chemical properties of the element alone are sufficient reason for assuming that the third electron is very loosely bound to the rest of the atom. This is also indicated by the low ionization potential of lithium as compared to helium. The great difference in the binding of this electron and the spectrum of the element strongly suggest that the third electron occupies a 2_1 or 2_2 orbit. As previously stated, the electron will rotate in the orbit that gives the atom

the lower energy state. Now, from the equation that shows the energy associated with an electron rotating in an elliptical orbit,

$$E_{r,k} = -\frac{2\pi^2 m Z^2 e^4}{h^2}\left[\frac{1}{n^2} + \frac{1}{n^4}\cdot\frac{4\pi^2 Z^2 e^4}{c^2 h^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right]$$

it is apparent that, for a single electron rotating about a nucleus of charge Ze the energy increases as n increases but that for a given value of n, *i.e.*, $n = 2$, the energy is greater for larger values of k.

Hence, it is probable that the third electron of the lithium atom occupies a 2_1 instead of a 2_2 orbit. Let us also examine the spectrum of lithium. Like other elements which resemble it in chemical properties, four sequences of terms—S, P, D, and F—combine to produce the sharp, principal, diffuse, and fundamental series of spectral lines. These different lines correspond to differences between terms, each of which can be represented (page 257) by an expression

$$\frac{R}{(m + \alpha)^2}.$$

We are now ready to offer an explanation of the quantity $(m + \alpha)$. It is apparent that this quantity replaces the value of n in the expression for a term of the hydrogen series

$$\frac{R}{n^2},$$

where n, of course, is the quantum number associated with the orbit related to this term; $m + \alpha$, therefore, is also a quantum number and if the atom which is the source of the spectral lines were entirely "hydrogen-like," we might expect, as in the case of hydrogen, to find, instead of $m + \alpha$, a quantum number that is an integer n or m. The quantity α, however, is a fraction which must be added to the integer m. We may speak of $(m + \alpha)$, therefore, as the effective quantum number n_e of the term

$$\frac{R}{n_e^2}.$$

We must compute the frequencies, or wave numbers, of the different S, P, D, and F terms of the lithium spectrum, therefore,

by the use of effective quantum numbers; or, knowing the values of these terms from spectral data, it is possible to calculate the values of n_e.

Our entire scheme is based upon the assumption that we are dealing with a hydrogen-like atom. This assumption may be justified by the following considerations: The third electron of the lithium atom revolves in an orbit, which for the most part lies far outside both the nucleus and the two first-quantum electrons; the actual nucleus appears to consist of the nucleus proper plus its two nearest electrons. Considered in this light,

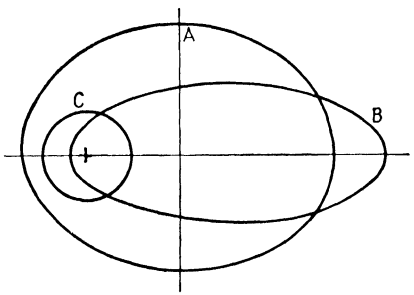


FIG. 113.—The screening effect. *A*, non-penetrating orbit; *B*, penetrating orbit; *C*, atomic core.

the third electron rotates around a nucleus that has a single positive charge e equal to that of the hydrogen nucleus. If the third electron rotates in *circular* orbits of quantum numbers larger than 1, it is evident that the effective nuclear charge will be +1 in each case, since the third electron does not penetrate within the region between the nucleus and the two electrons in 1_1 orbits. Penetration does occur in *elliptical* orbits, however, and for these, the effective nuclear charges will not be 1. Neither will it be 3 (the actual nuclear charge of the lithium atom), since, even in elliptical orbits, the outer electron is far removed from the nucleus during the greater part of its period of rotation and, therefore, is influenced by the atomic core (nucleus + 1_1 electrons) in accordance with the ordinary laws of a Coulombian field of force. As the electron reaches perihelion, however, it penetrates the atomic core, and the *screening effect* of the 1_1 electrons decreases; the nuclear charge acting upon it increases. For such orbits, therefore, we may think of the nuclear charge

as something less than 3 and more than 1. With these allowances, we should expect the spectrum of lithium to show resemblances to the hydrogen spectrum. The values of n_e will differ from n, and the divergences should give us some idea of the respective orbits which are related to the different terms of the spectrum.

The values of n_e for the F terms of the lithium spectrum are 4 and 5.003, which means that n_e in these cases is practically the same as n(4 and 5) for the hydrogen atom. It is likely, therefore, that the electrons responsible for these terms rotate in *circular* orbits or elliptical orbits for which k is almost equal to n and for which the principal quantum numbers are 4 and 5, since the effective nuclear charge must be the same or about the same as for the hydrogen atom.

The value of n_e for the D terms of the lithium spectrum are 2.998, 3.998, 4.999, and 6.000. These correspond to values of n equal to 3, 4, 5, and 6. We may assume, therefore, that the lowest member of the D terms has a quantum number $n = 3$ and that the corresponding orbits are all circular or are at least orbits of a small degree of eccentricity.

The departure of the values of n_e from integers is somewhat greater in the cases of the P terms. This can mean only that the electrons responsible for these terms are a little more firmly bound in their orbits than they are in hydrogen orbits whose quantum numbers are integers. The values of n_e for these terms are 1.959, 2.955, 3.953, and 4.952. The closer binding of electrons in these orbits can be explained, upon the basis of our previous comparison of the lithium and hydrogen atoms, as due to the increased effect of the nucleus. The effective nuclear charge must be slightly greater than in the F and D terms, a fact that indicates a decreased screening effect of the electrons in the 1_1 orbits and, hence, elliptical orbits.

The S terms have values of n_e as follows: 1.588, 2.595, 3.598, 4.599. These are considerably different from integral values. Now, the lowest S term must correspond to the normal state of the third electron of the lithium atom. The value of n_e for this term is 1.588. Let us remember that this orbit must be the one that gives the lowest possible energy state of the atomic system. This orbit cannot be assigned a two-quantum orbit

of the same character as that given the lowest P term, since the binding of this electron is very much stronger than for the lowest P term. For the reasons already mentioned and also because it is less firmly bound than the two inner electrons, we cannot think of it as a 1_1 orbit. The only possible orbit is the ellipse to which we assign the quantum number 2_1. This means, then, that the lowest P term corresponds to a circular 2_2 orbit.

The great difference in the binding of the electron in a 2_1 and in a 2_2 orbit (n_e for lowest P term = 1.959; n_e for lowest S term = 1.558) emphasizes the validity of our assumption that the electrons in elliptical orbits are more strongly bound than electrons in circular orbits for which the value of n is the same. This same effect should be noticeable in atomic systems containing greater numbers of electrons. In some of these, it is likely that the binding of an electron in an elliptical orbit of great eccentricity, such as a 4_1 or 5_1 orbit, may be stronger than the binding in a less eccentric orbit of smaller quantum number, such as 3_2 or 4_3. For this reason, electrons may be expected to enter 5_1 orbits, although 4_3 orbits, for example, are still vacant (see Table X, page 286).

The lowest terms of the four sequences S, P, D, and F, therefore, correspond respectively to orbits that may be described as follows: S, 2_1; P, 2_2; D, 3_3; F, 4_4. Furthermore, we believe that the different S terms correspond to 2_1, 3_1, 4_1, 5_1, etc., orbits; the P terms, to 2_2, 3_2, 4_2, 5_2 orbits; the D terms, to 3_3, 4_3, 5_3 orbits; and the F terms, to 4_4, 5_4, 6_4, orbits.

Reasoning in a similar manner, we may determine with some degree of assurance the distribution of electrons in other atoms. Thus, for the other alkalis (Table IX), we may reason that a single valence electron is responsible for the spectral lines and that its different possible orbits correspond to the different spectral terms of the S, P, D, and F sequences. In other words, each of these elements is hydrogen-like. If the effective quantum numbers are very nearly whole numbers, we may assume that the electron rotates in hydrogen-like orbits for which $n_e = n$ (approximately) and that the orbits do not penetrate the atomic core. If the value of n_e is radically different from an integral value, however, we must assume that the orbit is elliptical. Furthermore, the binding will be stronger the greater the eccen-

tricity of the ellipse. Upon this basis of interpretation, we find that the F terms of sodium, potassium, rubidium, and cesium correspond almost exactly to values of n_e equal to whole numbers from four to seven. The value of n_e for the D terms of the sodium spectrum are likewise very nearly integers ranging from three to six (Table IX).

TABLE IX.—EFFECTIVE QUANTUM NUMBERS

Values of N_e				Spectral term notation			
S	P	D	F	S	P	D	F
			Na				
1.63	2.12	2 99	4.00	3_1	3_2	3_3	4_4
2 64	3 13	3 99	5 00	4_1	4_2	4_3	5_4
3 65	4 14	4 99	6.00	5_1	5_2	5_3	6_4
4 66	5.14	5 99	....	6_1	6_2	6_3	7_4
			K				
1.77	2 24	2 85	3 99	4_1	4_2	3_3	4_4
2 80	3.26	3 79	4.99	5_1	5_2	4_3	5_4
3.81	4 27	4 76	5 99	6_1	6_2	5_3	6_4
4.66	5.27	5 75	6 99	7_1	7_2	6_3	7_4
			Rb				
1 80	2 29	2.76	3 99	5_1	5_2	3_3	4_4
2 84	3 32	3.70	4 98	6_1	6_2	4_3	5_4
3 85	4.34	4 68	5.97	7_1	7_2	5_3	6_4
4.85	5.35	5.67	6.97	8_1	8_2	6_3	7_4
			Cs				
1.87	2 36	2 55	3.97	6_1	6_2	3_3	4_4
2 91	3 40	3 52	4 97	7_1	7_2	4_3	5_4
3 93	4 42	4.52	5 97	8_1	8_2	5_3	6_4
4 94	5 42	5 52	6.97	9_1	9_2	6_3	7_4

EVIDENCE SUPPLIED BY X-RAY ABSORPTION AND EMISSION SPECTRA

The Bohr theory was modified by the assumption that each quantum group of electrons is divided into a number of divisions

called subgroups, the number of such divisions being equal to n, the principal quantum number of the group. The electrons in a subgroup have the same principal and also the same azimuthal quantum numbers; they revolve in the same kinds of orbits. The electrons of two different subgroups of the same main group have the same principal but different azimuthal quantum numbers. They rotate in slightly different kinds of orbits. One may rotate in a circular and another in an elliptical orbit; or two or more electrons may rotate in elliptical orbits of different eccentricities—in orbits whose major and minor axes are in different ratios to one another. We have already shown (page 252) how Sommerfeld's theory of elliptical orbits predicted and was, in turn, confirmed by the resolution of spectral lines.

It has been found, however, that n subgroups for the *nth* level will not suffice to explain either the valence of atoms or all the lines in the spectra of the elements, particularly all the lines in the x-ray absorption spectra.

X-rays have much shorter wave lengths (approximately 100–0.1 Å.) than "optical" rays (approximately 100,000–1,000 Å.). The wave numbers and frequencies of x-rays are, therefore, much larger than those of light. Hence, x-ray quanta are much larger than light quanta. The absorption of a light quantum may result in the removal of an electron only from an outer quantum level of the atom. The larger x-ray quantum may remove an electron from even the innermost groups.

If the atoms of an element are exposed to a beam of x-rays composed of many different frequencies, an absorption spectrum of the beam can be secured. Those frequencies which correspond to the characteristic emission lines of the element will be absorbed from the beam; the various quanta—$h\nu_1$, $h\nu_2$, $h\nu_3$, $h\nu_4$, etc.—will be absorbed by electrons that move from the K, L, M, or N level to quantum orbits farther removed from the nucleus.

If, however, the beam of x-rays contains a frequency which, when multiplied by h, gives a quantum sufficient to move an electron, let us say, from the K to the M level, it probably will also contain frequencies that will enable the electron to move from the K to the N, or even to other quantum orbits. Each of these shifts is the result of the absorption of a definite frequency. But if, as is usually the case, the L and M levels (and

perhaps even the N level) contain their maximum number of electrons, no frequency will be absorbed from the beam of x-rays, unless the beam contains a frequency that will enable the electron to move beyond the limits of the atom. The normal states of the atoms of the heavier elements usually contain electrons in the K, L, M, N, and O levels; for all elements lighter than radon and heavier than xenon, for example, the K, L, and M levels are completely filled; and for some of the heaviest of these elements, the N level is also filled (page 288). We may regard the outermost group of quantum orbits as the limit of the atom; hence, if an electron is removed to a quantum orbit farther removed from the nucleus (orbit of greater quantum

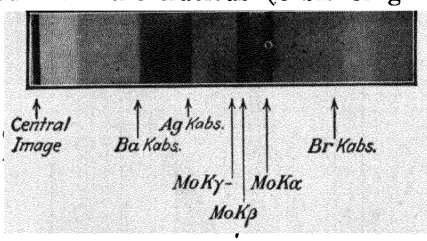


FIG. 114.—X-ray absorption spectrum produced by using a molybdenum anticathode and a crystal of barium sulfate as a reflector. The photograph shows the K absorption edges of barium, silver, bromine, and certain K emission lines of molybdenum. (*Pauling and Goudsmit, "Structure of Line Spectra," McGraw Hill Book Company, Inc.*)

number) than the orbits of this outermost group, we may think of the electron as having been removed beyond the atom, although, of course, in a theoretical sense, there is no definite boundary to the atom. To remove the electron beyond the atom's boundaries requires a definite minimum frequency. Any greater frequency, of course, may also remove it from the atom; the velocity of the expelled electron depends upon the magnitude of the frequency that is absorbed. Hence, a whole band of frequencies is absorbed instead of a single line. Each absorption band has, however, a very sharp head, and the line forming the head of a particular band corresponds to the frequency that is just great enough to separate the electron from the atom.

The study of the absorption bands of x-ray spectra led to the discovery that there are more bands in all except the K series than can be explained upon the basis of principal quantum numbers or even principal and azimuthal numbers.

Thus, x-ray absorption bands furnished further information concerning the necessary subdivisions of the quantum groups of electrons. Only one absorption-band head in the K series

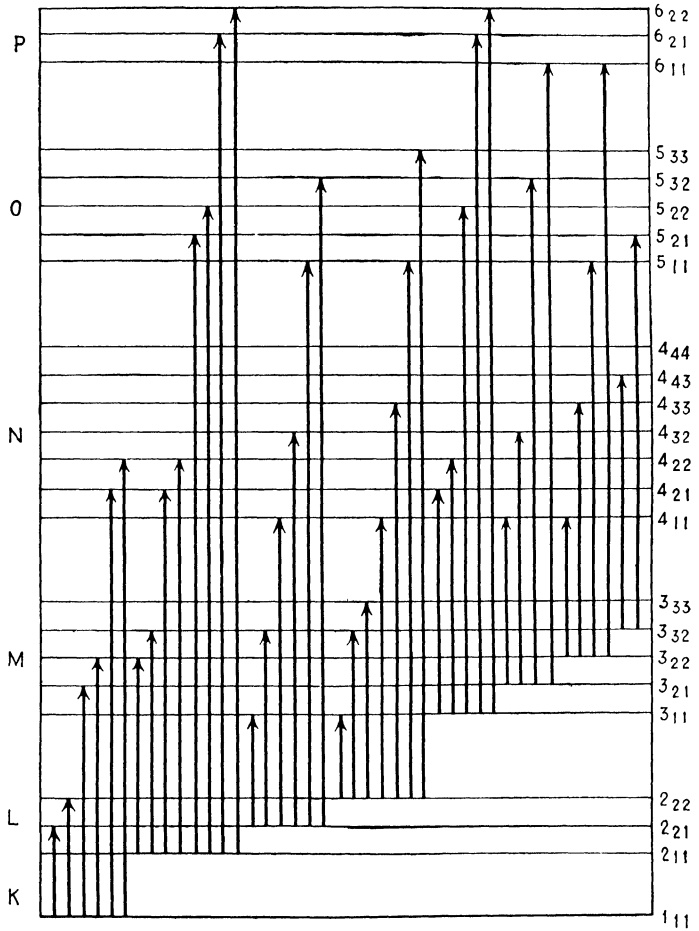


FIG. 115.—X-ray energy levels and spectral lines.

was recognized. Instead of a single head in the L series, however, three were discovered; these corresponded to an equal number of limiting frequencies of this series. Five modifications were revealed for the M and seven for the N series. It appeared, therefore, that there are $2n-1$ absorption-band heads for each

series of characteristic x-ray lines. Later, it was found that there are five absorption-band heads for the O series and three for the P series.

In addition to the complexity of absorption-band heads, close observation of x-ray emission spectra revealed many more lines than could be accounted for on the basis of single L, M, N, and O energy levels (Fig. 115). Instead of explaining the origin of lines in the x-ray spectrum upon the basis of a single quantum number, it thus becomes necessary to add subordinate numbers, as in the case of optical spectra (page 258). Each main level is associated with principal quantum number n. Slight modifications within a given level are indicated by a subordinate number k and by a third, the so-called inner quantum number j. The energy state corresponding to a particular orbit may, therefore, be indicated by the symbol n_{k_j}. The principal number n differs by unity for successive levels. The subordinate number k may be any integer equal to or smaller than n. The inner quantum number j may be equal to or one less than k. This system of notation is based, of course, upon the older system of quantum numbers using the values of k and j as they were originally used by Sommerfeld. The system of notation now in general use is one in which k is replaced by l (see page 298) and j is somewhat differently interpreted. The question of the values of j is discussed on page 298. The introduction of the quantum number j satisfied not only certain observed conditions in x-ray absorption and emission spectra but also aided in the explanation of the multiplicity of optical spectral lines (page 261) and for the normal Zeeman effect (page 292).

The use of three quantum numbers allows $2n-1$ *possible* modifications of the energy levels corresponding to the principal quantum numbers n. This is the same as the number of heads of the absorption bands in a given series of the x-ray absorption spectra. Of course, $2n-1$ energy levels (for a given value of n) do not appear in all atoms. Furthermore, certain selection principles (page 253) governing electron transitions limit the number of lines actually observed. Thus, transitions may occur between modifications of different levels provided that k changes by unity and j changes either by unity or does not change at all. The possible transitions, according to the rules of selection, are

shown in Fig. 115. Only two transitions between the L and K levels are possible. There are seven lines, however, which must be accounted for by transitions between M and L levels. The principles of selection are based, of course, upon actual observations of spectral lines and their relationships. Although there may be no basis for the physical explanation of the principles, they are entirely acceptable because of their agreement with the observed facts.

Structures of Atoms Based upon Three Quantum Numbers

According to the system which employs three quantum numbers to define the quantum state of all electrons, we may have for the nth level the following subdivisions: $N_{1,1}$; $N_{2,1}$ and $N_{2,2}$; $N_{3,2}$ and $N_{3,3}$; $N_{4,3}$ and $N_{4,4}$; $N_{n,n-1}$, and $N_{n,n}$. If the first three levels of an atom are complete, for example, the third level consists of the following subgroups: $3_{1,1}$; $3_{2,1}$ and $3_{2,2}$; $3_{3,2}$ and $3_{3,3}$. The second level consists of the subgroups $2_{1,1}$; $2_{2,1}$ and $2_{2,2}$. The first level consists, of course, of a single group $1_{1,1}$.

To demonstrate the difference between the electronic distribution based upon the system of three quantum numbers and that based upon two, let us fix our attention upon the subdivisions of the third quantum level. According to the old plan of two quantum numbers, three kinds of orbits are possible for this level: 3_1, 3_2, and 3_3. The third, or outside, orbit is circular, and the others are elliptical. With the introduction of a third quantum number, there is still just one kind of outer orbit; this is designated as $3_{3,3}$. But the others are double and elliptical. Thus, instead of the single orbit of the 3_2 level, we have $3_{3,2}$ and $3_{2,2}$ orbits; and in the place of the single 3_1 orbit, we now have $3_{2,1}$ and $3_{1,1}$ orbits.

Quantum orbits:					
2 quantum numbers....	3_1		3_2		3_3
3 quantum numbers....	$3_{2,1}$	$3_{1,1}$	$3_{3,2}$	$3_{2,2}$	$3_{3,3}$
Maximum number of electrons in each division:					
3 quantum numbers....	2	2	4	4	6
2 quantum numbers ...	2		6		10

TABLE X.—DISTRIBUTION OF ELECTRONS IN THE ATOMS OF ALL THE ELEMENTS

Element	n, 1 (K)	n, 2 (L)		n, 3 (M)			n, 4 (N)				n, 5 (O)			n, 6 (P)			n, 7 (Q)
	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$	$5s$	$5p$	$5d$	$6s$	$6p$	$6d$	$7s$
H	1																
He	2																
Li	2	1															
Be	2	2															
B	2	2	1														
C	2	2	2														
N	2	2	3														
O	2	2	4														
F	2	2	5														
Ne	2	2	6														
Na	2	2	6	1													
Mg	Core			2													
Al				2	1												
Si				2	2												
P				2	3												
S				2	4												
Cl				2	5												
A				2	6												
K							1										
Ca							2										
Sc						1	2										
Ti						2	2										
V						3	2										
Cr						5	1										
Mn						5	2										

| | | |

TABLE X.—DISTRIBUTION OF ELECTRONS IN THE ATOMS OF ALL THE ELEMENTS.—(*Continued*)

Element	*n*, 1 (*K*)	*n*, 2 (*L*)		*n*, 3 (*M*)			*n*, 4 (*N*)				*n*, 5 (*O*)			*n*, 6 (*P*)			*n*, 7 (*Q*)
	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
La											2	6	1	2			
Ce										1	2	6	1	2			
Pr										2							
Nd										3							
Il										4							
Sa										5							
Eu										6							
Gd										7		8	1	2			
Tb										8							
Ds										9							
Ho										10							
Er										11							
Tu										12							
Yb										13							
Lu										14							
Hf										14	2	6	2	2			
Ta													3	2			
W													4	2			
Re													5	2			
Os													6	2			
Ir													7	2			
Pt													9	1			
Au													10	1			
Hg													10	2			

Core

TABLE X.—DISTRIBUTION OF ELECTRONS IN THE ATOMS OF ALL THE ELEMENTS.—(*Continued*)

Element	*n*, 1 (*K*)	*n*, 2 (*L*)		*n*, 3 (*M*)			*n*, 4 (*N*)				*n*, 5 (*O*)			*n*, 6 (*P*)			*n*, 7 (*Q*)
	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*	6*p*	6*d*	7*s*
Tl	Core													2	1		
Pb														2	2		
Bi														2	3		
Po														2	4		
Rn														2	5		
														2	6		1
Ra																	2
Ac																1	2
Th																2	2
Pa																3	2
U																4	2

The distribution of electrons among the divisions of the *M* level is suggested at the bottom of page 285.

For the element radon, which contains 2-8-18-32-18-8 electrons in the six different levels, the complete distribution of electrons among the possible subdivisions is shown in Fig. 116.

As an illustration of how this grouping of electrons in the radon atom has been suggested, let us imagine that we have secured the x-ray absorption spectrum of this element. We recall that x-ray absorption spectra indicate, in general, a maximum of one, three, five, and seven modifications of the *K*, *L*, *M*, and *N* levels, respectively. Now, if all of these modifications are represented in the observed bands for radon—and let us assume

	K	*L*			*M*					*N*					*O*					*P*		
Energy level	$1s$	$2s$	$2p_2$	$2p_1$	$3s$	$3p_2$	$3p_1$	$3d_2$	$3d_1$	$4s$	$4p_2$	$4p_1$	$4d_2$	$4d_1$	$5s$	$5p_2$	$5p_1$	$5d_2$	$5d_1$	$6s$	$6p_2$	$6p_1$
	1_{11}	2_{11}	2_{21}	2_{22}	3_{11}	3_{21}	3_{22}	3_{32}	3_{33}	4_{11}	4_{21}	4_{22}	4_{32}	4_{33}	5_{11}	5_{21}	5_{22}	5_{32}	5_{33}	6_{11}	6_{21}	6_{22}
Number of electrons in each group ...	2	2	2	4	2	2	4	4	6	2	2	4	4	6	2	2	4	4	6	2	2	4

FIG. 116.—Distribution of electrons in the radon atom.

that they are—we can assume that these four levels are completely filled in this atom. Although there may be 12 modifications of the *O* level, bands corresponding to only five of these are observed. Hence, we conclude that only five subgroups of this level contain electrons. Similarly, there is evidence of only three real subgroups of the *P* level.

The general scheme of the distribution of electrons (Table X) among the subdivisions of the different groups of an atom was first suggested by Stoner from a consideration of spectral data and almost simultaneously by Main-Smith from a consideration of chemical properties. The two views are practically identical, although they were arrived at by entirely different lines of reasoning. Both were based upon the principle that the maximum number of electrons in a subgroup is equal to twice the inner quantum number of the corresponding energy level. The electronic distribution thus provided offers considerable aid in the explanation of the valences of the elements (see Table X).

The Physical Interpretation of the Inner Quantum Number.— We have observed that three quantum numbers are necessary in the definition of the different energy states of an atom. If we are to retain the mechanical model of the atom which was introduced by Bohr, it is essential that each quantum number should be associated with a periodic motion of some kind in the atom. Let us consider the case of an atom containing one optical electron which revolves about an atomic core. The periodic motions which are associated with the numbers n and k have already been discussed. They have to do, respectively, with the angular momentum which is associated with the motion of the electron in its orbit and with the precession of the ellipse. The inner quantum number j has been associated with the rotation of the plane of the orbit about an axis, which we may call the axis of the core (Fig. 117). Let us assume, then, that the core possesses an angular momentum (page 239) which may be thought of as the resultant of the momenta of all the electrons constituting the core. The total angular momentum of the atom is made up of that of the core plus that of the optical electron. In order to explain the inner quantum number, we must further assume that the total angular momentum depends upon the orientation of the orbit of the optical electron with respect to the orbits of the other electrons in the atom. This orientation calls for definite angles of inclination of the plane of the orbit to the axis of the core. The imposition of the quantum condition, demanded by the inner quantum number, upon the total angular momentum means that this inclination must be limited to certain definite angles:

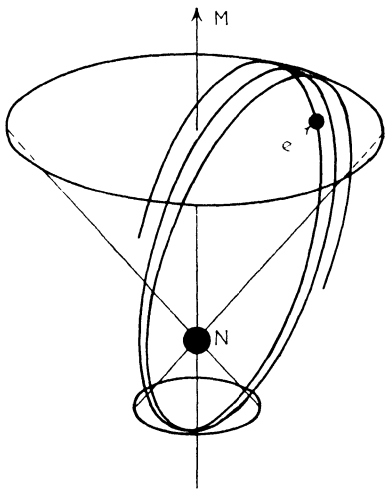


FIG. 117.

$$\text{Total angular momentum} = \frac{jh}{2\pi},$$

where j has different values corresponding to different angles of inclination. Hence, for the same values of n and k, the energy states of the atom may exhibit slight modifications. The number of such modifications is limited to the finite values of j. It must be remembered, however, that this mechanism is purely theoretical.

Although the use of a third quantum number was of great value in explaining many features of the multiplet structure of spectral lines, it was by no means entirely successful. The existence of multiplet terms of three or more components still remained unexplained. Another difficulty was also encountered in attempting to account for the effects of a magnetic field upon the lines of a spectrum. The effect of a magnetic field called for the assignment of quantum numbers not allowed by the system of notation that employs n, k, and j. For this reason, it will be desirable to discuss such effects at this time.

The Zeeman Effect.—The effect of a magnetic field upon spectral lines was first observed by Zeeman in 1896. When the source of light is placed in a strong magnetic field, each single line of the spectrum is split up into three components, provided that the lines are viewed at right angles to the direction of the field. One of the three components, the central line, has the same wave length as the line observed in the absence of a field. The other two components lie to the right and left of the first component and represent wave lengths that are longer and shorter, respectively, than the wave length of the original line. If the source of light is viewed in a direction parallel to the magnetic field, only two components are observed. The central line is missing. In either case, the light of any of the observed wave lengths is polarized. This resolution of a spectral line by a magnetic field is called the *Zeeman effect.* The resolution that we have described is called the *normal* Zeeman effect. More often, however, more than three components of a line viewed at right angles to the magnetic field are observed. Resolution into more than three components is spoken of as the *anomalous* Zeeman effect. It is with the latter that the three quantum-number system encounters its greatest difficulty.

Lorentz's Explanation of the Zeeman Effect.—Lorentz, long ago, offered an explanation of the Zeeman effect in terms of the

classical electromagnetic theory of light. The assumption is made that light vibrations are produced by the vibrations of electrons within the atom which lies in the magnetic field. We can think of these electronic vibrations as resolved into vibrations that lie in the direction of the magnetic field and vibrations that are perpendicular to the lines of magnetic force. Those that are parallel to the lines of force are not affected by the magnetic field. Hence, light corresponding to such vibrations will appear in the normal position (unchanged wave length) when the source of the light is viewed at right angles to the magnetic field. Since the vibrations do not emit light in the direction of the lines of force, no light is observed in this direction. Hence, no line corresponding to the original wave length is observed in the longitudinal direction. The light corresponding to these vibrations, moreover, is plane-polarized, since all the vibrations producing it are in one plane.

The vibrational components which lie in a plane at right angles to the lines of force may be looked upon as two circular vibrations in opposite directions. The frequency of a charged particle that rotates in either of these circular paths will be altered by the magnetic field. This effect is due to the same magnetic force that causes an electron (page 82) to move in a circular path in a plane at right angles to the direction of the field. The radius of this circle depends upon the strength of the field, the velocity, mass, and charge of the particle. Since the two circular vibrations are in opposite directions, the period of one will be retarded, and the other will be accelerated by the influence of the field. Hence, two lines corresponding to the different frequencies are observed either in the longitudinal or in the transverse direction. If they are observed in the direction of the lines of force, they will appear circularly polarized. In the transverse direction, however, the circular vibrations give plane-polarized lines, since circles viewed in this direction appear as lines.

Effect of a Magnetic Field upon Electron Orbits.—The orbital motion of an electron may be compared with a current flowing in a circular or elliptical loop of wire. In the presence of a magnetic field, we may expect the orbital motion of the electron to be disturbed in a manner somewhat similar to the disturbance

produced by a similar field upon the electrical current. The effect of a uniform magnetic field is to cause a precession about the lines of force of the magnetic field to be superposed upon the orbital motion of the electron in the absence of a magnetic field (Fig. 117). We may use a spinning top as an analogy. Let us disregard the effect of friction. The gravitational field replaces the magnetic field. If there were no gravitational effect, the top would continue to rotate about the same axis. But gravity is always tending to make the top fall over, and hence its effect is to cause the axis of the top to be inclined

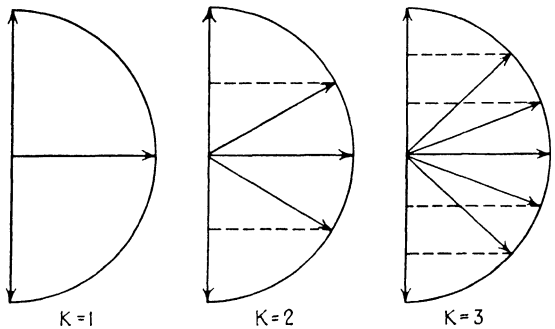


FIG. 118.—Orientation of planes of electron orbits with respect to lines of force of magnetic field.

slightly to the direction of the field and to produce a precession about the vertical line representing the axis of the field. The inclination of the top's axis to the direction of the gravitational field depends upon its kinetic energy. Similarly, the effect of an electrical or magnetic field upon an electron that revolves in a Bohr orbit depends upon the plane in which the orbit lies. These planes are distinguished by the degree of their inclination to a preferential axis, which in the case of a magnetic field is to be regarded as a line in the direction of the lines of force. Now, if the plane in which the electron's orbit lies rotates about this axis, it is evident from Fig. 118 that the movement of the electron can be resolved into its motion in the plane of the orbit and its motion in a plane perpendicular to the axis. Of course, the motion in the actual orbit plane is quantized, and the quantum conditions demanded by the equation

$$2ma^2\omega = nh$$

must be fulfilled. This is the same equation as the one given on page 240, except that here we have used $ma^2\omega$ instead of mva to express angular momentum. This can be done, since angular momentum is proportional to the product of the angular velocity ω and ma^2 (mass $\times$ square of radius), and since angular velocity can be expressed as orbital velocity divided by a:

$$\text{Angular momentum} = ma^2\omega,$$

$$\omega = \frac{v}{a},$$

$$ma^2\frac{v}{a} = mva.$$

The quantum mechanics also requires that the motion in the plane perpendicular to the axis also satisfy the requirements of this equation. This requirement means that the electron can revolve in orbits that lie only in planes that permit the satisfaction of these conditions. If these conditions are fulfilled, the actual planes of the orbit can be inclined only at certain angles from the axis. If the quantum conditions for the motion in the actual orbit are

$$2\pi ma^2\omega = nh, \tag{1}$$

the conditions required for the motion in the perpendicular plane are

$$2\pi ma^2\omega \cos\alpha = nh \cos\alpha, \tag{2}$$

where α is the angle between the axis and line which is normal to the plane of the orbit. Furthermore, $nh \cos\alpha$ must, according to quantum conditions, be a whole-number multiple m of h. Hence,

$$nh \cos\alpha = mh, \tag{3}$$

or

$$n \cos\alpha = m_1, m_2 \cdots \tag{4}$$

where m_1, m_2, . . . represent different integers. If $n = 1$ (electron rotates in one-quantum orbit), the plane of the orbit must be either parallel or perpendicular to the axis. This is readily seen from Eq. (4). If the plane is parallel to axis, $\cos\alpha = 1$, and

$$n \cos\alpha = 1$$

If the plane is perpendicular to the axis, $\cos \alpha = 0$, and

$$n \cos \alpha = 0.$$

No other values of $\cos \alpha$ will give integral values of m. If the electron rotates in a two-quantum orbit, however, the plane of the orbit may be inclined at angles of 0, 60, or 90 deg., since ($\cos 60° = \frac{1}{2}$),

$$2 \times 1 = 2,$$
$$2 \times \tfrac{1}{2} = 1,$$
$$2 \times 0 = 0.$$

The number m has come into rather general use at the present time as a quantum number that measures the angular momentum about an axis of symmetry when the atom is acted upon by a magnetic field.

Explanation of the Zeeman Effect in Terms of the Quantum Theory.—The quantum theory's explanation of the Zeeman effect considers the rotation of the plane of the electron's orbit about a preferential axis (page 291). This axis is supplied by the action of the magnetic field. If we consider the one-quantum orbit of an electron, it has been shown (page 295) that the plane of the orbit must be either parallel or perpendicular to the direction of the field. We may consider that the magnetic field does not influence the size or shape of the orbit, or the velocity of the electron in its orbit, provided that we make allowance for this effect by imposing upon the electron a second quantized rotation of the orbit's plane around the direction of the field as an axis. The rotation about this axis has an angular velocity equal to $eH/2mc$. The orbit in the actual plane remains a quantum orbit for which $n = 1$. The kinetic energy of the electron, however, is slightly different from the energy of an electron revolving in an orbit that is not influenced by a magnetic field. If the plane of the orbit is parallel to the direction of the field, the field will not change the kinetic energy of the particle. But if the plane is at right angles to the axis, the plane's rotation may be in the same direction as the movement of the electron in its orbit or may be in the opposite direction. If the rotation of the plane is in the same direction as the rotation of the electron in its orbit, the effect is an increase in

the actual velocity referred to a fixed axis. If the rotations are in different directions, the actual velocity is diminished. These differences in velocity cause, therefore, a change in the energy of the electron corresponding to the change in velocity. Now, if an electron falls into such an orbit as we have described, the energy radiated will depend upon the difference between the energy states of the electron in its original orbit and the energy state of the orbit into which it falls. In a magnetic field, therefore, there are two slightly different final energy states for the one-quantum orbit which lies in a plane perpendicular to the direction of the field. Hence, instead of a single spectral line corresponding to a wave number which can be defined as

$$\nu = \frac{2\pi^2 Z^2 e^4 m}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right),$$

two lines will appear corresponding to the wave numbers

$$\nu_1(\nu_2) = \frac{2\pi^2 Z^2 e^4 m}{ch^3} \pm \frac{eH}{4\pi mc^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

The three lines that appear when the source of light is viewed at right angles to the magnetic field are thus explained satisfactorily by the application of the quantum theory.

The Spinning Electron.—The introduction of a third quantum number j did not solve the problem completely. Difficulties were still encountered in interpreting the Zeeman effect, particularly the anomalous effect, and also the multiplet spectral terms when these consist of more than two components. Some advance in the right direction appeared to be offered by the suggestion of the spinning electron. According to this hypothesis, a fourth quantum number s is introduced. This symbol represents the number of units of angular momentum possessed by an electron because of the spin upon its own axis. The angular momentum due to this effect is expressed as $\frac{1}{2}\, h/2\pi$. Since the spin can be in only two directions (clockwise and counterclockwise), s may have two values $+\frac{1}{2}$ or $-\frac{1}{2}$.

The value of j takes on a slightly different interpretation when the quantum number s is introduced. The number j represents the resultant of the angular momenta of spins of all the electrons of the system and the angular momenta of the electrons in their

orbits. According to this new system of numbers, k is replaced by $k - 1 = l$ in designating the quantum number which is determined by the angular momentum ($ma^2\omega$) associated with the orbital motion of the electron. The symbol l designates, therefore, the orbital quantum number. The older number k may be used for this purpose in the case of the hydrogen atom and in designating differences in the terms involved in the relationships of the various optical series of spectral lines. But the number l must be used in dealing with more complex atomic systems and more complex spectral problems, such as multiplet structures. When the atomic system contains more than one

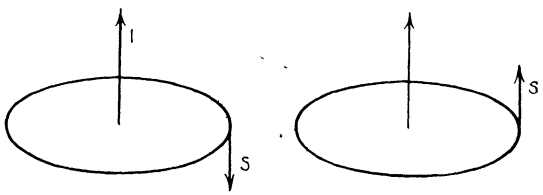


FIG. 119.—Orientations of spin momentum (vectors) with reference to angular momentum (vector l). A magnetic field is produced by the motion of the electron in its orbit and also by the electron spinning upon its axis. The potential energy of the system depends, therefore, upon the orientation of the field arising from the electron's spin with respect to the field associated with the electron's orbital motion.

electron, differences arise in the values of the orbital quantum number due to penetration of the inner electron groups (core) by the orbits of outer electrons. For the alkali metals, for example, this condition results in a more rapid precession of the elliptical orbits and to a wider separation of the energy levels which correspond to the different values of l than is true for the simple hydrogen atom. In describing spectral series, the letters S, P, D, and F correspond to the following values of l:

$$(S)l = 0;\ (P)l = 1;\ (D)l = 2;\ (F)l = 3.$$

If, for example, we consider a sodium atom as a system consisting of a single-valence electron rotating about the remainder of the atom as a core, j becomes the resultant of s and l for the electron. The values j, therefore, must be $l + \frac{1}{2}$ or $l - \frac{1}{2}$. According to the selection principle, l must vary by unity and j by unity or 0. Thus, if the values of l for the S, P, D, and F levels are 0, 1, 2, and 3, respectively, it follows that for the S

level $j = \frac{1}{2}$ or $-\frac{1}{2}$. The latter is excluded, since a negative value of j has no meaning. For the P terms, j may be $1 - \frac{1}{2}$ or $1 + \frac{1}{2}$. Hence, for this level, two terms differing in their values of j are permissible. Two lines are predicted, therefore, by combinations of P and S terms:

$$P_{\frac{1}{2}} - S_{\frac{1}{2}} \qquad \text{and} \qquad P_{\frac{3}{2}} - S_{\frac{1}{2}},$$

since j must change by 1 or 0.

If $l = 2$ for the D terms, j may have the values of $2 + \frac{1}{2}$ and $2 - \frac{1}{2}$, or $\frac{5}{2}$ and $\frac{3}{2}$. Three combinations of P and D terms are thus permitted:

$D_{\frac{5}{2}} - P_{\frac{3}{2}}$; j changes by 1.
$D_{\frac{3}{2}} - P_{\frac{3}{2}}$; j changes by 0.
$D_{\frac{3}{2}} - P_{\frac{1}{2}}$; j changes by 1.

Three combinations can also be shown for F and D terms.

A System of Four Quantum Numbers for Single Electrons of Atoms in a Magnetic Field.—In dealing with atomic systems that are acted upon by moderately strong magnetic fields, the state of a single electron can be best explained by consideration of l and s separately instead of dealing with the resultant j of the two. In weak fields, the resultant j (of l and s) may still apply, since the field is not sufficiently strong to overcome the forces existing between the electron and the core. It will be remembered that j is taken in such cases as the resultant of l and s, since the states represented by these two numbers exert an influence upon each other, the resultant representing the combined effect of the two influences. In strong fields, the electron and the rest of the atom (the core) are each influenced separately. Instead of using a single magnetic quantum number m (page 296) to represent the quantization of the total angular momentum about an axis of symmetry, m is "split" into two factors. Of these, the m_l component will represent the effect of the magnetic field upon the angular momenta of which l is a measure. And the m_s component represents the field's effect upon the spin momentum of the electron.

It should be noted that the four quantum numbers based upon the system of notation we have just presented apply to a single electron in an atomic system. The state of the entire system

must be defined in a different manner, since many electrons must be considered simultaneously, and these are not without interacting effects. Thus, there are so-called anomalous multiplet terms which can be accounted for only by the assumption of simultaneous transitions of two electrons (from the valence level to two different lower levels). The combined effect of these double transitions appears as a radiation of a single frequency. We cannot go into a lengthy discussion of these matters in a treatment of this kind. We may note, however, that a quantum number L is used to designate the resultant of all the l values for the different electrons in the atom. The value of L gives the system S, P, D, F, etc. The number S is the resultant of the s values for all the electrons. The third and last number is the inner quantum number j, which states the total number of units of angular momentum about an axis and is determined as the resultant of L and S.

In designating the different states of a single electron in an atom that is acted upon by a magnetic field, four quantum numbers are employed. The meaning of these numbers may be summarized as follows: (1) the principal quantum number n, which is often called the total quantum number; (2) the secondary quantum number represented by the symbol l, which expresses the effect of the precession of the elliptical orbits of the electron upon the quantum condition of the electron; (3) the number m_l, which designates the component of l along the lines of force of magnetic field H or in the direction of an electrical field X; and (4) m_s, which designates the component of s in the direction of H or X. When no magnetic or electrical field exists, m_l and m_s have no meaning. In general, the values of these different quantum numbers may be represented by the following scheme, which takes into account the generally accepted selection principles:

n may have the value 1, 2, 3, 4, etc.
l may have the values $n - 1$, $n - 2$, $\cdots$ 0.
m_l may have the values l, $l - 1 \cdots (1 - l)$, $-l$.
m_s may have the value $+\frac{1}{2}$ or $-\frac{1}{2}$.

The two values of m_s are due to the fact that there are just two directions in which the electron may spin; these are, of course, 180 deg. apart.

TABLE XI.—POSSIBLE ENERGY STATES OF THE ATOMS

n	1	2					3								
l	0	0	1			0	1			2					
m_l	0	0	1	0	−1	0	1	0	−1	2	1	0	−1	−2	
m_s	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$	$+\frac{1}{2}, -\frac{1}{2}$
Number of energy states for each set of quantum nos	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Number of states for each value of l	2	2	6			2	6			10					
Number of states for each value of n.	2	8				18									

For hydrogen, if $n = 1$, then $l = 0$, since l cannot be greater than $n - 1$. Furthermore, since $l = 0$, which means that there is no precession of the ellipse about the nucleus and that the orbit is circular, the magnetic field has no effect upon the angular momentum, *i.e.*, upon the orientation of the plane of the orbit; and hence, $m_l = 0$. But m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$, depending upon whether the electron spins with the magnetic field or against it. For this atom, therefore, the states of the single electron can be described by the following assignment of quantum numbers:

State 1	State 2
$n = 1$	$n = 1$
$l = 0$	$l = 0$
$m_l = 0$	$m_l = 0$
$m_s = +\frac{1}{2}$	$m_s = -\frac{1}{2}$

Now, if $n = 2$, then l may be either 0 or 1; if $l = 0$, $m_l = 0$; but if $l = 1$, $m_l = 1$, 0, or -1. Of course, m_s for any of these cases may be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

Making use of Pauli's exclusion principle, which states that *there cannot be two electrons which have the same values for all four quantum numbers*, the distribution of electrons in levels and sublevels is described in Table XI for the first three groups.

The arrangement of the electrons in atoms, in accordance with this plan, will be discussed in connection with the valences of the elements in Chap. XIV.

References

See references for Chaps. X and XI

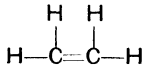
CHAPTER XIII

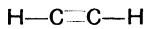
VALENCE

The study of valence is not so simple as it may appear when first we learn to employ it in writing chemical formulas and equations. It deals with many baffling questions concerning the structural features of molecules and the combining capacities of different kinds of atoms. It may be interesting, at least, to note some of the specific questions that an adequate theory of valence must answer.

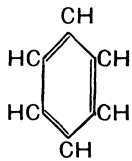
Why does chromium form the oxides CrO, Cr_2O_3, and CrO_3 but not Cr_2O or CrO_2? Why does sodium form only one true oxide, Na_2O? What is the valence of sodium in Na_2O_2, and what is the structure of peroxides in general? Why does manganese form compounds corresponding to the oxides MnO, Mn_2O_3, MnO_2, MnO_3, and Mn_2O_7, while the compounds of sulfur in the same periodic groups correspond to SO_2, SO_3, and S^{-2}? Why is the formula of sulfuric acid H_2SO_4 and not H_6SO_6, as it might be according to the older theories of valence? How is ammonia attached to the zinc ion in $Zn(NH_3)_4^{+2}$? How is NH_4^+ formed from NH_3? What is the valence of nitrogen in each of its oxides and in nitrites and nitrates? Why does the presence of an ethyl group C_2H_5 in place of one hydrogen atom in H-OH make ethyl alcohol so unlike water? What is the structure of the hydrates, and what is the nature of the valence forces in such compounds? Why is stannic chloride a volatile liquid, while the chlorides of other metals, which have smaller molecular weights, are solids? Why is mercuric chloride practically a non-electrolyte, while calcium chloride is an excellent conductor when fused and when dissolved in water? Why does calcium oxide react with water to form a fairly strong base, while carbon dioxide forms a very weak acid? Why do the metallic characteristics of the elements increase within a family with increasing atomic weight? What is the real nature of the

linkage between carbon atoms in compounds such as ethylene and acetylene?





How nearly does the structure usually assigned to benzene

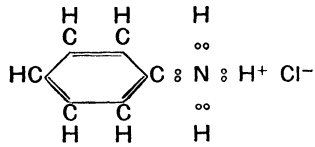


represent the real arrangement of atoms within the molecule?

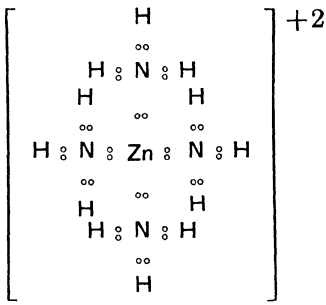
The desire to answer these and similar questions is not prompted by idle curiosity. They deal with fundamental chemical problems. In fact, we cannot be sure that a compound exists in the molecular state or what its exact nature is until we have an explanation of how the atoms that constitute the substance are united or how they are otherwise related. We once thought that crystals of sodium chloride are composed of molecules having the formula NaCl, but x-ray analysis has taught us that these molecules do not exist in these crystals.

A Brief History of the Concept of Valence.—Chemists have been interested in the forces that cause atoms to form molecules ever since they became certain that molecules exist. The philosophers of old Greece thought that "atoms" combine under the influence of love and that atoms that hate one another do not combine. Not long ago, discussions of "avidity," and still more recently of "chemical affinity," were quite in order. These terms were used in a vague way to explain the fact that certain elements combine readily while others combine less readily or not at all. Thus, hydrogen and oxygen were said to possess great affinity for each other, while chlorine and oxygen showed less affinity, chlorine and bromine still less, and hydrogen and helium none at all. Terms such as affinity, love, and hate were used because there was no better way of explaining the forces or conditions that cause elements to combine.

At the present time, the term chemical affinity has almost completely disappeared from the literature of chemistry. It



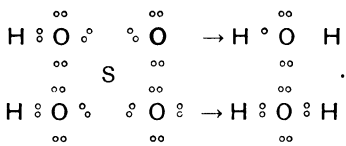
Similarly, ammonia may combine with ions of metals to form complex ions, which are sometimes called the *ammines*. Thus, zinc ion, Zn^{+2}, combines with four molecules of ammonia to form $Zn(NH_3)_4^{+2}$:



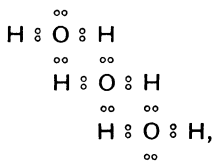
The zinc ion has lost the two electrons that the atom normally possesses in the fourth-quantum group. Now, the zinc atom, like the atoms of most of the other elements, can share four pairs of electrons. These four pairs are offered by the four ammonia molecules, each of which possesses one unshared pair. The complex ion has an electrovalence of two, which is the same as the valence of the simple zinc ion, since the addition of four neutral molecules of ammonia does not affect the charge.

Water molecules may form coordinated linkages by means of the unshared electron pairs of the oxygen atom. Hydrated salts are formed in this manner. The water that is attached to the salt molecule, or rather to an atom in the molecule, has been called "water of crystallization." This name is used incorrectly, since it is not necessary for the formation of crystals. Water molecules may be attached by *coordinated* bonds either to the positive ion, as ammonia is attached to zinc ion, or to an atom in the negative ion of the salt; hence, there is considerable variation in the number of water molecules in different hydrated salts. The sulfate ion displays a pronounced tendency to combine with

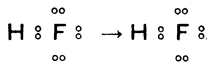
water molecules, as shown in the combination with hydrogen sulfate:



It appears that hydrogen shares two pairs of electrons with oxygen in this compound. This means that hydrogen exhibits a covalence of two. This is also the case when two or more water molecules combine (polymerize), forming $(H_2O)_2$ or $(H_2O)_3$,



and in H_2F_2,



VALENCE, STRUCTURE, AND THE PERIODIC TABLE

Hydrogen to Neon.—The valence of hydrogen is positive one or negative one. If the atom loses its single electron, the ion H^+ results. If the atom gains another electron, thus completing the first-quantum group, the ion H^- is formed. In practically all of its ionizing compounds, hydrogen forms the positive ion. In a few, such as LiH, however, hydrogen appears to gain an electron and to act, therefore, as a negative ion.

Helium has zero valence. Each atom of this element contains two electrons outside the nucleus, and the indications are that both of these lie in the first quantum group. This group appears to be completely filled by two electrons; hence, there is no tendency for the atoms of this element either to gain electrons or to lose those that it has.

Lithium has three electrons per atom—two in the first quantum group and one in the second. The second group may contain

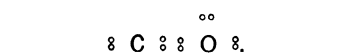
eight electrons. A single member does not go very far toward the completion of this group and is not very firmly held. Lithium is, therefore, strongly electropositive in character. It has little attraction for electrons, but, on the other hand, it does have a pronounced tendency to lose electrons, forming lithium ions, Li^+. The small ionization potential of lithium (page 273) shows that this is true.

The beryllium atom possesses two electrons in the first and two in the second quantum group. The valence of beryllium, therefore, is positive two. Similarly, the valence of boron is three, although this element exhibits this valence only by sharing electrons. The valence of carbon is four, and that of nitrogen is five; at least, these are the maximum (theoretical) valences of these elements; but, like that of boron, the valences of carbon and nitrogen are covalences rather than electrovalences. Similarly, oxygen *might* have a valence of six and fluorine seven, but both of these are ruled out by chemical facts. Compounds in which these elements display such valences are unknown. Neon, containing eight electrons in the second level, has zero valence.

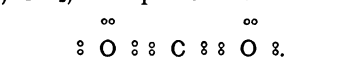
Beryllium forms the ion Be^{+2}, where two electrons are transferred to a more electronegative element, such as chlorine. The elements from boron to fluorine, however, almost never occur in solutions as positively charged ions, such as B^{+3}, C^{+4}, N^{+5}, O^{+6}, and F^{+7}. Some of these do exhibit the valences indicated, but in such compounds the atoms are usually linked covalently rather than electrovalently. Boron occurs in borates, BO_2^- and $B_4O_7^{-2}$; carbon is found in carbonates, CO_3^{-2}, or in hydrocarbons, such as CH_4, and in other organic compounds; nitrogen, in NO_3^-, NO_2^-, NH_3, $-NH_2$, etc.; oxygen, in oxides and acidic radicals, such as SO_4^{-2}, CO_3^{-2}, ClO_3^-; and fluorine in salts, such as sodium fluoride where it is negatively electrovalent. In general, very few ions with valences greater than three or four exist. There are a few ions, such as As^{+5} and Sb^{+5}, which appear to have lost five electrons per atom, but these never occur in large numbers and are readily converted into covalent forms, such as AsO_4^{-3}. There are a few well-known tetravalent cations. Among these is Sn^{+4} in $SnCl_4$, but even this compound in the pure state appears to be atomic rather than ionic. Ions with a valence of 3, such as Al^{+3} and Fe^{+3}, are some-

what more numerous, but the compounds of these elements are likely to be atomic rather than ionic. Their chlorides resemble in some respects carbon tetrachloride, CCl_4, in which the molecules never dissociate to form C^{+4} and Cl^- ions. All the bonds are due to shared electron pairs. There appears, then, a limit to the positive charge that an atom can carry; the usual charge is one or two units. The reason for this limitation is not difficult to find. Each electron which is removed from an atom leaves that atom with a positive charge, and since positive attracts negative, the removal of the second electron is more difficult. The removal of the fourth or fifth electron from an atom that already carries three or four units of positive charge is almost impossible.

Let us turn again to the table (page 286) which shows the distribution of electrons in the different levels and sublevels of the atoms of different elements. Let us examine more closely the relation between the structures of the atoms and the corresponding valences in this first series of the elements of the periodic table. Carbon contains four electrons in the second quantum group, but these four are not equivalent to one another. Two electrons revolve in $2_{1,1}$ orbits and two in $2_{2,1}$ or $2_{2,2}$ orbits. These two sets of electrons are not equally firmly held by the nucleus. Those that revolve in $2_{1,1}$ orbits are slightly less easily removed from the carbon atom than the others. Hence, carbon may have only the two electrons of the $2_{2,1}$ or $2_{2,2}$ orbits involved in combinations with oxygen or other elements; or it may have all four so involved. In carbon monoxide, CO, carbon shares two electrons with oxygen, forming two pairs of shared electrons which constitute the double bond:



In carbon dioxide, CO_2, four pairs of electrons are shared:

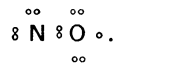


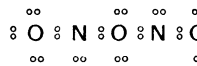
Carbon may be said, therefore, to have valences of two and four.

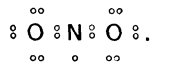
Nitrogen possesses subgroups of two and three electrons in the second level and so might exhibit combining tendencies in which either five or three electrons are involved in covalences. The subgroup of three electrons may be further subdivided into

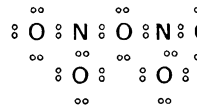
two grouplets containing one and two electrons, respectively. In this way, valences of one, two, and even four can be accounted for. As shown in the following formulas, which are suggestive for the oxides of nitrogen and for nitrates and nitrites, covalences of one, two, or three appear to predominate. The valence of five, which is suggested by the older valence theory for such compounds as N_2O_5 and HNO_3, appears unnecessary. The arrangement of electrons should not be considered as real but rather, they are arrangements which seem probable in the light of the properties of these compounds.

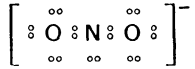
N_2O

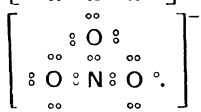
NO 

N_2O_3 

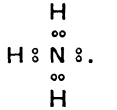
NO_2 

N_2O_5 

NO_2^- 

NO_3 

Ammonia has the following structure:



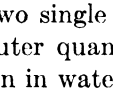
It appears, therefore, that nitrogen may exhibit different covalences with four as a maximum. The old problem of whether the valence of nitrogen is three, four, or five disappears.

In combining with three hydrogen atoms, nitrogen completes the second quantum group, since the atom then has eight elec-

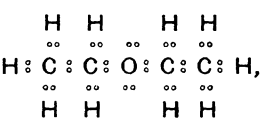
trons in this level. It will be noted, however, that there is a "lone," or unshared, pair of electrons in the ammonia molecule. This may be utilized in further combination with hydrogen or other atoms (page 313).

It will also be noted that molecules like NO and NO_2 contain one electron each which cannot be accommodated in any of the electron pairs within the molecule. These are called "odd" molecules, since they contain an odd number of valence electrons. Thus, NO contains 11 electrons, 6 for oxygen and 5 for nitrogen; and NO_2 contains 17, 12 for oxygen and 5 for nitrogen. Odd molecules are unstable. Nitric oxide molecules combine with one another, for example, to form molecules of N_2O_2; and NO_2 forms N_2O_4. In each of these compounds, the two "odd" electrons of the molecules form another shared pair. This is the bond that unites the two single molecules.

Oxygen completes the outer quantum group by sharing two electron pairs with hydrogen in water molecules:



or with other elements that possess electron-sharing characteristics, such as carbon in CO and CO_2 and nitrogen in its oxides. In the water molecule, in the ether molecule,



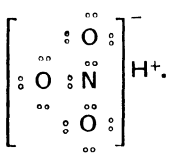
and in many others, the oxygen atom possesses two lone or unshared pairs of electrons, which, like the unshared pair in the ammonia molecule, may act more or less as latent valences. Other atoms, or radicals, may become attached at these points, giving rise to new and more complicated structures (page 315). Thus, oxygen may have a covalence of four. In this respect, it is similar to nitrogen.

Fluorine can actually acquire an electron from electropositive elements (metals). Thus, it attains a charge and produces electrovalent compounds. Like carbon, nitrogen, and oxygen, the atom of fluorine can exhibit a maximum covalency of four by

sharing four pairs of electrons. In forming four covalences, all of these elements attain a completed second quantum group of eight electrons. This group does not hold more than this number; hence, four is the maximum covalence of these elements.

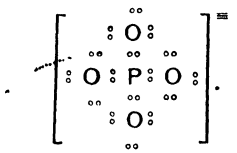
Sodium to Argon.—The valences of the elements that lie between sodium and argon in the periodic table can be accounted for in the same manner as the valences of the corresponding elements of the first series. Aluminum, like boron, should show a valence of three. Unlike boron, however, aluminum does show an electrovalence; the ion Al^{+3} is found in aqueous solution. The difference between boron and aluminum in this respect is in keeping with the relative sizes of these two kinds of atoms. Since the aluminum atom is the larger, the outer electrons are less firmly held and more easily removed than the electrons in the valence level of the boron atom. Like the compounds of boron, many pure aluminum compounds, even aluminum chloride, appear to be atomic rather than ionic. Aluminum chloride, $AlCl_3$, does not conduct the current of electricity in the pure fused state, although it does when it is dissolved in water. This fact has led to the opinion that the covalence of aluminum is converted into electrovalence when the salt dissolves. The effect of the solvent upon the kind of valence that aluminum displays may be due to the combination of water molecules with the aluminum atom by means of coordinated bonds, thus satisfying the covalence of aluminum and leaving the atom free to act electrovalently toward chlorine or other negatively charged ions.

Silicon closely resembles carbon, and phosphorus resembles nitrogen. One difference, however, should be noted between nitrogen and phosphorus. In nitric acid, HNO_3, nitrogen forms three covalent bonds with oxygen:



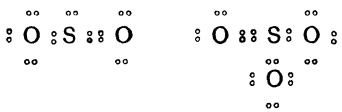
The valence of the NO_3 radical is negative one, since it contains 24 electrons, while the neutral oxygen and nitrogen atoms together possess only 23–6 for each oxygen and 5 for the nitrogen

atom. The radical, therefore, contains one electron in excess of the number required for neutrality; hence, it exhibits an electronegative valence of one toward H^+ or other positively charged ions. Phosphoric acid is H_3PO_4. Here phosphorus shows the usual maximum covalence of four:

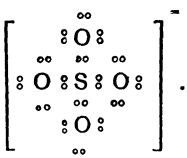


The electrovalence of the PO_4^{-3} group is three, since the group contains 32 electrons, whereas only 29 are required for neutrality. Metaphosphoric acid, HPO_3, contains a phosphorus atom with the same covalence as the nitrogen atom in nitric acid. If nitrogen formed four covalences with oxygen, we might expect the acid H_3NO_4. This acid of course, does not exist, because, no doubt, of the relatively small size of the nitrogen atom and the resulting tendency toward a covalence of three instead of four.

Sulfur shares three pairs of electrons with oxygen in SO_2 and four in SO_3:



In the former, one, and in the latter, two of the bonds are probably coordinated covalences. In SO_4^{-2}, sulfur also exhibits a normal covalence of four, two of the bonds being coordinated links:

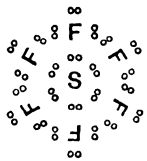


The sulfate ion possesses a negative valence of two, since it contains 32 electrons, whereas the four oxygen and one sulfur atom normally possess only 30.

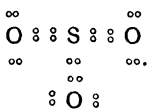
In hydrogen sulfide, H_2S, sulfur acts in much the same manner as oxygen in the water molecule H : $\overset{\cdot\cdot}{S}$: H. Hydrogen sulfide

ionizes slightly in water, forming first H^+ and SH^-, just as water forms H^+ and OH^- ions. The SH^- ion, unlike OH^-, further ionizes (very slightly) to form H^+ and S^{-2} ions.

Covalences Greater than Four.—There are several evidences that sulfur (and many other elements as well) forms compounds by sharing six pairs of electrons instead of four. Sulfur hexafluoride, SF_6, is an excellent example of such compounds:



Even sulfur trioxide, SO_3, may contain six bonds, as in



Whether it does or not we cannot be quite sure. In fact, we cannot assign it a definite structure. If the sulfur atom does have six covalences, as it must have in SF_6, these 12 electrons are probably not contained in the same quantum group as the eight electrons which are involved in four covalences. The group of 12 probably lies in an expanded or larger quantum group, farther removed from the nucleus.

Many elements appear to be capable of forming expanded valence groups, in which 12 (six pairs), and in a few cases even 16 (eight pairs), electrons are involved in linkages. Among compounds of this sort the following examples may be given:

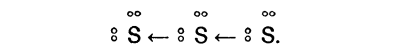
$Co(NH_3)_6Cl_3$
$Na_3Co(NO_2)_6$
$H_2(SiF_6)$
$K_2(PtCl_6)$
$K_4Fe(CN)_6$
SF_6
$Mg(OH_2)_6Cl_2$
$Na_3(AlF_6)$
$Na_3(TaF_8)$
MoF_6
OsF_8

Covalences of two, three, five, and seven are also sometimes shown in the compounds of some of the elements. The following are examples of such valences:

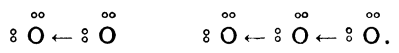
TaF_5
$AsCl_5$
$SbCl_5$
$K_4(RuCl_7)$
BCl_3
$Mg(C_2H_5)I$
$Zn(C_2H_5)_2$
$InCl_3$
PF_5
PH_3
$Al(CH_3)_3$
$K_2(BiCl_5)$

It appears, therefore, that an atom usually forms four or six covalent bonds. These bonds constitute a quantum group of 8, or an expanded group of 12, electrons. The lightest of the elements often form only two or three covalent links, as in $Mg(C_2H_5)I$, BF_3, NH_3, etc. Quantum groups of 10, 14, and 16 electrons can also be formed, but since they occur less frequently, they are evidently not so stable as those that contain 8 or 12.

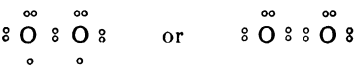
Diatomic and Polyatomic Molecules of Elements.—Sulfur atoms may combine with one another by means of coordinate links:



In like manner, complex molecules, like S_8, are built up. Oxygen, also, might combine with itself by means of coordinate links between its atoms to form O_2 and O_3:

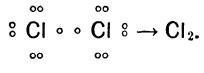


Oxygen might also have the structure



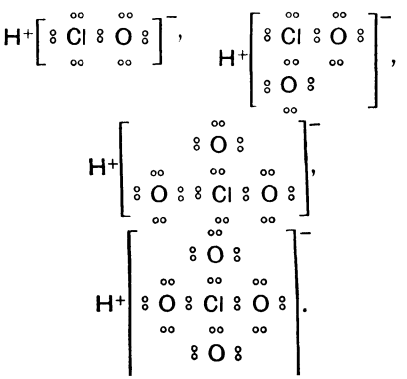
and the molecule of ozone might be

Other elements may combine with themselves in the same manner, if their atoms possess fewer than four pairs of electrons in the outermost quantum group or if the number of electrons in this group is odd. Thus, two chlorine atoms combine to form a molecule by means of a true covalent link.



Helium, He, neon, Ne, and the other inert gases do not form diatomic molecules. Since each atom of these elements has a completed quantum group, there is no opportunity to form covalent bonds by sharing electrons or to form coordinated links by accepting whole pairs of electrons from other atoms. Of course, it is theoretically possible for the neon atom, for example, to form a bond with some atom that can accept a pair of its electrons, as the nitrogen atom does with the hydrogen ion in forming NH_4^+. Such a linkage would result in the formation of the ion NeH^+. Just why this combination does not occur cannot be explained adequately, but the fact that it does not points to the great stability of the octet of electrons in the outer group of the neon atom.

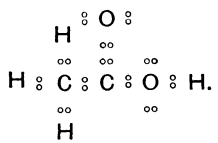
The Acids of Chlorine.—Chlorine's usual valence is negative one; it is like fluorine. It may, however, display various covalences in which it shares electrons with electronegative elements, such as oxygen. Thus, we may have the following oxyacids of chlorine:



Acids and Bases.—Hypochlorous acid HClO, structurally, is closely related to sodium hydroxide, NaOH. Yet, one of these compounds is a very strong base, and the other is an acid. Let us assume that the structures of the molecules of these compounds are $\overset{\cdot\cdot}{\underset{\cdot\cdot}{:Cl:}}\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:\!H$ and $Na:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$, respectively. These formulas picture the hydrogen atoms of the two molecules as attached to the oxygen atoms, although in the latter the valence is, at least in part, in the form of an ionic bond between Na^+ and OH^-. If both of these compounds were entirely covalent, or atomic, in character, neither would form H^+ or OH^- ions in solution. The fact that ClOH dissociates to form ClO^- and H^+ ions shows that the bond between H and O is more easily ruptured than that between Cl and O, for if ClOH acted as a base, it would dissociate as $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H^-$. In sodium hydroxide, however, the bond between H and O is stronger than that between O and Na. We are speaking here of the strength of the bond in terms of how firmly the two atoms are held together by the bond, of how easily they may be separated; this means, then, that the kind of bond we are considering is a covalent rather than an electrovalent one. Because of the location of the weaker bond, NaOH dissociates to form Na^+ and OH^- ions: $Na^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H^-$. If it acted as an acid, it would dissociate as $Na:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^- H^+$. The relative strengths of the bond between oxygen and hydrogen and the bond between oxygen and the third element (Cl or Na) determines whether the substance acts as an acid or as a base. The difference in the strengths of these bonds depends, in turn, upon the character of the element that is attached to the oxygen, especially upon its ability to attract electrons. If the atom is one like chlorine, which is strongly electronegative, the pair of electrons will be strongly displaced toward the electronegative atom (chlorine in this case). This displacement of this pair of electrons away from oxygen causes (according to Lewis' view) the oxygen atom more strongly to attract the other pairs of electrons around it. This results in a displacement of the pairs of electrons (which

join the oxygen and hydrogen) toward oxygen and away from hydrogen, weakening this bond and causing the ionization of the molecule into positive and negative ions, such as ClO^- and H^+. On the other hand in sodium hydroxide, sodium, unlike chlorine, repels rather than attracts electrons; hence, the electron pair between sodium and oxygen is displaced probably a little way toward hydrogen. This bond is strengthened by the shift, since formerly the electron pair was considerably removed from the hydrogen atom because of the much greater attraction of the oxygen atom for the electrons. A shift of the electrons to a position nearer the midway point between the two atoms produces a stronger covalent bond, since it results in a more equal sharing of the electrons. A shift toward one atom and away from the other means that the two atoms act more nearly like ions, since one of them tends toward complete ownership of the electrons. The break in the sodium hydroxide molecule comes, therefore, between sodium and oxygen rather than between oxygen and hydrogen and produces hydroxyl rather than hydrogen ions. In this case, the electron shift is so pronounced in the direction of the oxygen atom, and away from sodium, that the bond may be regarded as electrovalent in character.

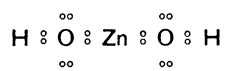
Acetic acid is a weak organic acid. This indicates that the hydrogen of the carboxyl group of the acid is attached to oxygen by a covalent rather than an electrovalent bond and that this bond is fairly strong.



If one hydrogen atom of the CH_3 group of the acetic acid molecule is replaced by an atom of chlorine, this chlorine atom will displace the bonding electron pair, between itself and carbon, away from the carbon atom. The carbon atom then attracts the other pairs of electrons around it more strongly and displaces the pair between the two carbon atoms toward the carbon atom to which chlorine is attached. Thus, the effect of the chlorine is transmitted to the second carbon atom and finally to the oxygen atom

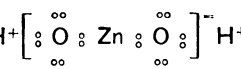
to which hydrogen is attached. The ultimate effect is the displacement of the electron pair between oxygen and hydrogen toward the oxygen atom and away from hydrogen. This bond is, therefore, weaker in monochloroacetic acid than it is in acetic acid; the former should be more completely ionized than the latter. The facts that solutions of monochloroacetic acid are better conductors of electricity and have lower freezing temperatures and higher boiling temperatures than solutions of acetic acid of the same concentrations prove that the former is more completely ionized. Similarly, dichloroacetic acid and trichloroacetic acid are even stronger than monochloroacetic acid. This fact indicates that the displacement of electrons in the direction of chlorine and away from carbon increases with the number of chlorine atoms attached to the carbon atom.

Certain elements such as zinc, tin, chromium, lead, and aluminum neither repel nor attract electrons very strongly; in other words, the electronegativity of these elements is weak and is not much more or much less pronounced than their electropositive character. In zinc hydroxide, for example, the bond between zinc and oxygen and that between oxygen and hydrogen are approximately equally strong. Neither bond is very easily ruptured. Hence, we may conclude that there is no pronounced displacement of electrons within the molecule.

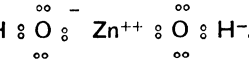


Zinc hydroxide can dissociate, therefore, as an acid or as a base with almost equal ease or, perhaps we should say, since zinc hydroxide is neither a strong acid nor a strong base, with almost equal difficulty:

Acid,



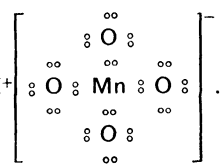
Base,



Such hydroxides are said to be *amphoteric*, since they produce both the ions of an acid and those of a base in solution. Since they produce both hydrogen and hydroxyl ions, and since the product of the ionic concentrations of these two ions in any

solution cannot exceed the ionization constant of water (about 1×10^{-14}), it follows that the concentration of neither of these two ions in any solution of these hydroxides can be very great, unless the concentration of one or the other ion is considerably reduced.

Potassium to Krypton.—Although the $3_{3,2}$ and the $3_{3,3}$ orbits contain no electrons as yet, the single electron of the outermost quantum group of the potassium atom goes into the fourth level and revolves in a $4_{1,1}$ orbit. The valence of potassium is positive one (K^+). Calcium contains two electrons in $4_{1,1}$ orbits and forms Ca^{+2} ions by the loss of these electrons. Spectral data indicate that in scandium one electron enters a $3_{3,2}$ or $3_{3,3}$ orbit while two remain in $4_{1,1}$ orbits. In titanium, two electrons remain in $4_{1,1}$ orbits and two enter the empty subgroups of the third level; thus, titanium has valences of two, three, and four. In the succeeding elements of this series (vanadium, chromium, manganese, iron, cobalt, and nickel), the number of electrons in the $4_{1,1}$ orbits remains the same as in calcium, scandium, and titanium, while the number in the $3_{3,2}$ and $3_{3,3}$ orbits gradually increases. Vanadium has three electrons in these orbits, chromium five, manganese five, iron six, cobalt seven, and nickel eight. Thus, vanadium has valences of two and three; chromium two, three, and six; and iron two, three, and six (in ferrates). It appears, therefore, that in the elements from scandium to nickel, all the electrons in the fourth level and those in the $3_{3,2}$ and $3_{3,3}$ orbits of the third level can take part in forming covalences. This leaves an unchanging core which is bounded by the 3_2 orbits of the third level. In potassium permanganate, for example, these valences are demonstrated by the following electronic formula:



Other examples are given below to illustrate the covalences of the elements in this list and the electrovalences of the complex ions that they form:

$TiCl_4$
$K_4^+[Fe(CN)_6]^{\equiv}$
$K_3^+[Fe(CN)_6]^{\equiv}$
$K_3^+[CoCl_6]^{\equiv}$
$K_3^+[CrCl_6]^{\equiv}$
$[Co(NH_3)_6]^{+++}Cl_3^-$
$[Cr(H_2O)_6]^{+++}Cl_3^-$.

Whenever any of these elements loses electrons to electronegative elements, such as chlorine, it appears, however, that two or three is the maximum number that can be removed from any of their atoms in the course of ordinary chemical reactions. Thus, we have salts such as $CrCl_2$, $CrCl_3$, $FeCl_2$, $FeCl_3$, $NiCl_2$, $CoCl_3$, etc., in which dissociation occurs, forming di- or trivalent ions of the metals. This fact indicates that the bonds in these compounds are electrovalent in character and that the two electrons of the fourth quantum group are easily removed. It is also possible to remove electrons from the $3_{3,2}$ and $3_{3,3}$ orbits during reactions with oxidizing substances such as free chlorine. Thus, ferrous chloride is oxidized to ferric chloride by the removal of one more electron from the iron atom. This electron comes, of course, from an orbit of the third group. That only one electron is easily removed from the third quantum group is probably due to the fact that the separation of an electron from an ion that already possesses three units of positive charge requires more energy than the oxidation reaction can supply. This explanation is the usual one, but there is another which is entirely in keeping with the principle (page 276) concerning the relative energy of electrons in elliptical orbits of great eccentricity (such as 4_1 orbits) and those of lesser eccentricity but smaller quantum numbers (3_2 orbits). According to this suggestion, we might expect electrons from 3_3 orbits to be more easily removed than those in 4_1 orbits. If this be the case, the charge of an ion, such as Fe^{++}, is due to the removal of 3_3 electrons. Higher valences might involve 4_1 electrons.

Many of the ions of this group are colored, a fact that means that certain wave lengths are absorbed by the atom and that, therefore, only certain colors are transmitted. Since the frequencies in the visible light range are relatively small, the quanta

of energy absorbed are correspondingly small. The absorbed energy is defined by the equation

$$E = nh\nu,$$

in which ν is small, a fact that means that the small quantity of energy absorbed is used in relatively short shifts in the positions of the electrons and that only electrons in the outer quantum groups of the atoms are involved. In K^+, the outermost quantum group of electrons is complete. Hence, a relatively large quantity of energy would be required to remove an electron from this group to a higher one. Potassium ion, therefore, does not absorb any of the colors of light, and the ion is colorless. But in chromium, manganese, iron, cobalt, and nickel, the outermost group is not filled. For atoms of these elements, only relatively small quantities of energy are necessary to remove electrons from this level to a higher one. This is readily accomplished by the absorption of small quanta, or the relatively small frequencies, of visible light. Hence, the ions of these elements are colored. It is remarkable that the ions cease to be colored as soon as the third quantum group is filled. Cuprous salts (Cu^+, 2–8–18–(1)) are not colored, while cupric salts (Cu^{++}, 2–8–17(1)–(1)) are highly colored. Zinc ion and the ions of the elements immediately following zinc in the periodic table are colorless, since the third group in each of these is completely filled. Zinc, for example, has the structure Zn^{++}, 2–8–18.

It is interesting, too, that these elements are paramagnetic up to nickel. Even Cu^{++} is paramagnetic, although Cu^+ and all the succeeding elements up to krypton are diamagnetic. Paramagnetism, like color, also appears to be associated with incomplete quantum groups of electrons. This fact may be due to the balancing of the magnetic moments of the electron orbits in the completed groups, while in the incomplete groups a complete balance cannot obtain.

Zinc, gallium, germanium, arsenic, selenium, and bromine closely resemble the corresponding elements in the preceding series. Arsenic, for example, forms AsH_3, $AsCl_5$, $AsCl_3$, H_3AsO_3, and H_3AsO_4, all of which closely resemble the corresponding compounds of phosphorus and somewhat less closely those of nitrogen. Arsenic, however, does exhibit slightly greater elec-

tropositive characteristics than phosphorus and much more strongly electropositive characteristics than nitrogen. Whereas PCl_3 and PCl_5 are typically atomic compounds, $AsCl_3$ and $AsCl_5$ partake slightly more of the nature of salts; to some extent, at least they display the properties of ionic compounds. Similarly, whereas phosphoric, H_3PO_4, and phosphorous, H_3PO_3, acids have practically no basic properties (they do not act as $P(OH)_5$ and $P(OH)_3$), arsenic, H_3AsO_4, and arsenious, H_3AsO_3, acids do show slightly greater tendencies to ionize as bases ($As(OH)_5$ and $As(OH)_3$) in the presence of large concentrations of hydrogen ion.

Likewise, selenium and bromine, while closely resembling sulfur and chlorine, respectively, in many chemical properties, are slightly more like the metals than the latter are. In general, we may say that metallic and basic characteristics increase as we go down from one member to another in any of the groups of the periodic table. Arsenic is more like a metal than phosphorus. Antimony and bismuth, in the same group with these two elements, still more closely resemble the metals in many ways. Bismuth chloride, $BiCl_3$, for example, shows very definite electrovalent and saltlike characteristics and resembles the chlorides of phosphorus and nitrogen very little. This change in metallic characteristics is in keeping, of course, with the idea that electrovalence (loss of electrons in this case) is more easily attained in large atoms than in small (page 312).

Rubidium to Xenon.—In the series of elements from rubidium to xenon, the members closely resemble those of the preceding series, both in the structures of their atoms and in their properties. As before, the first electrons (rubidium, strontium) enter the fifth quantum group and revolve in $5_{1,1}$ orbits instead of entering orbits in the unfilled groups of the fourth level. Then comes a group of elements (Yt to Ag) whose electrovalence is usually two or three and whose ions are colored and paramagnetic. All these elements exhibit covalences that involve electrons of the fifth and also the fourth quantum groups. These elements are like those between scandium and copper of the preceding series.

As we proceed toward silver, the electrons that are added go into the unfilled subgroups of the fourth level ($4_{3,2}$ and $4_{3,3}$ orbits), until these groups are filled in the silver atom, which has the structure 2–8–18–18–(1). Cadmium, the next element,

has the structure Cd, 2–8–18–18–(2). Spectrographic data indicate that in indium, the third electron instead of entering the $4_{4,3}$ or $4_{4,4}$ orbit goes into the $5_{2,1}$ or $5_{2,2}$ subgroup. Indium, therefore, has the structure 2–8–18–18–(2)(1). The $5_{1,1}$ orbits are completed by the two electrons already added in cadmium. The valence of indium is three, therefore, although it can be one if only the electron of the $5_{2,1}$ orbit is removed. Tin has the structure 2–8–18–18–(2)(2). This element may, therefore, show the valence of two or four. The structure of Sb is 2–8–18–18–(2)(3); that of Te is 2–8–18–18–(2)(4). Tellurium, therefore, resembles sulfur, which has the structure 2–8–(2)(4). If all six of these electrons are shared, tellurium may have a covalence of six as sulfur has in SF_6. Thus, we have $Te(OH)_6$, telluric acid, and salts, such as $M_3^{++}TeO_6$. Tellurium, in accordance with its increased atomic dimensions, shows a greater tendency to act as Te^{++++} ion. Thus, tellurium tetrachloride, $TeCl_4$, in the fused state acts as if it were ionized to some extent. Iodine has a negative electrovalence of one, since it tends to acquire one electron in completing the group of four electrons for the $5_{2,2}$ subgroup. The atom of iodine has the structure 2–8–18–18–(2)(5) in which the last subgroup may be further divided into two divisions containing, respectively, two and three electrons. Xenon has the structure 2–8–18–18–(2)(6).

Cesium to Radon.—Beginning with cesium, the next electron enters a $6_{1,1}$ orbit instead of the incomplete subgroups of either the fourth ($4_{4,3}$ and $4_{4,4}$) or fifth ($5_{3,2}$, $5_{3,3}$, $5_{4,3}$, $5_{4,4}$, $5_{5,4}$, $5_{5,5}$) level. Barium has the structure 2–8–18–18–8–(2), and lanthanum 2–8–18–18–8, 1–(2). In the latter, the extra electron of the fifth level goes into a $5_{3,2}$ orbit. Cerium has the structure 2–8–18–18, 1–8, 1–(2); here the added electron takes a place in the previously empty $4_{4,3}$ orbits of the fourth quantum group. This is the beginning of the rare earth group, which consists of the elements from cerium to lutecium. As we pass from one member of this group to the next, the successive electrons fall into $4_{4,3}$ and $4_{4,4}$ orbits:

Pr 2–8–18–18, 2–8, 1–(2)
Nd 2–8–18–18, 3–8, 1–(2)
Il 2–8–18–18, 4–8, 1–(2)
Sm 2–8–18–18, 5–8, 1–(2)

. . . . . .

Gd 2–8–18–18, 6, 1–8, 1–(2)

. . . . . .

Lu 2–8–18–18, 6, 8–8, 1–(2)

With lutecium, the fourth quantum group is completely filled, and additional electrons must go into either the fifth or the sixth level. Since the rare earth elements are exactly alike as regards the quantum orbits of their electrons in the fifth and sixth levels, they are also much alike as regards chemical behavior. Since only the two electrons of the $6_{1,1}$ and the one electron of the $5_{3,2}$ orbits are involved in forming valences, all these elements have a valence of three.

Beginning with hafnium, the fourth level is completely filled; additional electrons go into the $5_{3,2}$ and $5_{3,3}$ orbits of the fifth group. Thus, the distribution for hafnium is 2–8–18–32–8, 2–(2), and for tantalum it is 2–8–18–32–8, 3–(2). Tantalum, therefore, resembles vanadium, 2–8–8, 3–(2). The structures of the atoms of the elements next in the order of atomic numbers are

W 2–8–18–32–8, 4–(2)
Re 2–8–18–32–8, 5–(2)

. . . . . .

Pt 2–8–18–32–8, 8–(2)

These elements resemble chromium, manganese, iron, cobalt, and nickel. They also resemble the elements of the second long series between molybdenum and palladium.

Beginning with gold, the $5_{3,2}$ and $5_{3,3}$ orbits are filled, and there is one electron left over for the $6_{1,1}$ orbit. Some of the electrons can be removed, during chemical reactions, from the $5_{3,3}$ orbits. This is indicated by the fact that gold has an electrovalence of three as well as one. The mercury atom has the structure 2–8–18–32–18–(2) and may have a valence of one or two, which means, perhaps, that the two electrons of the sixth level revolve in different kinds of orbits. Assuming that the two outermost electrons enter $6_{1,1}$ orbits, these orbits are now filled, and the third electron which goes into the sixth group enters a $6_{2,1}$ or $6_{2,2}$ orbit. This gives thallium the structure 2–8–18–32–18–(2, 1). This element is both univalent and trivalent, depending upon whether an atom loses only the electron in the 6_2 orbit or those

of the 6_1 orbits as well. The structures of the elements following thallium are as follows:

Pb 2–8–18–32–18–(2, 2) Valences of 2 and 4; compares with Sn

Bi 2–8–18–32–18–(2, 3) Valence three

Po and No. 85

Rd 2–8–18–32–18–(2, 6) Inert

Number 87 to Uranium.—With radon, the 6_2 orbits are filled, and this element is inert; all elements that have this 2, 6 distribution in the outermost group are inert. As usual, the next electron (in No. 87, the last member of the alkali group) enters the $7_{1,1}$ subgroup of the seventh level. Radium, the second element of this series, like barium, strontium, and calcium, has an electrovalence of two; it is really more electropositive than any of these, because of the greater size of its atom. Its structure is represented by 2–8–18–32–18–8–(2). In actinium, the added electron probably falls back into a 6_3 orbit, leaving two electrons in the $7_{1,1}$ subgroup.

Ac 2–8–18–32–18–8, 1–(2)

Th 2–8–18–32–18–8, 2–(2), or, perhaps, 2–8–18–32–18–8, 3–(1)

. . . . . .

Ur 2–8–18–32–18–8, 5–(1)

The structures just given appear the most probable for the elements from actinium to uranium, but, as in the case of the corresponding elements of the preceding series, the added electrons might fall into 5_4 orbits. Thus, thorium might have the structure 2–8–18–32–18, 1–8, 1–(2) and uranium 2–8–18–32–18, 3–8, 1–(2). If the latter arrangement is the true one, these elements should represent the beginning of another series of elements closely resembling the rare earths. The first-mentioned structures appear more likely, since these elements resemble one another neither in the matter of valence nor in their chemical properties. Thorium, for example, has a valence of four, while uranium forms six covalences in many of its compounds.

Effect of Kind of Valence upon the Properties of Compounds

Ionization.—Electrovalent compounds consist of ionic combinations of atoms or radicals. The ions that are involved are

electrically charged because of the transfer of electrons from one to the other. In the solid state of the compound, these ions are usually held together, because of their electrostatic attraction, in the form of some crystal lattice (page 159). Each negative and each positive ion occupies a definite position in the lattice with reference to a certain number of the ions of the opposite kind of charge. Thus, in a crystal of sodium chloride, each sodium and each chlorine ion (except those on the very faces of the crystal) is located at the center of a unit cubic lattice with six ions of the opposite kind located at the centers of the six faces of the cube. If such a solid is fused, the melting point is the temperature at which the lattice structure disintegrates more or less completely into its constituent ions. The increased kinetic energy of the particles at the higher temperature permits them to break away from the positions that electrostatic forces cause them to take relative to one another at a lower temperature. If the substance is dissolved, the solvent may change the attraction of the particles for one another, since the electrostatic force between any two particles, which are charged positively and negatively, respectively, depends in part upon the nature of the medium that separates them. If two point charges A^+ and B^- are separated by the distance d, and if the medium that occupies the space between them possesses the dielectric constant D, then the electrostatic attraction F between them can be defined as follows:

$$F = \frac{e_1 \times e_2}{d^2 \times D},$$

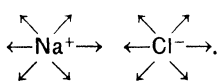
where e_1 and e_2 are the quantities of charge located at A and B, respectively. The force of attraction varies inversely, therefore, with the value of the dielectric constant D. The attraction between ions, for example, is small if the medium is a substance, such as water, which has a high dielectric constant; that of water is approximately 80. The attraction is great if the medium is benzene, carbon tetrachloride, ether, ethyl acetate, etc., all of which have dielectric constants of approximately two or three. Later, we shall discuss the dielectric constant as a property related to the structure of the molecules of a compound (page 340).

It is apparent, therefore, that a compound in which the valence forces are of an electrostatic character ionizes when dissolved in a solvent which weakens the attraction between the ions of the crystal lattice. If the solvent cannot do this, then the substance does not ionize in that solvent. In fact, it may not dissolve (page 339).

Covalent, or atomic, compounds (in which ions do not exist in the solid state) do not liberate ions in solutions, unless the solvent, in one way or another, causes the covalences of the compound to be converted into electrovalences. Such a change does sometimes appear to occur. Thus, stannic chloride in the pure, liquid state is a nonconductor of electricity and exhibits many other properties that normally belong to atomic compounds, such as high volatility and solubility in benzene and other solvents of low dielectric constant. But when stannic chloride is dissolved in water, it forms a conducting solution. Similarly, pure hydrogen chloride, aluminum chloride, and ferric chloride act as atomic compounds in the pure state and as ionic compounds in aqueous solutions.

One may use ionization, therefore, as a means of determining whether a given substance is electrovalent or covalent, ionic or atomic, in character.

Volatility.—Electrovalent, or ionic, compounds have relatively great external fields by means of which they exert an influence upon neighboring molecules. This external field is caused by the high degree of polarization of such substances. Perhaps it would be better to drop the idea of the molecule entirely in these cases and to speak of the individual ions of which the substance is composed. The attraction of each ion in the substance is not satisfied by being directed toward one ion of the opposite kind but is exerted equally in all directions.



This results, as we have seen in our study of crystalline sodium chloride (page 161), in the formation of very complex crystalline structures. In these crystals, the molecules of sodium chloride lose their individual identities and are interwoven to make a

structure of indefinite size—a "giant molecule," so to speak. This is an extreme case, of course, where the external fields are very strong and cause a very close association of the parts of the compound.

In covalent, or atomic, compounds, the external fields are weak, and in some cases there may be no such fields at all. In the hydrogen molecule, for example, the electrical forces are probably almost completely satisfied within the molecule. There is no polarization; there are no positive and negative portions of this molecule to exert electrical forces in an external field.

Since the molecules[1] of ionic compounds have strong external fields, and since such molecules are bound more or less closely together by electrostatic attraction, more energy is required to separate them. Covalent compounds, on the other hand, consist of molecules that act more or less independently in the absence of external fields. Covalent, or atomic, compounds, therefore, are relatively volatile and boil at low temperatures. Ionic compounds are less volatile and have much higher boiling temperatures. All salts, since they are ionized and, hence, are electrovalent, boil at very high temperatures. Thus, the halides of the metals have boiling temperatures several hundred degrees higher than the boiling temperatures of the halides of the nonmetals carbon, phosphorus, silicon, and certain elements like tin, aluminum, and iron (page 339). We are inclined to say, therefore, that the latter are atomic compounds in their pure states (see Table XII). If volatility depends only upon the mass of the molecule, sodium chloride should boil at a lower temperature than stannic chloride or even carbon tetrachloride. That this is not the case means certainly that volatility is dependent, at least in part, upon the molecular structure of the compound. The structure of the molecules aids or hinders, as the case may be, in the separation of the molecules from one another.

Solubility.—Molecules that have strong external fields are generally less soluble than those with weak fields. Here, again, the deciding factor is the binding of the molecules together by

[1] We recognize the uncertainty attached here to the use of the term *molecule*. The word is used to represent the *particles* of which the substance consists, whether they be molecules or parts of molecules.

TABLE XII.—BOILING POINTS OF HALIDES
(Degrees Centigrade at 1 Atmosphere)

Element	Fluoride	Chloride	Bromide	Iodide
Sodium	1695	1490	1390	1300
Silicon	− 90	57	150	300
Boron	−101	18	91	210
Aluminum	800	180	260	350
Tin (stannic)	700	114	200	300
Arsenic (-ous)	63	130	221	400
Antimony (-ous)	.....	224	280	401
Bismuth	.....	447	453	
Titanium (tetra)	>400	136	230	>360

electrical forces which are not entirely satisfied within the molecules themselves. Covalent compounds should be more soluble, therefore, than those in which the valences are of electrostatic origin. All other conditions being equal, one should expect an atomic compound such as naphthalene to be more soluble in all solvents than an ionic compound such as sodium chloride. Since the external fields are weak in naphthalene, there is very little cohesion to be overcome in the separation of the molecules. In salt, however, the external field which is responsible for the crystalline form of the substances is very strong. Sodium chloride does not dissolve in benzene, or in any other solvents like benzene, because these substances do not weaken the electrostatic forces between sodium and chlorine ions. Neither should sodium chloride dissolve to any great extent in water or other solvents of high dielectric constants, unless the salt chemically combines with the solvent, or unless the solvent weakens the external fields of the ions, just as it does in promoting ionization. The effect of a medium upon the electrostatic force between two charges that it separates depends upon the dielectric constant of the medium. Thus, salt, like many other electrolytes, dissolves in water because water *does* have a high dielectric constant and fails to dissolve in other solvents because they have low dielectric constants. This matter will be discussed in greater detail in the next section of this chapter. Atomic compounds do not dissolve appreciably in water, as a general rule, although they may dissolve in benzene and many

other solvents of a similar character. These compounds, because of the absence of extensive external fields, should dissolve in *all* solvents. Their failure to dissolve in water may be caused by the association of the water molecules with one another. The association of the molecules of the solvent with one another crowds out molecules of the solute and often causes separation into two layers in the case of liquids. If both solvent and solute molecules associate, solubility of the solute in the solvent may be increased by the association of one kind of molecule with the other. In some cases, association may result in the formation of new kinds of molecules. Thus, the solubility of ammonia in water may be due in part, at least, to the combination of these two substances to form NH_4OH. Similarly, the solubility of many salts in water, and in other solvents, may be influenced by the formation of hydrates, such as $CuSO_4(H_2O)_5$ and similar compounds.

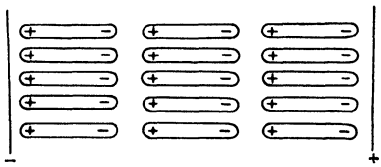


FIG. 120.—Water dipoles.

Dielectric Constant.—The dielectric constant of a substance is measured by comparing its effect upon the attraction between two unlike charges with the effect of some other substance, such as air. The effect of the medium that separates two charges is thought to be due to the orientation of molecules of the medium in the electrical field (see Fig. 120). Orientation means that all the molecules in the field will line up parallel to one another. When we think of this kind of orientation, we are thinking of the molecules as acting as dipoles. Naturally, only polar molecules—molecules that act as dipoles and, hence, possess electrical moments—are oriented in this manner. A molecular dipole is a molecule in which there is an excess of positive charge at one place and an excess of negative charge at another. A molecule of this kind consists of two "poles," a positive and a negative. We may think, then, of the dipoles as a line with a center of positive charge at one end and a center of negative charge at the other. Examples of such dipoles are found in the molecules of water and ammonia. There is no electrical moment in molecules, such as H_2, CCl_4, and CH_4, where the distribution of the charge is symmetrical. In water, in ammonia, and in other substances that possess high dielectric constants, the distribution of charge is

not symmetrical. There must be a greater accumulation of positive charge around one center in the molecule and of negative charge around another. The electrical moment of the dipole depends upon the extent to which these two centers are separated and upon the magnitude of the charges.

If molecular dipoles are brought between two point charges A^+ and B^-, they are oriented; *i.e.*, they arrange themselves in a "head-to-tail" series through the space that separates the charges. This orientation results in much the same effect as placing more plates in a condenser; more plates increase the capacity of the condenser. The attraction between A^+ and B^-

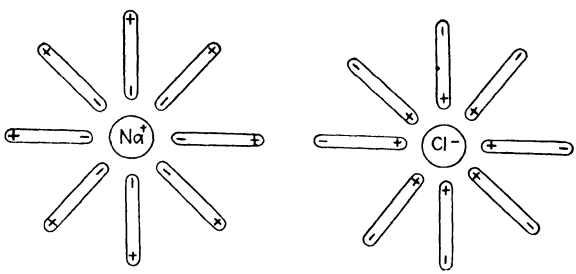


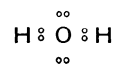
FIG. 121.—The separation of ions by molecular dipoles of a solvent.

is reduced, because of the orientation of solvent molecules. If the attraction remains the same, the charges on A^+ and B^- must be increased. This amounts to an increase in the capacity of the system.

When crystals of sodium chloride, or other ionic compounds, are mixed with a solvent, such as water, the electrostatic forces that exist between ions in the crystal are weakened by the orientation of the water dipoles between the ions. And since the forces upon which its structure depends are weakened, the crystal lattice dissolves. Since there can be no orientation of molecules of substances such as carbon tetrachloride and benzene, sodium chloride and other ionic compounds do not dissolve readily in such solvents. The external fields, which cause the ions to take definite positions in the crystal and cause such substances as sodium chloride to have low volatility and low solubility, maintain their full strength in the presence of solvents whose molecules are nonpolar in character. Hence, their crystal structure is maintained, and the substances do not dissolve.

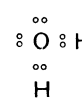
Thus, it appears that the solubility of a salt and its ionization are determined largely by the structure of the molecules of the solvent. Although some salts dissolve slightly in solvents of moderately high dielectric constants, such solutions do not necessarily reveal corresponding degrees of ionization. Our usual methods of determining the extent of ionization of a solute depend upon the movement of ions as well as their number. Even in aqueous solutions, the extent of ionization, as usually determined, is less than 100 per cent of the solute. We must conclude, therefore, that the solvent may weaken the forces between ions sufficiently to break down the crystal lattice without entirely overcoming these electrostatic forces. Only to the extent that the attraction of the ions of the salt for one another is overcome by the orientation of solvent dipoles do the ions act independently of one another and mix with the molecules of the solvent. Obviously, a solvent such as water which possesses a high dielectric constant will dissolve more sodium chloride per cubic centimeter and will permit the ions of sodium and chlorine to act more independently of one another than a solvent such as methyl alcohol which has a much lower dielectric constant (approximately 35). All electrolytes appear, therefore, more extensively ionized in water than in methyl alcohol. There may be as many ions in one solution as in the same volume of the other. But in water, the ions of the electrolytes have less attraction for one another and hinder one another's movements less than in alcohol.

External fields may result from covalent links within a molecule. Only in a relatively few kinds of molecules can one assume that the shared electron pair belongs equally to the two atoms. In most cases, one of the atoms is more electronegative than the other; hence, it more strongly attracts the electron pair and causes a displacement of the electrons in its direction. Thus, in the water molecule, which we usually represent by the following electronic formula

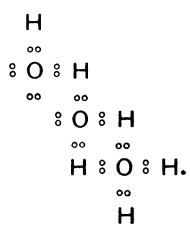


oxygen is certainly more electronegative than hydrogen. This displacement of electrons results in more or less electrical disturbance within the molecule. Oxygen becomes slightly negative

with respect to hydrogen, although the transfer of electrons is not complete and no ions are produced within the molecule. As pictured above, however, the distribution of the positive and negative charge in the water molecule is symmetrical. The centers of both kinds of charge coincide at the center of the oxygen atom. Such a molecule would not have an electrical moment and, hence, would not have an external field. If this were the true picture of the molecule, water should be a typically nonpolar compound; in particular, it should be very volatile, since it has a very low relative mass. Now, water does not have the properties of nonpolar substances. It boils at 100°C. and is, therefore, not very volatile, although its constituent elements boil at temperatures much farther below zero than its boiling temperature is above. These facts point to the presence of an external field for the water molecule and, hence, to an unsymmetrical distribution of the electrical charge within the molecule. For example, the molecule might have the following structure:

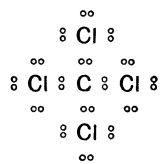


in which the negative charge of the particle is located at the center of the oxygen atom but the positive charge is centered at another point, which, as we have drawn the figure, would be somewhere below and to the right of the oxygen atom. This model of the water molecule is more in accordance with its behavior as a dipole. As such, it may orient itself with others of its kind in an electrical field. The high dielectric constant of water justifies this assumption. Still greater electrical disturbances may result when two or more molecules of water combine through coordinated covalences between the oxygen atom of one molecule and the hydrogen atom of another.



This tendency toward association reveals the external field of the water molecule. If water molecules had no external fields, they would not associate. It is this same external field that causes water to have a relatively high boiling temperature.

In the molecule of carbon tetrachloride, CCl_4, the chlorine atoms attract electrons more strongly than the carbon atom; hence, the electrons are displaced toward chlorine and away from carbon.

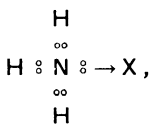


This means that chlorine becomes slightly negative with respect to carbon. The distribution of the charge is symmetrical, however, and the molecule does not have an electrical moment; it does not act as a dipole.

The methyl chloride molecule, CH_3Cl, contains only one atom of chlorine. Hence, this molecule is not symmetrical with respect to the distribution of its charges; the chlorine atom is slightly negative with respect to the CH_3 group. Methyl chloride, therefore, is more polarized and has a greater external field than carbon tetrachloride. Since the methyl group is much more electronegative than sodium, potassium, or other metals, it exerts a stronger pull upon the binding electrons than these elements. The electrons are not completely transferred to chlorine, as they are in sodium chloride, for example. For this reason, methyl chloride does not ionize and possesses, on the whole, the properties of an atomic compound. This means that the bond between chlorine and the carbon atom of the methyl group is covalent. The dielectric constant of methyl chloride, however, is larger than that of carbon tetrachloride or of methane. This condition is in keeping with the electrical disturbance in the molecule and the unsymmetrical distribution of electrical charge, which results because of the different electronegativities of carbon and chlorine.

Coordination compounds, on the whole, are more highly polarized than covalent compounds but much less than electro-

valent compounds. In the molecule of ammonia, for example, the nitrogen atom is more electronegative than hydrogen. Because of the presence of the unshared electron pair and because, perhaps, of the arrangement of the hydrogen atoms about the nitrogen atom in space, the charge is not symmetrically distributed about the atom of nitrogen. The positive and negative charges are centered at slightly separated points. The polar characteristics of ammonia become more apparent if we regard the molecule as a figure in three-dimensional space rather than a figure drawn on a sheet of paper in two dimensions. Ammonia, like water, therefore, is a polar compound, although it is certainly not an electrovalent compound. Consequently, as solvents, water and ammonia have many properties in common. This similarity is due, no doubt, in part, to the presence in each molecule of an atom which possesses at least one unshared electron pair. When this pair forms a bond with another atom, as in



greater electrical disturbance occurs, and a stronger external field results. The increase in the strength of the electrical field results because the centers of the positive and negative charges of the molecule are further separated. The NH_3 group becomes slightly positive toward X by sharing the electron pair with this atom or radical; the X atom or group becomes slightly negative by acquiring partial possession of these electrons, since it was neutral before it was attached.

Coordinated covalence produces greater electrical disturbances than normal covalence. Hence, coordination compounds resemble electrovalent compounds in many respects more strongly than covalent compounds do. Thus, compounds containing coordinated linkages possess higher dielectric constants and are slightly less volatile than similar compounds in which the linkages are formed by normally shared electron pairs. The differences in the effects of coordinated and covalences are most apparent in isomeric compounds. In many cases, it is possible to use

differences in the properties of such compounds to distinguish between the type of valence in different isomers.

Molecular Volume.—The molecular weight of a compound divided by its density gives the molecular volume. Since the atoms of an ionic compound are closely held together by electrostatic attraction, the molecular volume of such compounds is smaller than that of similar compounds in which the valence is due to the sharing of electrons. Coordination compounds possess smaller molecular volumes than similar covalent compounds, since each coordinate bond results in some electrical disturbance, which, in turn, produces greater external fields and stronger binding forces to pull molecules closer together.

MacLeod showed that surface tension and density are related as shown by the equation

$$\gamma = C(D - d)^4,$$

where γ is the surface tension, C is a constant, D is the density of the substance in question, and d is the density of its saturated vapor. This equation may also be written as

$$C^{\frac{1}{4}} = \frac{\gamma^{\frac{1}{4}}}{(D - d)}.$$

Sugden undertook to use this equation for the purpose of correlating the chemical composition of a substance with its density and surface tension. He multiplied the value of the fourth root of MacLeod's constant by M, the molecular weight, thus obtaining the equation

$$P = \frac{M}{(D - d)} \gamma^{\frac{1}{4}}.$$

P is called the parachor of the substance. The quantity $M/(D-d)$ has the dimensions of volume and, if d is small, becomes almost equivalent to the molecular volume M/D. Sugden determined the values of P for different (liquid) substances at temperatures at which the substances have the same surface tension. He found that the observed values of P could be calculated as the sum of constants for each of the atoms in the molecule plus the constants due to influences such as unsaturation, ring structure, and the general nature of the linkages

between the atoms. The value of an atom was found to be independent of its position in the molecule; and, hence, the parachors of position isomers were found to be identical. Sugden found the following effects for different kinds of valences and different ring structures.

Triple bond	+46 4
Covalent double bond	+23 2
Coordinated bond	− 1 6
Three-membered ring	+15 5
Four-membered ring	+11 6
Five-membered ring	+ 9 3
Six-membered ring	+ 7 7

The values of the parachors of a few of the elements studied by Sugden are as follows:

Carbon	4 8
Nitrogen	12 5
Oxygen	20 0
Chlorine	54 3
Bromine	68 0
Iodine	91 0
Hydrogen	17 1
Phosphorus	37 7

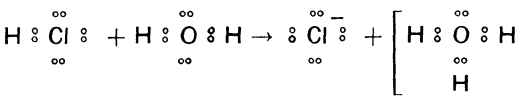
The parachor of a compound can be calculated from the constants of the different atoms and the types of valence in its molecules. The constants of the elements as given above are for combinations in which they are united by normal covalent linkages of single electron pairs. Thus, the parachor of methane is calculated as $4.8 + (4 \times 17.1) = 73.2$. That of the unsaturated hydrocarbon ethylene is

$$(2 \times 4.8) + (4 \times 17.1) + 23.2 = 101.2.$$

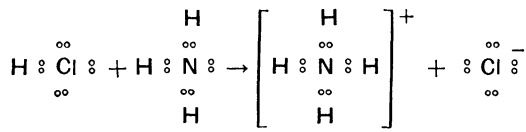
The calculated values agree with the parachors determined experimentally by Sugden within limits of approximately 1 per cent. These results covered several hundred organic and a few inorganic liquids.

Since the parachors are determined for liquids at temperatures usually far below those at which the vapor state exists, the volume represented by $M/(D-d)$ must be regarded as an "extrapolated molecular volume." As such, it serves very well for comparisons of various structures and types of linkage.

The Oxonium-ion Theory of Acidity.—We have become accustomed to measuring the strength of an acid or base in terms of its ionization. Thus, hydrochloric acid is called a stronger acid than acetic, because the solution of hydrochloric acid is a better conductor of electricity, has a lower freezing temperature, a higher boiling temperature, and greater osmotic pressure than a solution of acetic acid of the same concentration. Now, hydrogen chloride in the pure state appears to be a covalent compound; it is very volatile, it dissolves in benzene, and it does not conduct the current. But in water hydrogen chloride is very highly ionized. It has been suggested that the following reaction occurs when this substance is dissolved in water:



This means, of course, that free hydrogen ion does not exist in solution; instead, the hydrogen ion either remains attached to the anion of the original acid molecule, or this bond is broken, and the hydrogen ion becomes attached to $H:\ddot{O}:H$, forming $H:\ddot{O}:\overset{+}{H}$, which is called an *oxonium ion.* This ion closely resembles the ammonium ion and is produced in the same manner.



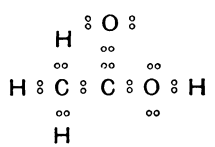
Hydrogen chloride does not ionize in such solvents as benzene, because the molecules of such solvents contain no atoms that possess unshared electron pairs, as do the atoms of oxygen and nitrogen in water and ammonia molecules. Hence, the hydrogen atom remains attached to the anion of the original acid molecule, since there is no possibility of its combination with the molecule of the solvent.

In aqueous solutions, many strong acids, such as HCl, HBr, HNO_3, and $HClO_4$, are almost equally strong. The strength of the acid to which we refer here, of course, is that which is

indicated by the ionization constant of the acid. This condition of equality is probably due to the fact that, in water, the reaction between each of the acids and water is practically complete in each case. Hence, in each solution, approximately the same ionic conditions exist. If the concentrations of the solutions of the different acids are of the same normality, there is approximately the same concentration of oxonium ion in each. This ion, therefore, contains practically all the protons of the solution. It is this ion in each case which acts as the real acid toward basic substances which are added in neutralization reactions. From every point of view, therefore, these acids may be regarded as possessing almost equal strengths in aqueous solutions.

Let us define such substances as water and ammonia as *basic* solvents. The molecules of these substances are distinguished by their ability to combine with protons. In this respect, they differ from benzene, carbon tetrachloride, and similar solvents whose molecules do not possess this ability.

In weaker acids, the bond that unites hydrogen with the anion of the original molecule is stronger than the bond between hydrogen and chlorine in hydrogen chloride. It is more difficult, therefore, for the oxygen atom of the water molecule to remove the hydrogen atom by forming a coordinated bond. Hence, more hydrogen ions remain attached by their original bonds and fewer combine with the oxygen atom of the water molecule. In aqueous solutions of acetic acid, for example the bond uniting hydrogen and oxygen



is stronger than the coordinated covalence of the oxygen-hydrogen bond in the oxonium ion. Relatively few ions, therefore, are produced in an aqueous solution of acetic acid. Acetic acid is a weak acid as measured by its ionization constant. The older ionization theory explains the small ionization constant of this acid by assuming that an *equilibrium* exists between a small number of hydrogen and acetate ions on the one hand and a large number of undissociated molecules of the acid on the other.

The difference between this point of view and our present concept of ionization is essentially one that involves the manner in which ions are produced in the solution. The Arrhenius theory assumed that a certain number of molecules spontaneously dissociated until the conditions of equilibrium were established. The new theory assumes that ions are produced only to the extent that molecules of the solvent combine with the hydrogen ions, thus breaking the bonds that held the hydrogen in its original combination in the acid molecule. Thus, instead of free hydrogen ions (protons), the solution contains oxonium ions $(H_3O)^+$. If an atom of chlorine is introduced into the acetic acid molecule, replacing one of the hydrogen atoms of the methyl group, the bond between oxygen and hydrogen in the acid molecule appears to be weakened, since this acid is much more strongly ionized than acetic. As a result of the decreased strength of this bond, more hydrogen combines with the molecules of water, and more ions are formed. Monochloroacetic acid is said, therefore, to be stronger than acetic acid. In terms of the oxonium theory, the solutions of monochloroacetic acid must contain more H_3O^+ ions than an equally concentrated solution of acetic acid. The greater concentration of H_3O^+ ion means that the introduction of a chlorine atom into the acetic acid molecule weakens the bond between the hydrogen and oxygen atoms of the carboxyl group of the acid molecule. This permits more hydrogen ions to combine with the molecules of the solvent.

If, on the other hand, some basic group such as the NH_2 radical replaces one hydrogen atom in the methyl group, the hydrogen is even more firmly held in the acid molecule than it was in the original acetic acid molecule. This decreased strength may be due to the combination of the hydrogen ion, when once the bond between this atom and the oxygen atom of the acid is broken, with the nitrogen atom of the NH_2 group.

The amino-acids are usually regarded as a mixture of two forms in equilibrium. In the case of glycine, for example, these forms are the so-called *undissociated* acid, CH_2NH_2COOH, and the *ionic* form, $NH_3{}^+CH_2COO^-$. The evidence in favor of the existences of these two forms strongly indicates the two possible linkages by which the hydrogen atoms may be held within the acid molecule. To the extent that it is held by either

of these linkages, of course, it cannot combine with molecules of the solvent. The formation of ions is thus rendered less likely in a solution of aminoacetic than in one of acetic acid. The former, therefore, is weaker than the latter.

Let us now consider briefly the matter of acidity from a different point of view. There are other ways of measuring and expressing the strength of an acid than in terms of the number of ions that it produces in solution. We might measure it, for example, by its ability to furnish hydrogen ion for the reaction with some basic substance. Let us define a base as a substance that reacts with hydrogen ion; ammonia is a base because it reacts with hydrogen ion to form ammonium ion. Many other substances, which were not formerly considered as bases, must be so considered on the basis of this definition; thus, water is a base because it combines with hydrogen ion to form oxonium ion. Now, if an acid is dissolved in a basic solvent, such as ammonia or water, in which the hydrogen ion almost completely combines with molecules of the solvent, less hydrogen ion is available for the reaction with a second base, such as an indicator. On the other hand, if the same acid is dissolved in a nonbasic solvent, such as benzene, whose molecules contain no hydrogen-accepting atoms, all the hydrogen ions remain attached to their original acid molecules. When a basic indicator, or any other base, is added, the reaction of the hydrogen with the added base is not hindered by the competition of the unshared electrons of the solvent molecule; there is none of these. One competitor for the hydrogen ion is absent, and so the hydrogen either combines with the molecules of the added basic substance or remains attached by the bonds that form the acid molecules in the pure state. The only possible reaction is that between the undissociated acid molecule *HA* and the basic molecule *I*.

$$HA + I \rightarrow IH^+ + A^-.$$

Thus, the extent of this reaction depends entirely upon the relative strengths of the H—A and the I—H linkages. The latter is the same for all acids. Hence, acids that appear equally strong in a basic solvent may show individual differences in a nonbasic solvent. Hantzsch has shown that these differences are very real. He finds that acids such as HCl, HNO_3, and

$HClO_4$, which are approximately equally strong in water, are very different in nonbasic solvents. These differences are demonstrated, of course, by the reactions of the different acids with basic indicators. From this point of view, an acid that appears strong in water (by this means of measuring strength) may be even stronger in nonbasic solvents, such as benzene. Furthermore, acids that are weak in water may be fairly strong in other solvents.

Many other factors enter into the determination of acidity. We have pointed here only to a very broad view of the direction in which our modern theories of electrolytic dissociation are leading us in the study of acidity. Our chief interest is to point out the part that the valence forces prevailing in the solutions of different substances play in the determination of the character of the solution. One of the most important of the other factors, no doubt, is the dielectric constant of the solvent.

This treatment of acidity has revised somewhat our ideas concerning acids and bases. Any substance that accepts protons is a base. A substance that can furnish the proton to the base is an acid.

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Many of the books referred to in Chaps. X to XI contain chapters devoted to the various problems of chemical constitution and structure.

CHAPTER XIV

THE NEW QUANTUM MECHANICS

The Defects of the Bohr Theory

Bohr's theory of atomic structure was destined for only a brief period of supremacy. With the help of the original quantum theory of Planck, with which it was intimately associated, it succeeded in producing a rather general distrust of the wave theory of light and furnished a reasonable basis for the study of the simpler parts of the spectra of the elements. Bohr's theory soon became, however, the subject of severe criticism. There developed a growing lack of confidence in its ability to explain fully all the problems connected with the structure of the atom. New ideas were sought.

The Bohr theory has not been discarded entirely; the fundamental concepts of the theory have been retained. As nearly as it is possible to have a model based upon the new treatment, the Bohr model is still acceptable in most of its details. But the present methods of formulating and expressing atomic theory are so radically different from the old that they can scarcely be called modifications. They are as bold and revolutionary in the advances that they make as Bohr's assumption of nonradiating orbits was in its day.

Among the many defects of the Bohr theory, one stood out as, of course, most important of all to the chemist. The attempt to correlate the Bohr theory with chemical behavior soon showed that the explanation of chemical reactions requires something more than the original form of this theory could provide. Although it went a long way toward explaining the valences of the different elements and their periodic relations, the theory left many problems unsolved. Why are the valences of fluorine, for example, not the same as those of the other halogens? For fluorine does not show the combinations that other halogens do in compounds such as $NaClO$, $NaClO_2$, $NaClO_3$, and $NaClO_4$.

Oxygen does not have the positive valences of four and six which characterize the other elements of its group. The shared electron pair has proved very useful in dealing with the valences of elements in nonelectrolytes and weak electrolytes. But to say that it is, or could be, a physical reality is to claim more than is permissible even in accordance with the model of the Bohr atom. If an electron pair joins two atoms, then it must simultaneously belong to two nuclei. The electrons must revolve around both nuclei and must spend, presumably, a part of their existence in a quantum orbit of one atom and the remainder of the time in an orbit of the other. This view necessitates a rather complicated and uncertain state of affairs, especially as regards the energy states of the electrons. Furthermore, there is a great deal of uncertainty as to the mechanism of the doublet. Just how are two electrons united in the pair that is shared by two atoms? It was assumed, of course, in the original theory, that they were tied together in some way through the magnetic fields which each produced because of its rotation upon an axis. Yet it was exceedingly difficult to explain just how this magnetic effect could be maintained if the two electrons revolved about the nuclei of the two atoms. And so, although there seemed to be no sound physical explanation of the electron pair, the chemist used the idea as the only means by which the Bohr theory could be made to fit into an explanation of the mechanism of the reactions that occur between atoms. The new treatment of atomic mechanics, with which this chapter deals, fortunately does not render impossible the concept of the shared electron pair. On the other hand, it strengthens the position of this concept of valence (page 310) by providing a sound and reasonable explanation of the bond for which the suggestion of the shared electrons was first offered.

Turning now to the physical aspects of the problem, we find even more serious defects of the Bohr theory. Better to understand the difficulties that were encountered in all attempts to extend the theory, it may be well to review briefly at this time the conflict between the classical and the quantum theories of radiation.

An electron revolving in its orbit is a simple case of an electrical oscillator. During a revolution, the electron is displaced

(vertically, as shown in Fig. 122) more and more as it revolves, until the displacement reaches a maximum at B, whereupon it decreases again to zero at C. As the electron returns to its original position at A, the displacement again attains a maximum at D and again decreases to zero when the electron finally arrives at A. According to classical mechanics, the electron should emit radiation that has the same frequency as the frequency of its own rotation in the orbit, provided that the force that restores or urges the electron back toward its equilibrium position is proportional to the extent of the displacement. If, on the other hand, the restoring force varies with some power of the displacement, the

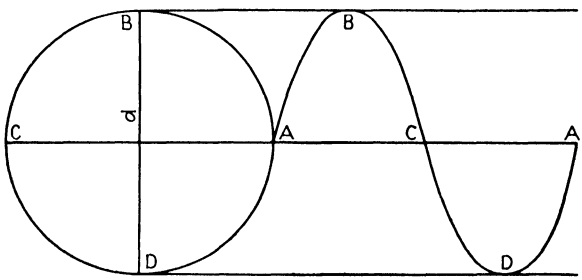

FIG. 122.

radiation no longer consists of a single frequency but is made up of several, all of which are multiples of the fundamental frequency. On this basis, we should expect, therefore, that all the frequencies of radiation arising from the oscillations of an electron should be simply related to a definite fundamental frequency. The complexity of spectral data, to which we have often referred, is proof enough that no such simple relation exists. Radiation is emitted from an atom in frequencies that bear no relation whatsoever to the rotation of electrons in their orbits.

The laws that govern the motion of electrons in their orbits of the Bohr atomic model are those of classical or Newtonian mechanics. As we have shown in the preceding paragraph, the frequencies of the radiation according to this system of mechanics should be simple multiples of a fundamental frequency. In other words, the frequency emitted should be a simple multiple of the frequency of the electron in its orbit. By applying the same system of mechanics, Bohr calculated the radii of electron orbits and the corresponding values of the energy levels of the

atom. And yet, the boldest and most important feature of his theory postulates that the radiation emitted by an atom depends upon the difference in the energy values of two orbits and is independent of the frequency of the electron's rotation in either orbit. This principle appeared necessary, since the frequency of each spectral line can be represented as the difference between two terms (page 234).

Although classical mechanics fails completely in explaining the general spectrum, it can be applied successfully to radiations of very long wave lengths. According to the Bohr theory, such wave lengths are emitted when transitions occur between quantum orbits of large radii. The frequency of the electron's rotation is relatively small in these large orbits. Hence, the frequency of the radiation *can* be, at least approximately, equal to the frequency with which the electron rotates in one of these orbits. This agreement with the requirements of classical mechanics in dealing with long wave lengths is known as the *correspondence principle.*

Ordinary mechanics also makes the intensity of radiation which attends the rotation of an electron in its orbit dependent upon the square of the amplitude of the displacement of the electron. Now, of course the intensity of the radiation is no more related to the frequency of the oscillation of the electron than is the frequency of the radiation. Furthermore, an electron that is continually changing its direction (Fig. 122) must, according to classical mechanics, radiate continuously and not discontinuously, as spectral lines indicate. Thus, an electron that is continuously losing energy by radiating should "spiral" down toward the nucleus, instead of dropping in this direction by definite "jumps" or transitions in its energy states.

Bohr believed that he was justified in altering the application of mechanics to his atomic model by assuming nonradiating states of the electron. But just how an electron could rotate without radiating energy was never explained by the Bohr theory. The assumption was justified, because it permitted the calculations of results that agreed with observations, although there was no sound basis for it. The fact remains, however, that Bohr's theory was in conflict with the very principles of mechanics upon which it was based.

In further submitting it to critical examination, we find that the theory of Bohr was best known for its explanation of the frequencies corresponding to the different spectral lines of hydrogen. Many difficulties were encountered, however, when an attempt was made to extend the theory so that it would explain optical and x-ray spectra of other elements. As a matter of fact, the difficulties arose even before the spectrum of hydrogen was completely disposed of. The hydrogen spectrum reveals a so-called fine structure with which the Bohr theory could not correlate without the introduction of rather improbable modifications and then only with questionable success. The spectral lines of neutral helium were also a serious stumbling block, although ionized helium was found to give a spectrum that could be fitted into the Bohr theory with considerable success. The success of the theory in the latter case was probably due to the fact that this ion, having lost only one electron, resembles the simple hydrogen structure in which a single electron revolves around the nucleus.

Bohr attempted to deal with other atomic systems, particularly those of the alkali metals, as simple hydrogen-like groups with one electron removed some distance from the rest of the atom. The orbit of this electron was supposed to penetrate the orbits of other electrons, but for the most part it was thought to lie far out and beyond these orbits. This idea was responsible for the introduction of values of the effective quantum number (n_e) in place of the usual values of n for the outer or so-called optical electron (page 276). Sommerfeld, Pauli, and others attempted to solve the problem by assigning four quantum numbers to each electron in the atom. In this way, they attained some success in explaining the multiplets of lines which occur in most spectra. But even this series of quantum numbers did not explain adequately the fact that there are evidently some states, as shown by spectral data, for which quantum numbers that are halves of whole numbers (such as $\frac{1}{2}$, $\frac{3}{2}$, etc.) must be assigned. It was also necessary to assume certain principles of selection, which controlled the character and number of electron transitions from one quantum state to another. More satisfactorily to account for these effects and for the multiplicity of terms in spectral data, magnetic quantum numbers were introduced to describe the

energy states of individual electrons. The system of quantum numbers thus derived called for a radically different quantum treatment of the atom as a radiating unit of matter and allowed a much more reasonable and complete distribution of electrons among the different energy levels of the atom. But they did not solve the whole problem.

Further trouble developed when attempts were made to use the theory in explaining the so-called anomalous Zeeman effect and certain other features of radiation, such as intensity and polarization. Because of all of these failures of the original theory, and in most cases of the later modifications also, Bohr's theory appears to have been a somewhat inconsistent mingling of classical mechanics and Planck's quantum theory. It was eminently successful in dealing with the simpler problems of spectral data and in providing a qualitative picture of the source of the radiation arising within the atom. It failed when applied to complex spectral problems. It also failed to provide an exact description of the operation of the mechanism by which energy is radiated and absorbed.

The Bohr theory did not explain just how and when radiation is emitted. The assumption was made that radiation is the result of a transition of an electron from one quantum orbit to another. But the theory could not show whether the radiation of energy occurs before, during, or after the transition. If the radiation occurs before or during a transition, then the final position of the electron is determined before the "jump" is completed or even before it starts. Some determining power, on the part of either the electron or some unknown force, must be assumed. Such an assumption is absurd. If radiation occurs after the transition, the equal absurdity arises of having an electron occupy a level to which its energy does not correspond. Furthermore, if radiation occurs after the transition, there can be no cause for the transition, which is assumed to be the result of a decrease in energy. If the electron jumps before a change in its energy occurs, there can be no explanation of the particular jump that is made. This condition would resemble the hypothetical case in which a boy jumps 10 feet and upon landing proceeds to spend the energy required to carry him through the air.

It is too much to expect that a perfect model of the atom can be conceived. As such, the Bohr atom was probably as satisfactory a model as can be made. But how far short of perfection this model really was can be seen readily from the foregoing considerations. All of the contradictions to which we have called attention between theories based upon classical mechanics and the observable facts of atomic behavior indicate that something is wrong. It appears that classical mechanics can be applied to machines and to large-scale phenomena but that for atomic systems it somehow falls short of meeting the situation completely. A new system of mechanics specifically adapted to the problems of atomic mechanics appears to be demanded. The new system which has developed in response to this demand is called the new quantum mechanics. It is given the name of quantum mechanics since it is based fundamentally upon the theory of energy quanta as opposed, for example, to the wave theory of radiation. It is called the new quantum mechanics because of its departure from Bohr's point of view in which he tried to reconcile classical mechanics with quantum theory. In the next section of this chapter, we turn our attention, therefore, to the new mechanics of the atom with the hope that it may throw more light upon many of the old problems. Let us expect to find that it is a step in the direction of a final solution rather than a complete attainment of the goal itself.

The New Quantum Mechanics of Atomic Systems

Introduction.—The revolt against the Bohr theory has taken various forms and has been headed by different leaders. But on the whole the different points of view appear to lead to a common ground of understanding. Although they differ in the course taken, they arrive at the same destination. All these theories are by their very nature difficult to interpret, except in terms of the mathematical language in which they are expressed. For this reason, we shall be content to present here the results that they yield and the philosophical considerations and part of the evidence upon which they are based. We shall not attempt the complete formulation of the theories themselves.

The theories may be classified under two heads: (1) the so-called matrix theory, which was developed by Born and

Heisenberg; and (2) the wave mechanics of de Broglie and Schrödinger. These differ in their methods of attacking the problem, but their points of view are much alike. Both theories discard atomic models. The concepts of atomic nuclei and quantized electron orbits were necessary for the Bohr theory. In its original form, at least, this theory was based upon a model that was relatively easily visualized. The extent to which this model had to be revised, as the theory was extended, fully indicates its deficiencies as an actual picture of the atom. At no time, of course, was it regarded as a model whose parts could be placed under observation. Devices measuring distance and time, such as meter sticks and clocks, could never be applied to its flying electrons. It was also obviously impossible to define the position and velocity, or the momentum, of any particular electron simultaneously, although this was exactly what the Bohr theory attempted to do. If the momentum is accurately defined, the electron could not be given a definite position, even if it could be observed. Or if the electron were given a definite position with reference to a system of coordinates, the momentum could not be defined without the introduction of an error infinite in its extent. The reason for this state of affairs may be explained as follows: To observe an electron with the purpose of determining its position, the electron must be illuminated. In illuminating it, we cause it to collide with light quanta and to recoil with a velocity depending upon the frequency of the radiation by which we had hoped to observe the particle. During the attempt at observation, therefore, the electron would be given kinetic energy which would cause it to be displaced from the position where it was previously located. Now, to observe an electron, wave lengths that are smaller than the dimensions of the particle itself would have to be used; and since the electron is extremely small, very small wave lengths, indeed, would have to be employed. But such waves would possess very great frequencies and would represent very large quanta of light energy; and hence, an electron would recoil from a collision with one of these quanta with a very high velocity. Since the momentum of the body is proportional to its velocity, the use of high-frequency radiation to define more accurately

the body's position causes an extremely great change in its momentum.

The new theories are interested only in observable atomic phenomena, which can be measured externally and which do not require the impossible devices that would have to be used for the measurements of dimensions within the atom. Since we cannot measure time and space within the atom, it is doubtful if they have any meaning as so applied. Time and distance have meaning only when we can tell how they are measured in comparison with other times and other distances. The theory of relativity raised serious doubts concerning our previous ideas of time and space as applied to objects in a system that embraces the whole universe. The newer theories of atomic structure raise the same questions concerning matter at the other end of the scale—within the atom. Born, Heisenberg, Schrödinger, Jordan, Dirac, and others look upon the atom as a whole, rather than as a dissectible system of several parts. They find for this system certain observable phenomena, such as the frequencies of the radiation that it emits, the heats of its chemical combinations, etc. They have used these data in an endeavor to find mathematical forms of reasoning which permit the results of such observations to be calculated theoretically. Their reasoning explains their observations, but the method of arriving at the explanations cannot be followed by strict and specific interpretations of the mechanical behavior of the system or any of its parts.

This new form of the theory does not discard all of the concepts of the older points of view. We may still think of the atom as a solar system if we wish, but we need not bother ourselves with the locations of the planetary electrons or their orbits. We may keep our notions of the different quantum states of the atom. We may still look upon radiation and absorption of energy as due to transitions of electrons from one quantum state to another. But we are not concerned with the exact physical description of either radiation or absorption. Instead of dealing with such phenomena as individual occurrences, we have learned in the new quantum mechanics to deal with them by statistical methods. Thus, instead of treating specifically the change of energy that accompanies a transition from a third to a second quantum orbit, we consider such a transition in terms of its

probability as compared with an infinite number of transitions of a similar character that may occur. Instead of dealing with the shared pair of electrons in a covalent linkage and fixing them exactly in position between two atomic nuclei, we must consider the probability that the electrons will occur in this position instead of the infinite number of other positions that they may occupy. The application of statistical methods also implies that we cannot consider the behavior of a single atom. We must deal with large numbers of atoms, and the probability that is determined must be regarded as the probability that electrons in one or more atoms of this number will act in a certain manner.

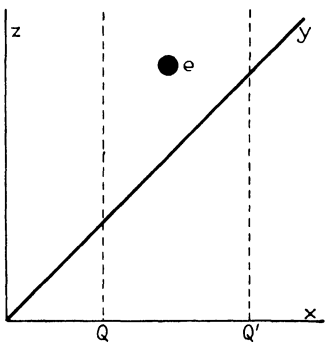

FIG. 123.—An electron's position or displacement is defined in terms of distances along the coordinates x, y, and z.

Matrix Mechanics.—In classical mechanics, we assign to the electron definite momentum and definite displacement in some system of coordinates whenever we speak of it as a part of an atomic system or as an isolated individual. The momentum p of the electron is determined by its mass and velocity. Its displacement is defined with reference to a certain system of coordinates as shown, for example, in Fig. 123. In the discussion that follows, we shall refer, generally, to displacement with reference to a single coordinate x in order that the problem may be simplified as much as possible. From the displacement and velocity of an electron at one instant of time, we are accustomed to predict the exact position and velocity of the same particle at some future time. This is what we do when we assign the electron an orbit that is definitely oriented in the space occupied by the system of which it is a part. When we treat the problem of the electron and its behavior within the atom by the methods of the new quantum mechanics, we decide first of all that simultaneous assignments of momentum and position to the electron cannot be made. For a given position, it is possible to say only that the velocity, or the corresponding momentum, lies within certain limits pp', the range of which depends upon the exactness

with which the position is defined. Likewise, for a definitely stated velocity, *i.e.*, stated definitely as within certain limits, the position is defined not as q but as within the limits qq'.

Recognition of these limitations in atomic mechanics led Heisenberg, in 1925, to develop a new system of mechanics, which because of its use of matrix algebra is called matrix mechanics. Heisenberg's purpose was to derive equations by means of which determinations could be made of the energy levels of the atom and of the intensities and frequencies of spectral lines. The equations may be regarded as dealing with the motions of electrons which in terms of the electromagnetic theory act as "virtual oscillators," producing the frequencies and intensities that are observed.

$$q = \begin{vmatrix} A_{11} & A_{12} & A_{13} & A_{14} & A_{15} \\ A_{21} & A_{22} & A_{23} & A_{24} & A_{25} \\ A_{31} & A_{32} & A_{33} & A_{34} & A_{35} \\ A_{41} & A_{42} & A_{43} & A_{44} & A_{45} \\ A_{51} & A_{52} & A_{53} & A_{54} & A_{55} \end{vmatrix}$$

FIG. 124. A matrix of q elements.

Confining our attention to the problem of a single particle which moves along one coordinate only, the displacement q of the particle at a given instant of time can be given by an equation such as

$$q = A_{nm}e^{2\pi i\nu_{nm}t},$$

in which ν is the frequency that corresponds to a transition from the nth to the mth energy level and A represents the corresponding amplitude or displacement of the virtual oscillator. Instead of employing individual values of q, Heisenberg dealt with q matrices. A matrix of this kind is an array or set of q terms or elements which are closely associated and which can be represented by a single symbol. A typical q matrix is shown above (Fig. 124).

This matrix can be continued indefinitely in the two directions indicated. The elements A_{11}, A_{22}, A_{33}, A_{44}, etc., lie on a diagonal line running through the matrix. These are the elements that correspond to the stationary or nonradiating states of the atom. There is, of course, no radiation when the designated energy levels are the same, as they are, for example, in the A_{22} element. The element A_{21} corresponds to the spectral line that is emitted because of a transition between the second and first energy

levels. Similarly, the A_{31} element corresponds to the spectral line that results from transitions between the third and first energy levels; and the A_{32} element, a transition between the third and second levels. Elements below the diagonal correspond to lines in the emission spectrum. Elements above correspond to lines in the absorption spectrum. Thus, the A_{12} element corresponds to a line in the absorption spectrum which is produced by a transition from the first to the second level. Although a single element of the matrix represents a single possible kind of transition, it will be noted that the incorporation of the element in the set of elements indicates that the single type of transition is not to be considered alone. It must be considered only as a single possibility out of a large number of other possibilities which are represented by the other elements of the matrix. Since A represents the amplitude of the oscillator, it is an intensity factor. Interpreting intensity statistically, this means that A is a measure of the probability that the indicated transition will occur or will occur in a certain fraction of the atoms (out of a great number) at one time. A matrix, such as the one shown, furnishes a means of recording the frequencies of the observed spectral lines and their intensities. This alone, and aside from the value of the method as a means of studying atomic structure, is a very worth-while feature.

Let us consider the case of an atom in an excited state. An electron has been displaced from its normal energy level to one farther removed, and the atom therefore is in a position to radiate energy. Let us first write an expression for the energy of this particle, using the terms of the older theory. The problem of a particle that acts as a linear harmonic oscillator may be treated by Newtonian, or classical, mechanics as follows. The total energy of such a particle can be expressed as the sum of its kinetic and potential energies. Its kinetic energy is given by the equation

$$E_K = \tfrac{1}{2}mv^2.$$

Its potential energy can be defined as a function of the single coordinate q along which the particle moves. If k is the restoring force per unit of displacement (along the coordinate), the potential energy can be expressed by the equation

$$E_P = \frac{kq^2}{2}.$$

Now, the value of E_K can also be expressed by an equation in which the momentum p is substituted for mv.

$$E_K = \frac{p^2}{2m}.$$

Hence, the total energy E_T can be expressed as a function of q and p.

$$E_T = \frac{p^2}{2m} + \frac{kq^2}{2}.$$

Using this equation for the total energy of the electron and introducing the equation that defines the quantum condition of the Bohr theory,

$$\oint pdq = nh,$$

the energy state of the oscillator is defined as

$$E = nh\nu.$$

Now, treating the same problem by Heisenberg's system of matrix representations, we recognize first of all that we cannot give a definite value to q. If an atom is in a position to radiate energy, it is impossible to determine into which energy level the electron may fall; and hence, the frequency of the corresponding spectral line is uncertain. We must deal with all the possible transitions between energy levels instead of a single transition. To do this, we use the matrix of q terms instead of single, finite values of q in calculating the energy state of the electron or virtual oscillator. To express the total energy of the particle, we consider it as acting in the manner of a simple harmonic oscillator and use the equation

$$E_T = \frac{p^2}{2m} + \frac{kq^2}{2}.$$

in which p and q matrices are used instead of determinant values of p and q. From the matrix of q elements (page 363), it is possible to derive a matrix consisting of q^2 elements. Each element in the latter is calculated from those of the q matrix in accordance

with the rules of matrix algebra. Similarly, matrices of p and p^2 elements can be formulated. From the p^2 and q^2 matrices, it is now possible to construct a matrix corresponding to a form of the equation that defines E_T, the total energy of the electron.

To determine the value of E_n, the energy corresponding to the state n, a new quantum condition complying with the laws of matrix algebra must be introduced. Heisenberg found that the following condition could be used to calculate results that agree with experimental observation:

$$pq - qp = \frac{h}{2\pi i},$$

in which $i = \sqrt{-1}$. The introduction of this condition in place of the Bohr quantum condition gives the following equation for E_n:

$$E_n = (n + \tfrac{1}{2})h\nu.$$

Heisenberg's quantum condition illustrates one of the differences between ordinary and matrix algebra. Since we have expressed the total energy of an electron as a function not of the ordinary, numerical values of q and p, which cannot be determined, but of p and q matrices, our calculations must be based upon the rules of the latter kind of algebra. The theory of matrices is a phase of algebra that was developed by Cayley. This branch of algebra has its own rules of addition, subtraction, multiplication, etc., and these differ from the rules of ordinary algebra. Multiplication in matrix algebra is not commutative. This means that the product of pq, for example, is not equal to the product qp, if these symbols represent the corresponding matrices instead of ordinary numerical values. A condition of this kind means that the symbols of a matrix represent operations rather than quantities and that the operations must be performed in the same order if the same results are to be obtained. The case is somewhat similar to the rule that a certain order of operations must be carried out in bringing about a definite chemical reaction. Thus, we do not get the same result when we mix iodine with water and then add phosphorus as we do when we first allow phosphorus to react with iodine, forming phosphorus tri-iodide, and then add water to hydrolyze the product, forming hydriodic acid.

Further attempts on our part to elucidate the application of matrix principles are probably not worth while. To readers who are already familiar with the theory of matrices such attempts would appear somewhat elementary, and for those who are not familiar with them we should be obliged to describe the entire development of a very difficult and strange phase of mathematical reasoning. It is evident that the method is one that treats the subject in a purely mathematical fashion and aims only at the calculation of results that can be compared with those actually observed in studying the atom's behavior. Heisenberg's treatment of quantum mechanics does not make use of electron orbits and electron velocities. Instead of these, it deals with the frequencies and intensities of the lines of the atom's spectrum. Heisenberg is concerned, therefore, with definitely observable values. From these he determines the different energy states of the atomic system by mathematical reasoning. His methods of arriving at the results in no way involve a physical basis upon which the differences in energy states can be explained. His theory does not attempt to describe the atom. Because it does not attempt to do this, it is not handicapped or encumbered by any of the many limitations that are encountered when one attempts, as Bohr did, to locate electrons within an atom with respect to a system of coordinates and to define the velocities of these electrons in terms of atomic space and time, which cannot be measured.

The Principle of Indeterminism and the Probability Interpretation.—The most significant idea of matrix mechanics is to be found in a deduction made by Heisenberg and upon which his whole theory, or system of mechanics, is based. This is the so-called principle of *indeterminism.* We have already suggested (page 362) that there is a certain indeterminism in the simultaneous definition of the position and momentum of an electron. But the principle is sufficiently important to deserve further discussion.

If q is one coordinate by which the position of an electron is defined, and if p is the electron's momentum, the mathematical matrix demands that qp is not equal to pq. Instead, $pq - qp$ is equal to a definite numerical difference $h/2\pi\sqrt{-1}$. This difference means that p and q cannot be defined accurately at

the same time. If p has a definite value, then q must have an uncertain one. In this case, the value of q can be expressed only within certain limits, such as q to q' or dq. If the position of the electron with respect to the coordinate is known or could be determined, then p could be expressed as somewhere within the limits p to p' or dp. If the measurement of p lies somewhere within the range dp and that of q somewhere within the range dq, Heisenberg states that the product $dp \times dq$ is of the order of h, Planck's constant. If dq is small, dp is large, and vice versa. If one is zero, the other is infinity; if the electron's position could be stated with zero error, then the error in the value of p would be infinitely great. This is the principle of indeterminism.

Let us apply, by way of analogy, the indeterminism principle to the possible reactions that can occur in a mixture of equal numbers of several kinds of atoms. We may think of this mixture as containing atoms of chlorine, carbon, hydrogen, oxygen, helium, nitrogen, sulfur, and sodium. Now, let us assume that atoms of the different elements may combine either two at a time or in all other possible ways. The events that occur in the mixture bear no relation whatever to events that have gone before. It is impossible, therefore, to determine just what a given atom will do, although we may have a complete history of that atom's behavior up to the time it is placed in the mixture. A great many different combinations are possible. The combination of hydrogen atoms, of one hydrogen and one chlorine atom, two hydrogen and one oxygen atom, and many other combinations involving hydrogen and the other elements result in the formation of several different kinds of molecules. When all reactions have ceased, however, we shall find a great many cases of certain combinations, a few of others, and perhaps none of others. It would be impossible to say of one certain hydrogen atom, for example, that it would combine with one certain chlorine atom. It would be impossible even to determine that this one hydrogen atom would combine with chlorine at all. It would be possible, however, to determine the definite probability that it would combine with some chlorine atom. There is even the definite probability (which is small, of course) that this atom will combine with one certain chlorine atom. When the reactions ceased, we could measure the distribution of the combi-

nations, and in this way we could test the precision of our predictions.

For like reasons, we cannot state definitely that an electron within an atom will do thus and so, that it will move from this orbit to that orbit, that it will be here or there. We can still think of it as rotating in an orbit, but we cannot state just what position it occupies in this orbit at a given instant. Neither can we think of this electron as rotating in one orbit and no other. There is the probability that the electron will act in each of the possible ways or occupy each of the possible positions. The new quantum mechanics offers a means of determining the probabilities of such events. The interpretation of this new system of mechanics as a basis for probability determinations is due largely to Born.

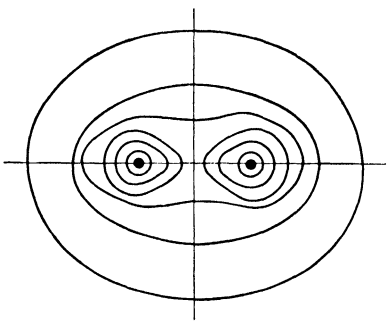

FIG. 125.—Stable configuration of two hydrogen atoms.

In the case of the hydrogen molecule, for example, it cannot be said that the two nuclei are joined by a pair of electrons which lie midway between them. If this could be done, the positions of the electrons would be defined absolutely, and this, as we have seen, is contrary to the principle of indeterminism. But it is possible to determine the average positions and, hence, the positions of greatest probability of the electrons. The most probable positions are found to lie midway between the nuclei. In other words, the distribution of the electronic charge within the molecule is symmetrical with respect to both nuclei. In Fig. 125, the lines around the nuclei of the atoms represent variations in the density of the charge in the molecule. To express the idea differently, we may say that these lines represent the probability that the electrons will be found within the areas bounded by these lines. The density, or probability, is greatest where the lines are closely drawn and least where they are farthest apart. In Fig. 125, the lines between the two nuclei lie close together. It is in this intermediate region that the electrons are usually found—but not always. The region

between the two positively charged nuclei is negatively charged. The density of the negative charge is concentrated here and exerts an attraction upon the two regions of positive charge. Thus, the two nuclei are joined together. This explanation of the covalent linkage of the hydrogen molecule must appeal to anyone as more reasonable than the shared-electron pair of the earlier theories of the atom's structure.

It is also possible that the two atomic nuclei may be surrounded by areas in which the density of the negative charge is differently distributed from the way it is in the case that we have described in the preceding paragraph. In Fig. 126, the lines lie close

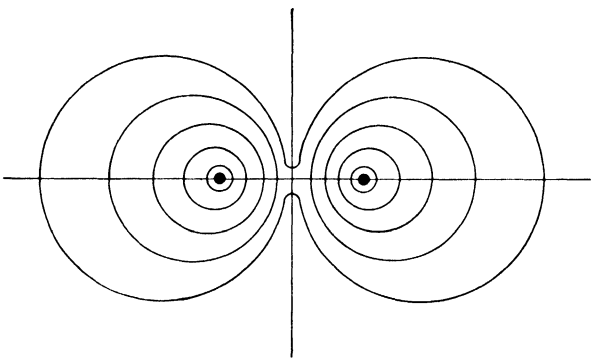

FIG. 126.—Unstable configuration of two hydrogen atoms.

together in the vicinities of the two nuclei but are far apart in the region between them. The negative charge is not concentrated in the region between the nuclei, and there is consequently no attracting field to hold the two nuclei together. Hence, the nuclei of the two atoms repel each other, and this type of combination is not stable.

Since it is impossible to determine with any degree of accuracy both the position and the velocity of an electron, it is even more impossible to determine just what the future position or velocity of the same electron will be. The new quantum mechanics denies, indeed, that any relation can be determined between any event within the atom and preceding events. All that can be determined and all that the Heisenberg matrix theory attempts to determine is the probability that the electron will occupy a position in a certain atomic arrangement. For a given electron,

there can be no certainty that it will, or will not, occupy this position. There exists only a definite probability that it will. If we know the exact velocity, or if we know this within very small limits, then the position, which we have called q, cannot be determined. All the different values of q are possible positions that the electron can occupy; and for future values of q, that value which is most probable is most likely to be the one actually observed. The quantum mechanics of Heisenberg is, then, simply a means of calculating the distribution of certain variables. It tells the probability that each of these may be the actual value and shows how the different probabilities are scattered through a wide range. Because of their character, Heisenberg's determinations are, therefore, said to be statistical values.

Wave Mechanics

We shall approach the subject of wave mechanics by first presenting the results of two lines of recent investigation. One of these appears to present decisive evidence of the corpuscular nature of radiant energy. The other indicates that particles of matter, such as electrons, possess the character of waves. We are about to speak, therefore, of particles of energy and waves of matter.

The Compton Effect.—Professor A. H. Compton succeeded in adding the finishing touch to the evidence in favor of the concept of light quanta, upon which the new quantum mechanics so fundamentally rests. Professor Compton allowed x-rays to impinge upon matter that contains free or loosely bound electrons. When he did this, he observed that secondary x-rays of slightly longer wave length than those of the impinging beam were produced. These results constitute the *Compton effect.*

According to the wave theory of radiation, no suitable explanation can be offered for the increase in the wave lengths of the scattered x-rays in the Compton effect. There is no change in the pitch of a reflected sound or in the frequency of reflected light. We can argue, in like manner, that there should be no change in the frequencies, or wave lengths, of x-rays that are scattered by the electrons in matter upon which the x-rays fall. Compton found, however, that there is a change in the x-ray frequencies under these conditions. To explain his observations, he assumed

that the beam of x-rays is composed of quanta, or photons, which we may regard as corpuscles of energy. He further assumed that the same principles of conservation of energy and of change in momentum apply to the encounter of a photon and an electron as apply to objects that can be observed readily, *e.g.*, the collision of two moving balls. A quantum represents a quantity of energy equivalent to $h\nu$. If the quantum is a particle, it possesses momentum equivalent to $h\nu/c$, c being the velocity of light. When a quantum collides with an electron, the electron gains momentum, and the light corpuscle is deflected with a

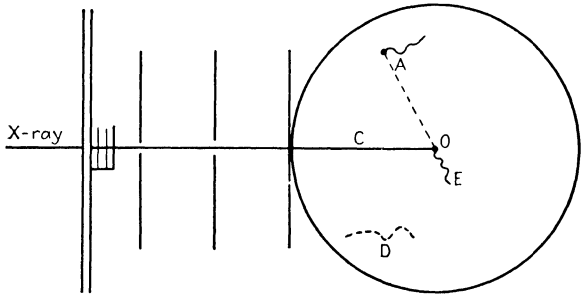

FIG. 127.—The Compton effect. A collision of a photon and an electron. *C*, primary x-ray; *O*, point of collision of primary photon and electron; *A*, point of collision of scattered photon and a second electron and path of second electron after the collision. *D*, typical of positions where the second electron is never observed. *E*, path of first electron after collision. [*After Compton, J. Chem. Ed.*, **6**, 1166 (1929)].

loss of momentum. Since h and c do not change, this means that the frequency must be lowered and that the wave length must be increased correspondingly as a result of the collision.

The photon glances off after the collision in one direction (Fig. 127) with momentum equal to $h\nu\theta/c$. The electron recoils in another direction with momentum equal to $m\nu/\sqrt{1-\beta^2}$, where β is the ratio of the velocity of the electron to the velocity of light. A part of the energy of the original photon is consumed in giving the electron its momentum. In accordance with the quantum theory, therefore, the scattered photon possesses a smaller quantity of energy than it possesses before the collision and must consequently represent a lower frequency, since a quantum is defined as $h\nu$. Compton first confined his efforts to the measurement of the frequencies, or the corresponding wave lengths, of the scattered x-rays. The original wave length is

observed at all the different angles of observation employed in the experiments, but most of the radiation possesses a greater wave length than the original beam. By means of C. T. R. Wilson's fog-track method, the recoil electrons were later located (Fig. 127). A feeble beam of x-rays was allowed to enter the fog-track chamber through a system of slits and filters. Because of the feeble strength of the beam, only a few recoil electrons were expected to make their appearance in the chamber. This proved to be the case. These recoil electrons were found to possess sufficient kinetic energy to ionize particles of gas in the chamber, and the ions thus produced acted as nuclei for the formation of fog droplets. Figure 127 shows at E a recoil electron which was moving at the time the photograph was made in the general direction OE following an encounter with a photon. It is evident that the electron did not continue to move in this direction for a very great distance. The change in the direction of its path was caused by deflection upon colliding with other particles in the chamber, for like all electrons the recoil electron is easily deflected. The scattered photon bounds away from its encounter with this electron in a direction opposite that taken by the electron. In the case shown in Fig. 127, we should look for the photon somewhere in the upper part of the chamber. It will probably strike another electron eventually. This second recoil electron will also be given momentum and will act as an ionizing agent, giving rise to a second fog track A. We can now draw the line OA as the path taken by the photon after the collision. Results confirming these predictions are actually observed. Hence, the scattering of x-rays must be regarded as the deflection of a material particle. The second electron is never found in the same general direction as the first, a condition that might well be the case if the x-ray acts as a wave.

Compton's experiments, therefore, add one more convincing proof of the corpuscular character of radiation. Not only did Compton find qualitative agreement between observation and experiment, but he was able to predict successfully the difference in the frequency of the original and the secondary rays upon the basis of his suggested explanation of the effect. It should be noted, however, that his results indicate the existence of the photon as a corpuscle of energy only at the time of the expendi-

ture of energy. The results offer no possible way of describing the character of the x-ray during the time that it is traversing space. During such times, the wave theory accounts well enough for its behavior.

The Ghost-field Explanation of Radiation.—If we accept the photon—and Compton's experiments and their results appear to leave little choice in the matter—we are faced with the problem of explaining interference and diffraction. The wave theory explains these phenomena very satisfactorily, and their reconciliation with the corpuscular view of energy appears to be a matter that presents grave difficulties. Einstein has offered an explanation which attempts to harmonize the two points of view. His interpretation makes use of the so-called "ghost field." This refers to the electromagnetic field which is associated with a ray of light. The name ghost is applied to this field because, as Einstein suggests, there is no energy in the field itself. The field serves only to direct the photons. According to the electromagnetic theory itself, the radiant energy at a given point is proportional to the sum of the squares of the electric and magnetic fields at that point. Now, if the strengths of these fields are great, Einstein's suggestion is that at this point a relatively large number of photons are present and at a point where the fields are weak only a few photons are directed. The strength of the electromagnetic field, therefore, is a measure of the number of photons at a point where the strength of the field is measured; or it can also be said that the strength of the field is a measure of the probability that a given photon will be present at that point rather than at some other, where the strength of the field is different.

If we accept this view, we must think of a point source of light as emitting photons in all directions. The intensity falls off as the distance from the source increases, because the emitted photons are scattered over more space. The probability that a photon will strike within a definite area decreases as the distance from the source increases. Regions in which electromagnetic waves are assumed, according to the wave theory, destructively to interfere become, according to this new point of view, regions in which the strength of the electromagnetic field is small; hence, only relatively few photons are directed to these regions. These

are the regions where the probability of the photon's presence is small. On the other hand, regions of constructive interference, or reenforcement, are regions of high probability. This explanation depends upon the fact that in all cases where effects of photons are measured, we must deal with vast numbers of individual particles. For these great numbers, the laws of probability hold very well. The accuracy might be considerably different if we should deal with one, or a few, photons at a time.

Einstein's assumption can be summarized in one statement: The probability of a photon's presence at a given point is measured by the intensity of the electromagnetic field at that point. If this theory is based upon a sound assumption, it offers a way out of the difficulty presented by the seemingly dual character of radiation as corpuscles and as waves. The value of the suggestion, for the present, lies in the success with which it explains features of radiation that previously were well enough explained by one theory but not by the other. In this respect, Einstein's interpretation is more successful than any other.

The Wave Motions Associated with Electrons.—The motion of light quanta may be regarded as occurring under the direction of electromagnetic waves which have a frequency ν as defined by the equation

$$\nu = \frac{E}{h} = \frac{mc^2}{h} \qquad \text{(page 97)}.$$

In this equation, m represents the mass of a light corpuscle or photon which is traveling with velocity c. But the mass of the particle when at rest is zero or very nearly zero. If the light quantum is directed by an electromagnetic wave of frequency ν, is it not possible that other particles of slightly greater mass, such as the electron, may also be directed in motion by somewhat similar waves? In answer to this question, de Broglie, in 1922–1923, conceived the idea that a particle possessing the mass m, when at rest, and the velocity v has associated with it an undulatory motion for which the wave length is defined by the following equation:

$$\lambda = \frac{h\sqrt{1 - \frac{v^2}{c^2}}}{mv},$$

where c is the velocity of light. If v is small, v^2/c^2 = (approximately 0), and $\lambda = h/mv$.

The representation by de Broglie of λ in terms of h/mv was based upon the following considerations: Bohr's quantum condition for the radius a of the normal orbit of the electron in the hydrogen atom can be stated as follows:

$$mva = \frac{h}{2\pi} \qquad \text{(page 240)},$$

or

$$2\pi mva = h$$

Now, if there is a wave that can be associated with the electron (of mass m and velocity v), de Broglie reasoned that the circumference $2\pi a$ of the orbit must be a multiple of λ and that for the simplest case

$$2\pi a = \lambda.$$

Substituting λ for $2\pi a$ in Bohr's quantum equation, it is readily shown that

$$\lambda = \frac{h}{mv}. \qquad (1)$$

In assuming that the circumference of the electron's orbit must be an integral multiple of λ, de Broglie was defining the stationary Bohr orbits as those that are integral multiples of h/mv. This was the first reasonable basis for explaining the conditions that cause only certain orbits to be nonradiating. We can compare the electron's orbital path with a vibrating string which is fastened at both ends. When the string vibrates, its doubled length is always a multiple of the wave length. If the ends of the string are to remain stationary, only those wave lengths are permissible that are definitely submultiples of the length of the string. In other words, the string may vibrate either as a whole or as a number of segments, provided that the segments are halves, thirds, fourths, or some other exact fraction of the whole length. In a similar manner, only those electron orbits can be stationary that are integral multiples of the wave length.

According to the relativity concept of the relation between mass and energy, the energy E of any particle is defined in terms of its mass, its velocity, and the velocity of light as follows:

$$E = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{2}$$

This equation can be written as $E = mc^2$, if v is small. Now, the energy that can be calculated from the mass by Eq. (2) can also be represented in terms of Planck's constant h and a frequency ν, if we apply the quantum conditions implied in the equation

$$E = h\nu.$$

From this relation it follows that

$$\nu = \frac{E}{h} = \frac{mc^2}{\lambda mv} \tag{3}$$

and

$$\lambda\nu = \frac{mc^2}{mv} = \frac{c^2}{v}, \tag{4}$$

where the product $\lambda\nu$ defines the velocity of the individual waves.

Accepting, then, the relativity relation of energy and mass and the quantum relations of energy and frequency, it should be possible to calculate by Eq. (3) a definite frequency for an electron moving with a definite velocity. To the extent, therefore, that this frequency is real, the electron may be regarded as possessing the characteristics of a wave. The frequencies calculated by the de Broglie equation are sometimes spoken of as *matter waves.*

Verification of Matter Waves.—C. J. Davisson and L. H. Germer of the Bell Telephone Laboratories have shown that electrons do act as waves or as if they were associated with wave motions. They allowed a stream of electrons to bombard crystals, the direction of the bombardment being normal to a face of the crystal. They found a high degree of similarity between the scattering of the bombarding electrons and the diffraction of waves by gratings. They state that

A description of the occurrence and behavior of the electron diffraction beam in terms of the scattering of an equivalent wave radiation by the atoms of the crystal and its subsequent interference is not only possible but most simple and natural.

The explanation of the diffraction of the beam of electrons involves the association of a wave length with the electron beam which falls upon the crystal. This wave length is in satisfactory agreement with the value h/mv of undulatory mechanics (see de Broglie's Eq. (1), above), provided that the velocity of the

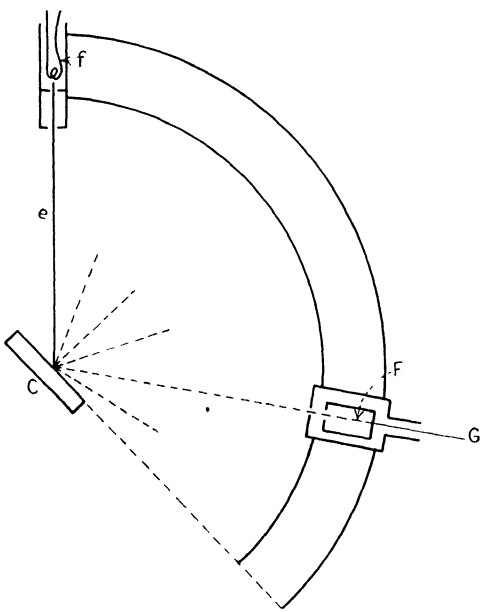

FIG. 128.—The reflection of electrons by crystals.

electron is small. Davisson and Germer employed practically the same methods as those used by the Braggs to determine the structure of crystals (page 166) and the wave lengths of x-rays diffracted by atoms within the crystal (page 163). The method that they used is shown in Fig. 128. The reflected electrons are detected by means of a Faraday cylinder attached to a galvanometer. This cylinder is moved through the arc shown in the figure. At different positions along this arc, corresponding to different angles between the lines *CF* and *e*, the galvanometer shows

different maxima of reflection. One should expect that the maximum intensity of the reflected electrons would be observed in a direction for which the angle of incidence is equal to the angle of reflection. When electrons are reflected from a nickel plate, however, there is no reflection at this angle. Figure 130 shows the relation of the intensity of the reflected electron beam to the square root of the potential difference under which the electrons bombard the surface of the crystal. The results shown

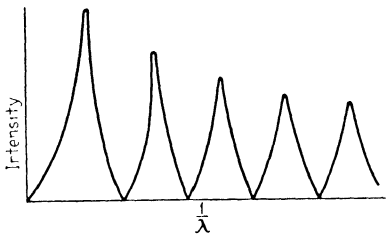

FIG. 129.—Reflection of x-ray beam.

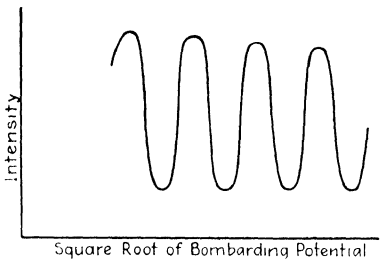

FIG. 130.—Reflection of electron beam.

in this figure, of course, are for a given angle of incidence. Now, the velocity of the bombarding electrons is expressed by the equation

$$v = \sqrt{2V\frac{e}{m}}, \tag{1}$$

where V is the potential difference and v, e, and m have their usual meanings.

When the results obtained by Bragg's method of studying the intensity of reflected beams of x-rays are expressed by a plot of the intensity of the reflection against the reciprocal of the wave length, maxima similar to those shown in Fig. 129 are obtained. This relation may be derived from the equation (page 165)

$$n\lambda = 2d \sin \phi, \tag{2}$$

which can also be written as

$$\frac{1}{\lambda} = \frac{n}{2d \cos \phi}. \tag{3}$$

This equation can be interpreted to mean that maxima for the intensity of the reflected beam are observed when λ has a value of

$$\frac{2d\cos\phi}{1}, \quad \frac{2d\cos\phi}{2}, \quad \frac{2d\cos\phi}{3}, \text{ etc.,}$$

or $1/\lambda$ has a value of

$$\frac{1}{2d\cos\phi}, \quad \frac{2}{2d\cos\phi}, \text{ etc.}$$

The maxima observed in the plot occur, therefore, at intervals equal to

$$\frac{1}{2d\cos\phi}.$$

For reflected beams of electrons (Fig. 130), the maxima also occur at equal distances apart. The similarity in the two sets of curves can be interpreted as meaning that electron reflection is actually a wave reflection for which $1/\lambda$ is proportional to $\sqrt{V}$. The value of λ for the electron wave can be expressed by combining Eq. (1) with the de Broglie equation

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

as follows:

$$\lambda = \frac{h}{m\sqrt{2V\frac{e}{m}}},$$

or

$$\lambda = \sqrt{\frac{h^2}{2me}}\,V. \tag{4}$$

Now, if the reflection of electrons can actually be regarded as the reflection of a wave motion, the values of λ calculated by Eq. (4) should agree with those calculated by Eq. (3). With certain corrections made in ϕ because of the refraction of electron beams as they emerge from the crystal, excellent agreement was obtained in the values of λ as calculated by these two methods. This agreement demonstrated experimentally the validity of de Broglie's concept of "electron waves."

Using de Broglie's equation, we can easily calculate the wave length of the undulatory motion associated with a given electron. An electron that falls through a difference of potential of 100 volts attains a velocity of about 6×10^8 cm. per second. If we take the mass of the electron as 9×10^{-28} g., its momentum mv is

$$(9 \times 10^{-28}) \times (6 \times 10^8) = 5.4 \times 10^{-19}$$

and

$$\lambda = \frac{h}{mv} = \frac{6.55 \times 10^{-27}}{5.4 \times 10^{-19}} = 1.21 \times 10^{-8} \text{ cm.}$$

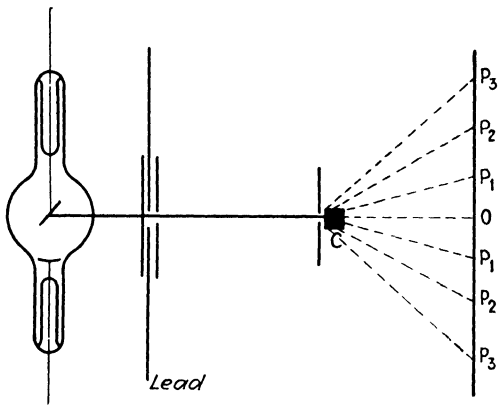

FIG. 131.—Hull's method of diffracting an x-ray beam by powdered crystals. Owing to the powdered state of the crystalline substances, all possible sets of planes act to diffract the beams of x-rays simultaneously. This produces concentric circles (P_1P_1, P_2P_2, etc.) about the center.

Davisson and Germer's experimental results, involving electrons of the same velocity, agreed satisfactorily with this value of λ.

G. P. Thomson has added important evidence confirming the wavelike characteristics of electrons. His results can be interpreted best by comparing them with those obtained by similar treatment of x-rays. Hull developed a method of diffracting a beam of x-rays by passing the beam through masses of powdered crystals (Fig. 131). Layers of atoms in the crystal act as a grating to diffract the x-rays, and a diffraction pattern (Fig. 132) is obtained. Interference patterns of this character have long been considered as conclusive evidence of the wave nature of light. Now, Thomson passed a beam of high-speed electrons

through a gold foil and obtained a photograph of several rings of diffracted electrons (Fig. 133). The similarity of the photographs obtained in the two series of experiments can mean only that these experiments deal with similar phenomena, that electrons, at least under the conditions that attend diffraction of their beams, act in the same manner as x-rays and possess similar characteristics. If x-rays are waves, then electrons must also possess the characteristics of waves. The wave lengths of these waves and their variations with the speed of the electrons are exactly those predicted by de Broglie's equation for the wave lengths of matter waves.

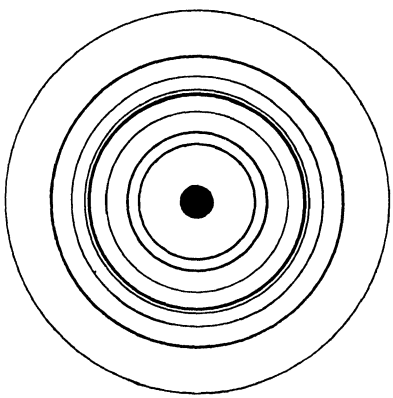

FIG. 132.—Diffraction of x-ray beam by aluminum crystals (Hull's powder method).

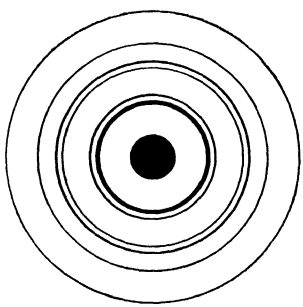

FIG. 133.—Diffraction of electron beam by gold crystals.

Still more recently, Johnson, Ellet, and Olson have found that atoms of hydrogen and other elements are reflected from crystal faces in a manner similar to that in which x-rays are "reflected" by crystals. Dempster has also succeeded in obtaining diffraction patterns of protons by passing beams of these particles into crystals of calcite.

Any observation of light is an observation of energy or a manifestation of that energy's presence. When we measure the intensity of light, all that we do is to measure the quantity of energy carried by the light—whatever light itself may be—in a definite region of space. We have found that, in accordance with the wave theory of light, we can express this intensity as proportional to the square of the amplitude of a theoretical light wave.

But we must not forget that the amplitude and, also, the wave itself are not realities; they are the products of our theory of light waves. Now, if light exists as corpuscles, or photons, evidently the intensity is proportional to the number of photons in the beam, and this number is also, therefore, proportional to the square of the amplitude of our theoretical wave. If light particles are replaced by electrons, or other particles, we may carry over from our study of optics the same principles of expressing intensity in terms of wave amplitude. Thus, we may calculate, upon the basis of the amplitude of an electron wave, the number of electrons that may be expected to be present in any portion of space as directly proportional to the square of the amplitude of that wave. Light waves and electron waves are each purely theoretical. One has no more or no less reality than the other. All that is new is the realization that light is corpuscular and that the principles of optics which we have used in expressing intensities of light in different portions of space may be applied to other kinds of particles.

Matter and Energy.—Consideration of the Compton effect leads us inevitably to the conclusion that energy is atomic in character; this conclusion is justified, at least, when we consider the encounter of energy with a particle of matter, such as the electron. On the other hand, the agreement of the results of diffraction experiments involving electron beams with the predictions of de Broglie's theory of matter waves leads just as inevitably to the conclusion that particles of matter are associated with undulatory motions, such as we have been accustomed to associate with radiant energy.

The further we study matter and energy the more closely we find them related. In the past, we were accustomed to think of energy as convertible only into other forms of energy and of matter as convertible only into other forms of matter. We have noted from time to time during our previous discussions of the character of matter and energy several indications that they are convertible one into the other. This idea is included, of course, in Einstein's relativity relation of mass and energy and was also derived by Lorentz by classical electrodynamics. We have found occasion to use it as a means of explaining the effect of packing upon atomic mass and in accounting for certain elec-

tronic-orbital perturbations resulting in the precession of elliptical orbits. We now find an even closer relationship in the behavior of photons of energy which act as particles of matter and of particles of matter which act as radiant energy. Very recent results tend to show that energy may be converted into matter. Thus, there is some experimental evidence that a very high-frequency photon may be converted into an electron and a positron when it encounters a very powerful nuclear field. The positron is defined as the exact counterpart of the electron but bearing a positive charge. Its charge is numerically equal to that of the electron, and its mass is also assumed to be the same as the mass of the negative particle. There is also some indication that collisions of high-speed particles, such as protons and neutrons, with atoms may sometimes result in the conversion of energy into mass. These are questions, however, that must await a considerable extension of knowledge before we can be quite certain of results and their causes.

Wave Mechanics

The wave mechanics of the atom is based upon de Broglie's theory of matter waves. This system of atomic mechanics was first developed by Schrödinger and, therefore, is sometimes called the Schrödinger theory. Like that of Heisenberg, this theory does not attempt to determine the location of an electron within the atom. It only measures the probability that the electron will be at a definite place, or rather within a definite region, during a certain period of time.

Schrödinger's Function ψ.—In Schrödinger's mathematical development, there appears a function $\psi(x,y,z)$. The term $[\psi(x,y,z)]^2$ $(dxdydz)$ is a measure of the intensity of the de Broglie wave motion. With the understanding that the maximum intensity occurs in the region of maximum probability, it follows that ψ^2 is also a measure of the probability that the electron may be found somewhere within the volume represented by $dxdydz$, where x, y, and z are coordinates of position and dx, dy, and dz are certain distances along these coordinates. These distances bound the volume under consideration.

The classical Bohr orbit for the electron is thus replaced by the square of Schrödinger's function ψ. This concept is inter-

preted most satisfactorily as a somewhat more precise mathematical treatment of the principle of indeterminism. Bohr's treatment dealt with definite orbits for the electron. The new theory replaces this orbit by a region about the nucleus within which there is a maximum probability that the electron will occur. This view does not limit the electron to this region, however, although the probability of occurrence is assumed to decrease very rapidly toward zero as the distance from the nucleus becomes greater than the values of r which are calculated by Bohr's theory. This interpretation of Schrödinger's function was not included in the original treatment but was added by

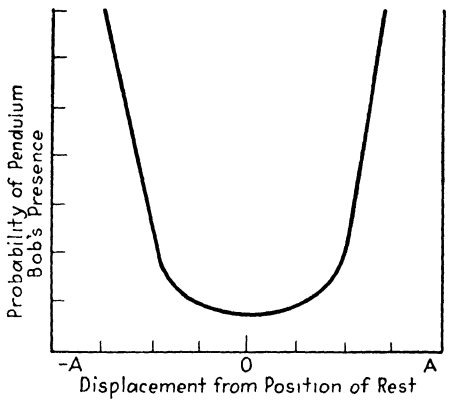

FIG. 134.

Born. Born's suggestion includes the idea that the intensity of the wave motions and the corresponding probability of occurrence of certain states of the system can be expressed in terms of ψ^2.

Now, the distribution of the density of the electron's charge within the atom depends upon the probability that the electron may be located in the different parts of the atom's structure. The charge density is greatest where the probability of the electron's presence is greatest and least where the probability is smallest. Hence, ψ^2 is proportional to the charge density. The term ψ is consequently a most important one in the formulation of Schrödinger's wave mechanics, but its physical nature practically defies interpretation, if indeed it can be assigned a physical explanation at all. In the classical theory, the electron, rotating

in its orbit, could be treated in the same manner as a pendulum. If we should consider the amount of time that the bob of the pendulum spent in each part of its swing, we could plot the probability that the bob would be found in a certain position against the displacement from the position of rest. The result would be similar to that indicated in Fig. 134. Now, treating the electron in a similar manner, and considering it as oscillating back and forth across its orbit, we should find a similar curve (Fig. 135) for the relation of the probability of the electron's occurrence and the displacement. This curve is designated as *B* in Fig. 135. Curve *C* shows the distribution of probabilities according to wave mechanics. The two curves emphasize the difference between the classical theory and wave mechanics.

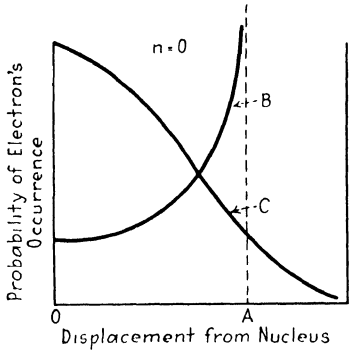

FIG. 135.

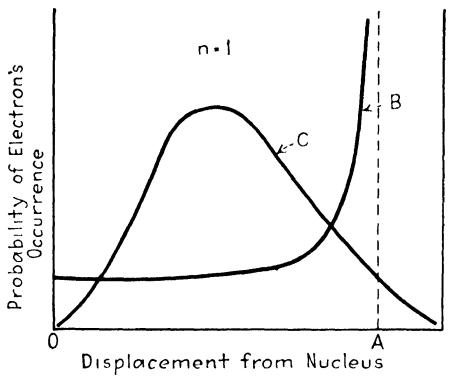

FIG. 136.

The relative probabilities of the occurrence of electrons for quantum states one and two are shown in Figs. 136 and 137.

Schrödinger's Wave Equation.—Schrödinger states the value of ψ in the form of the following partial differential equation:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0,$$

where m is the mass, $V(x,y,z)$ is the potential energy in the field of force of the nucleus, and E is the total energy of the electron. Solutions of this equation give values of $\psi(x,y,z)$ which are called Schrödinger's wave functions. If these solutions are finite and single-valued wave functions, E can have only certain values. The permissible values of E, which are thus determined, are oddly enough the same values of the total energy of the electron as those required in the Bohr theory, where the frequency of the radiation is related to the energy values of two independent quantum states by the equation

$$h\nu = E_2 - E_1.$$

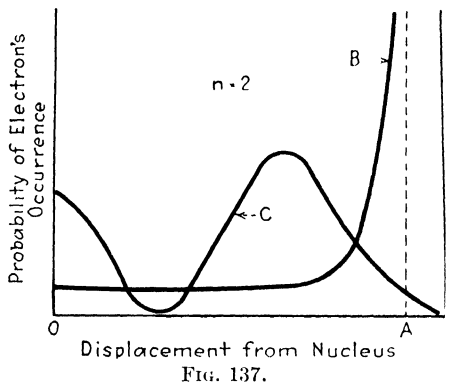

FIG. 137.

These permissible, or possible, values of E are called *Eigenwerte* and give values of ψ that are called *Eigenfunctionen*.

An Explanation of Radiation.—The Bohr theory denied the possibility of electron transfers between energy levels designated by certain combinations of quantum numbers by assuming certain arbitrary selection principles. In terms of the new quantum mechanics, these selection principles must be interpreted as meaning that certain transitions are possible but are considerably less probable than others. The new theory states that the probability of a definite transition is the average of the probabilities that electrons located at all points within a region to which the state n_1 can be assigned will undergo transitions to some other region of state n_2. We are thus relieved of solving the perplexing problems, which arose in the older theory, con-

cerning the actual course of events during the passage of an individual electron from one stationary orbit to another. We are also relieved of the task of accounting for the limitation of orbits to those of certain "stationary" energy values by the simple expediency of discarding the limitations. The new theory eliminates all consideration of individual events. Instead, all possible distributions of one or more electrons are considered simultaneously and are represented by the variations in space of the purely mathematical function ψ. This function is not for one electron alone. It is actually the product of the *Eigenfunctionen* of all the electrons which may constitute the atomic system under consideration. The system is treated as containing all the possible states simultaneously, which means that what we really consider consists of all the possible states simultaneously existing in different atoms. The square of ψ represents the variations of charge density for all the electrons which are regarded as coexisting. Hence, transitions between two states occur only when both these states exist in the system.

In terms of the Schrödinger theory, an atom becomes a region without definite boundaries through which waves are spread. The symbol ψ represents a complex algebraic quantity, which, although only in an indirect sense, stands for a wave. It represents a definite value of *something* possessed by the wave at some one place. The intensities of the waves that are spread through the atom are most intense where the Bohr orbits were assumed to lie. Beyond the boundaries usually assigned to the atom, the intensities are very small. For any one steady state of the atom, we may regard the wave associated with the atom and represented by ψ as a system made up of the vibrations of all the different portions of the atom. For this state, the frequency is equal to the energy divided by h. Each steady state of the atom, therefore, is represented by a characteristic ψ frequency.

Let us assume that in some atoms it is possible for a ψ vibration to exist which corresponds to the resultant of the interaction of two steady states; we may think of the ψ vibration as consisting of two components. The resultant ψ vibration corresponds to a beat note in sound. Since the wave lengths of the two vibrations are slightly different, the vibrations alternately neutralize and reenforce each other. A rather complex vibration results,

therefore, and its frequency is equal to the difference in the frequencies corresponding to the two stationary states. The amplitude of the resultant vibration slowly changes. Schrödinger shows that the complex vibration is attended by radiations of energy; *i.e.*, this vibration does not represent a steady state of the atom. It can be assumed, therefore, that the frequency of the radiation is the frequency of the "beats."

The question of radiation involves, therefore, a transition from one ψ-vibrational state to another instead of a transition of an electron from one orbit to another. This transition may occupy a very small period of time, probably less than 1×10^{-9} sec., but during this time the change is continuous rather than abrupt. The continuous character of the transition means that the new vibration first possesses a very small amplitude and increases as that of the old vibration decreases, until the latter has disappeared.

A Theory of Radioactive Disintegration.—In the chapter on radioactivity, we stated that the rate at which a given radioactive element disintegrates is independent of all external conditions and that the energy possessed by the expelled alpha particles is greater the shorter the half-life period of the element. Quantum mechanics offers the only explanation of these rather unusual facts.

Let us consider an alpha particle and the nucleus of which it is a part in an atom of radium. Let us think of the alpha particle as separated from the nucleus and moving toward it. Rutherford's experiments dealing with the deflections of alpha particles by atomic nuclei lead us to believe that the alpha particle is repelled by the nucleus until it comes to within a distance of about 1×10^{-12} cm. Somewhere inside that limit, the repulsion of the alpha particle changes to attraction. This assumption appears to be justified, since otherwise there could be no atoms of the radioactive elements. Let us draw a curve which shows, in a purely theoretical sense, the variation of the potential energy of the alpha particle with its distance from the nucleus (Fig. 138). As the alpha particle is moved nearer the nucleus from a distance considerably greater than 1×10^{-12} cm., its potential energy will increase, since work must be done upon it in bringing it closer to the nucleus that repels it. The potential energy

consequently reaches a maximum and then, at a distance from the nucleus less than 1×10^{-12} cm., begins to fall. The decrease in potential energy begins as soon as the alpha particle is attracted. This gives us the left-hand slope of the curve.

Let us now select some point (a_1) on the left-hand side of the curve to represent (theoretically) the potential energy of the alpha particle which is expelled when an atom of radium disintegrates. The point a_1 designates the distance from the nucleus and the potential energy of the alpha particle before disintegration. Upon the disintegration of the atom, the alpha particle must be transferred from the position a_1 to some position a_2, where it is repelled by the nucleus. The older theories of mechanics would lead us to the conclusion that the alpha particle in escaping must climb over the peak of the curve—the potential-energy hill. In doing so, the particle would have to have more potential energy than it actually possesses and, hence, could not escape. Quantum (wave) mechanics offers a plausible explanation. According to the basic principles of wave mechanics, a particle possessing the energy corresponding to the a_1 position on the curve is not limited to that position. There is only a certain probability that the particle possessing this quantity of energy will be found at a_1. There is also the probability that the particle may be found at a_2 and in other positions. Instead of having to climb the potential-energy hill—an impossibility—we may think of the alpha particle as passing right through the hill and escaping, therefore, with the same amount of energy it would possess if it had remained at a_1.

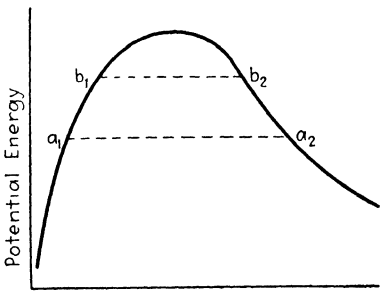

FIG. 138.—Radioactive disintegration.

Let us also consider an alpha particle at b_1. This condition may be used to designate the potential energy and distance from the nucleus within an atom of radium C', which disintegrates much more rapidly than radium. This alpha particle has more potential energy than the alpha particle in the radium atom. The distance between b_1 and b_2 is less than the distance between

a_1 and a_2, and there is consequently a greater probability that the alpha particle of the radium-C′ atom will be found at b_2 or at other points in the region where it is repelled by the nucleus. To retain our analogy of the potential-energy curve to a hill, there is less hill for the alpha particle possessing the potential energy corresponding to b_1 to pass through, and the time that must elapse before it appears at b_2 is relatively short. Upon escaping, it will possess the same quantity of energy as it would possess in position b_1. This is greater than the energy of the particle designated by a_1. Hence, alpha particles expelled from radium C′ have more energy and correspondingly longer ranges than those expelled from radium.

What Is an Electron?

All attempts to define the physical characteristics of the electron are probably unwise. They must, at least, be regarded as purely speculative. Yet we are so accustomed to rather definite physical models that we naturally seek an electron that can be visualized. Several pictures of the electron have been offered. A brief review of some of these may not be without merit.

According to one point of view, all space is filled with . . . ? What shall we say? Ether, subether, or just empty space? Perhaps, it does not matter much what we say; certainly we do not know that it is filled with anything. Anyway, let us think of this sea of something which fills all space as covered with very small waves whose frequencies are much smaller than those of any waves with which we are acquainted. If a certain group of these tiny waves combine, they produce regions of greater disturbance here and there in the surface of this endless sea of space. Some persons are of the opinion that these regions of disturbance may be what we are accustomed to think of as material particles, such as electrons. The energy of a particle of matter is determined by the frequency of the waves that produce the region of disturbance. According to this point of view, therefore, the electron is a group of waves. The individual and group waves to which we have referred may be compared with a disturbance on the surface of a large body of water. Such a disturbance consists of many individual waves traveling with a definite velocity. The group of waves that constitute the area

of disturbance travels, however, with a different velocity from that of the individual waves. There may be, for example, several areas of disturbance, each consisting of individual waves of definite velocity, on the surface of a lake. These may be traveling not only with different velocities but even in different directions.

If we are to regard the electron as a particle, it must lie somewhere within the area of disturbance. The energy associated with the group of waves appears to be concentrated at a point rather than scattered over the entire region covered by the waves. As the electron moves, the individual waves die out in front, but new ones continually spring up behind, thus maintaining the same region of disturbance. The only reason for associating the existence of a particle with the wave groups at all is more satisfactorily to explain the action of an electron when energy is involved. Otherwise, Schrödinger's theory would prefer the view that an electron represents an indefinitely bounded region consisting of a continuously distributed charge the density of which is proportional to the intensity of the waves.

The individual waves are thought to travel with a velocity greater than that of light. The velocity of the group is the velocity of the electron and is, therefore, less than that of light. The assumption that the velocity of the individual waves is greater than that of light is based upon the following considerations: From quantum conditions, energy can be defined in terms of $h\nu$ and, in accordance with relativity concepts, in terms of mc^2. There is a certain equivalency, therefore, between mc^2 and $h\nu$. If mass increases with velocity, this equivalency, however, no longer can hold true, particularly because increased velocity also means diminished frequency. Equivalency can be restored if the velocity of light is taken as the mean of the wave velocity and the velocity of the wave group, or the particle. It also follows that the velocity of the individual waves must increase as the velocity of the particle (wave-group velocity) diminishes.

The waves associated with an electron have often been compared to the waves produced in a violin string when the bow is drawn across the string. If the bow is drawn across the middle of the string, one wave is produced and its length is the length of the string. But if one's finger is placed in the middle of the

string, two waves are produced, one on either side of the center. In a similar way, other numbers of waves can be produced along the length of the string. In the case of an electron which rotates in an orbit, the major axis of the orbit corresponds to the string. De Broglie assumed that a standing wave is spread around the orbit of the electron. It was further assumed that the lengths of the possible waves thus associated with the electron were limited by the condition that the vibrating segments must be contained an integral number of times in the axis of the orbit. In this manner, the vibrations of the electrons are limited to those that are in resonance to the orbit. The orbits that fulfill the conditions and in which the electron can rotate correspond to the different stationary or steady states of the atom. Each of these represents a definite energy state for which three quantum numbers are used to express the nature of the wave system. The usual fourth quantum number expresses the spin momentum of the electron.

Summary.—What are we to believe? Are electrons waves or particles? Is radiation transmitted as waves, as we had thought, or does it always consist of particles, as quantum mechanics would have us believe? We have thought of the wave and the corpuscular theories of light as completely contradictory points of view. Sometimes one theory has appeared in the ascendency, sometimes the other. Each theory has proved somewhat deficient in explaining certain phenomena which the other dealt with more successfully. Perhaps we must make use of both theories in attempting to explain the nature of radiation. It appears to be necessary, also, to extend both concepts to include the behavior of material particles. At least, both points of view appear to be necessary for a satisfactory explanation of such phenomena as the diffraction of light photons, electrons, and atoms; the Compton effect; the photoelectric effect; and others of a similar nature.

So far, Einstein's suggestion of the ghost field is the only interpretation that offers an explanation of all these phenomena. This suggestion reconciles the two conflicting theories of radiation and at the same time takes into account de Broglie's matter waves. Wherever light photons appear or wherever they may go, one can think of them as directed by electromagnetic waves—

a ghost field, as Einstein calls it. The density of the photons in a given volume is determined by this ghost field. This means that the number of photons in a given volume is proportional to the sum of the squares of the strengths of the electrical and magnetic fields within that volume. Similarly, wherever electrons and other small particles may appear, they are directed by matter waves. The square of the ψ function of these waves determines the probability that an electron can be found in a given place.

The new theories discard the older picture of the electron, just as they discard the classical wave theory of radiation. These theories deal with terms that represent the propagation through space of groups of waves, not corpuscles of matter. The particle has been replaced, in other words, by a train of waves, and the motion of the particle, whether it be an electron or a photon, is represented by a plane wave. The wave length is determined by the momentum of the wave group, and the length of the train depends upon the accuracy involved in measuring the momentum. The wave that represents the photon is, of course, an electromagnetic wave, while that which represents the electron is expressed only by the symbol ψ of Schrödinger's equation.

The wave motions of which we have been speaking are sometimes called waves of probability. Thus, electromagnetic waves, such as light, are most intense where there is the greatest probability that a photon will strike and spend energy upon something, such as a grain of a silver halide in a photographic plate. Low intensity corresponds to small degrees of probability that such a grain will be struck by a photon. Similarly, we can think of the waves that represent electrons as being most intense where electrons are most likely to make their existence apparent by doing work or having work done upon them. These suggestions concerning the nature of the electron and its comparison with the photon must be regarded as purely speculative hypotheses. Supporting experimental evidence is lacking. Electrons and photons can be located only when they spend energy in doing work, as, for example, when they collide with each other. We can state that there are these regions in space time where energy appears, and we can think of electrons and photons as occupying these positions at the time that work is performed.

But outside the regions where energy is expended, we can have no definite evidence of the existence of the particles, whether they be electrons or photons. Hence, any assumption that we might make concerning the propagation of either electrons or radiation through space must be without any foundation of observable facts or reasons. In the absence of any more satisfying solution, it remains permissible, perhaps, to think of this problem as one involving the propagation of wave motions.

The Atom and the New Mechanics

The Hydrogen Atom.—For the hydrogen atom, the various energy levels are defined by Bohr's theory by the simple equation

$$E = \frac{-Rhc}{n^2},$$

where E is the energy, n is a whole number, c is the velocity of light, h is Planck's constant, and R is Rydberg's constant (page 234). The value of the energy as defined by this equation is negative, since it represents the quantity of energy that must be subtracted from a certain constant amount which is associated with some reference state. The amount so subtracted varies from level to level with the value of n. The smaller the value of n the larger the quantity subtracted from the reference quantity in calculating the actual energy value of any particular level (see also page 240).

Rydberg's constant R is defined by the following equation:

$$R = \frac{2\pi^2 e^4 Z^2 m}{ch^3}.$$

Now, for the lowest energy level of the hydrogen atom, Schrödinger shows that

$$\psi = \frac{1}{\sqrt{\pi a^3}} \cdot Z^{\frac{3}{2}} \cdot e^{-\frac{Zr}{a}},$$

where a is the radius of the 1_1 orbit of the Bohr atomic model, r is the distance from the nucleus to the probable position of the electron, Z is the atomic number, and e is the electronic charge. Since Z for hydrogen is unity, the value of ψ becomes,

$1/\sqrt{\pi a^3} \cdot e^{-\frac{r}{a}}$. If the above value of ψ is squared, or, more exactly, if the product of ψ and its complex conjugate is taken,

$$\psi^2 = \psi\bar{\psi}^* = \frac{Z^3}{\pi a^3} \cdot e^{-\frac{2Zr}{a}} = \text{(for hydrogen)}\ \frac{1}{\pi a^3} \cdot e^{-\frac{2r}{a}};$$

a value $\psi\bar{\psi}^*$ is thus obtained which determines the probability that the electron will be found at the distance r from the nucleus. This value, and hence the probability of the electron's occurrence, decreases rapidly toward zero with increasing values of r. There is, however, a small probability that the electron will be found at any distance, however large r may become.

Satisfactory solutions for ψ in the Schrödinger partial differential equations are obtained only when the values for the total energy (page 243) of the electron can be expressed by the equation $E = -\frac{2\pi^2 Z^2 e^4 m}{n^2 h^2}$. These values are the *Eigenfunctionen* of wave mechanics. They are often expressed as values of $\psi\bar{\psi}^*_{nlm}$, where *nlm*, the subscripts, indicate the quantum numbers that determine the character of the ψ vibration.

Quantum Numbers and Wave Mechanics.—The interpretation of quantum numbers in connection with the ψ vibration of the wave theory is necessarily different from that given in terms of the Bohr theory. In wave mechanics, these numbers appear not because they express any quantized conditions as in the older theory, but because they are necessary as variables in the different solutions for ψ in Schrödinger's partial differential equations. They are often referred to as "nodal" numbers. The nodal concept can be understood best by reference to Fig. 139, in which eigenfunctions for certain energy states of a linear oscillator are plotted as functions of x. The quantum number n in this case corresponds to the number of nodal points in a vibrating string. In fact, for one degree of freedom the problem can be treated in exactly the same manner as the vibrating string. In a string which is vibrating, the nodal point represents a point where the amplitude is zero. In the case shown in Fig. 139, a nodal point represents a value of ψ equal to zero. The number of such points in each curve of the plot (for small values of x) is equal to n. The coordinate x can be regarded as representing

n a rough sort of way the region in which ψ has its maximum ralue. For larger values of x, ψ diminishes exponentially to zero. t has been suggested that each quantum number (n, l, m) epresents the number of *nodal surfaces* of a particular kind vithin the atom. These surfaces may be those of spheres about he nucleus, cones with the nucleus at the apex, and planes hrough the nucleus. In a way, therefore, a semblance to the nterpretation of these numbers in the older theory is maintained. The fourth quantum number was interpreted in the older theory is representing the electron's spin with or against the direction n which the electron moves in its orbit. Wave mechanics can carcely offer even a suggestion of a physical interpretation of

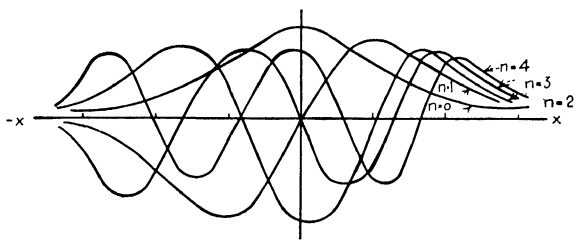

FIG. 139.

his quantum number. The mathematical treatment of the vave theory, however, has been extended successfully to include he wave function associated with this fourth variable. The reatment shows that for each type of vibration, there may be wo electrons within the atom. Each of these electrons exercise slightly different effect upon the state of the wave system.

Energy Levels of the Atom.—For the lowest energy level f the hydrogen atom, the quantum numbers have the following ralues: $n = 1$; $1 = 0$; $m_1 = 0$; and m_s can be either $\frac{1}{2}$ or $-\frac{1}{2}$, lepending upon the direction of the electron's spin with reference o the direction of the magnetic field. The principal quantum umber n, the azimuthal number l, and the two magnetic uantum numbers m_1 and m_s have their usual meanings, which ave been discussed on page 299. When $n = 2$, l may be equal o 1 or 0; m_1 may be 1, 0, or -1; and m_s may be either $\frac{1}{2}$ or $-\frac{1}{2}$. For any value of n, l may be any number from 0 to $n - 1$. For ny value of l, m_1 may be any number from l to $-l$. The value

of m_s, of course, may be either $\frac{1}{2}$ or $-\frac{1}{2}$ for any set of values of n, l, and m_l. By means of these quantum numbers and with the aid of Pauli's exclusion principle, which states that no two electrons in an atom can have the same set of quantum numbers or the same wave function, we can list the possible wave functions or the total number of energy states which are possible by listing the possible combinations of the four numbers. These are shown in Table XI.

Valence and the Wave Mechanics of the Atom

The problem of electrovalence is treated by wave mechanics in a manner that is similar to the older treatment. In this section, we shall consider, therefore, problems involving bonds which are generally called covalent linkages. These bonds are thought to result when two atoms approach each other very closely. Under these conditions, two electrons, one in each atom, may rapidly and continuously interchange positions. This interchange furnishes the linkage between the atoms. The interchange in the positions of the electrons may occur between two atoms that are separated by any distance. If this distance is great, the probability that an electron from one atom will be found within the boundaries of the other is very small. When the two atoms are close together, the exchange of electrons is more probable or takes place with greater frequency. When this happens, the probability that an electron will be in a definite position can no longer be calculated as it is for a single atomic system. The calculation of the probability must now take into account the electrostatic forces of the second as well as the first atom. Furthermore, the two electrons can no longer be considered independently.

Not all the electrons in an atom are able to form bonds by exchanging positions with electrons in other atoms. Furthermore, the formation of a valence bond between two atoms is possible only when these atoms possess electrons that have identical quantum numbers n, l, and m_l but different values of m_s. This means that two electrons, one on each atom, must spin in opposite directions. When this condition exists, two such electrons may couple to form the symmetrical distribution

of charge which is shown in Fig. 125 (page 369). This coupling results in a decrease in the potential energy of the system that consists of the two atoms.

In deciding what molecules can be formed by the combination of atoms, let us base our calculations, therefore, upon the rather simple idea that a stable molecule requires that *the total energy of the atoms combining must decrease as the atoms approach and combine.* In considering the valence of different kinds of atoms, we shall assume that some of the electrons in the outer level of an atom are unpaired or uncoupled in the sense that we have just described. Such electrons, if they lie in different atoms, may couple together, thus resulting in the chemical combination of their atoms. The valence of an element is defined, therefore, as the number of uncoupled electrons in the outermost electron group of its atoms. Let us now apply these principles to a few of the simpler elements and their combinations with each other.

Now, we mean by an uncoupled electron one for which there is no other that is identical in the first three quantum numbers and different only in the direction of spin. Thus, we can have two hydrogen atoms, each possessing an electron of quantum number $n = 1$, combining to form a molecule H_2. Urey has explained the stability of this molecule in the following manner: If the two hydrogen nuclei were forced completely together, the nucleus of a helium atom would result. The formation of the hydrogen molecule is just a step in this direction. The helium nucleus which would be formed in this manner would have a mass of two, and its nuclear charge or atomic number would be two. The formation of this nucleus from two protons could happen without any change in the value of n for the electrons that are associated with the protons in the hydrogen atom, since the helium atom contains two electrons for each of which $n = 1$, while each hydrogen atom possesses one electron for which the value of n is also 1. Reasoning in a similar manner, however, we must conclude that it is impossible, or at least improbable, that three hydrogen atoms should combine to form the molecule H_3. Such an event would mean that there are three electrons for the resulting atom, each of which originally possessed the quantum number $n = 1$. This condition is denied by Pauli's exclusion principle. There can be but two electrons for which

n has the value of 1 in any atom. These two electrons can have different sets of quantum numbers:

$$n = 1; l = 0; m_l = 0; m_s = \tfrac{1}{2}. \quad (1)$$
$$n = 1; l = 0; m_l = 0; m_s = -\tfrac{1}{2} \quad (2)$$

A third electron would have to possess either one set of these quantum numbers or the other; or a third electron would have to be transferred to another energy state, where its quantum number n would have a value greater than 1. The first of these alternatives is out of the question. The second appears to be just as impossible as the first, since such a change would necessitate an increase in the energy of the system and is contrary to the rule of stability which we have adopted as most consistent with the facts.

Four hydrogen atoms can combine to form an atom of helium, since both extranuclear electrons of the helium atom have values of n equal to unity. In forming the helium nucleus, however, four positively charged hydrogen nuclei have to be forced very closely together. This would have to be accomplished in opposition to the repulsion that exists between the hydrogen nuclei. This repulsion becomes very great at the small distances that separate the hydrogen nuclei in the nucleus of the helium atom. For this reason, the formation of helium from hydrogen is not likely to occur under ordinary conditions.

Helium shows little tendency to combine with other atoms, since its two electrons (for each of which $n = 1$, $l = 0$, and $m_l = 0$) can take no further part in spin coupling unless one of them is promoted to a higher energy level ($n > 1$). The promotion of an electron is not likely to occur, however, since an increase in energy would be required, and the molecule resulting from the coupling of such an electron would be unstable. Thus, helium hydride, if prepared, should prove to be exceedingly unstable.

In the hydrogen molecule, the two electrons spin in opposite directions as indicated by the two possible values of m_s, $\frac{1}{2}$ and $-\frac{1}{2}$. In any atom, two electrons with their spins oppositely directed form a closed and stable pair; and hence, they exert no attraction for a third electron. This means, then, that electrons that are coupled cannot exert valence forces and, therefore,

play no part in the formation of molecules. A single electron which finds in its own atom no other electron that has the same first three quantum numbers but whose spin is oppositely directed to its own can pair with such an electron in another atom and thus form a valence bond. This is the shared electron bond of the Lewis and Langmuir theories. In the lithium atom, for example, there is a single electron in the valence level, for which $n = 2$. The pairing of this electron within the lithium atom itself is impossible, since the two other electrons, both of which are in the $n = 1$ quantum state anyway, are paired together and form a closed system from which the third electron is excluded. Lithium, therefore, has one electron capable of coupling with an electron of another atom. The valence of lithium, therefore, is one. There are two electrons in the outermost group of the beryllium atom. For these, $n = 2$. If these two electrons have sets of quantum numbers

$$n = 2;\ l = 0;\ m_l = 0;\ m_s = \tfrac{1}{2}$$
$$n = 2;\ l = 0;\ m_l = 0;\ m_s = -\tfrac{1}{2},$$

respectively, they will form a closed pair. In this case, the valence of the atom is zero. But if one electron has the quantum numbers

$$n = 2;\ l = 0;\ m_l = 0;\ m_s = \tfrac{1}{2}$$

and the other electron has the set

$$n = 2;\ l = 1;\ m_l = 1;\ m_s = \tfrac{1}{2},$$

each electron can attract another electron from another atom. In this case, the valence of the beryllium atom is two.

Similarly, the carbon atom possesses four electrons in its valence level, each electron possessing the principal quantum number two. Two of these electrons have an l quantum number of zero, and two have l numbers of one. The m_l quantum numbers can be one, zero, or minus one. The possible sets of quantum numbers that can be assigned to the four electrons of the carbon atom, again considering Pauli's exclusion principle, are shown as follows:

Two Electrons, Coupled	Two Electrons, Coupled
$n = 2$	$n = 2$
$l = 0$	$l = 1$
$m_l = 0$	$m_l = 1$
$m_s = \frac{1}{2}$ for one electron and $-\frac{1}{2}$ for the other.	$m_s = \frac{1}{2}$ for one electron and $-\frac{1}{2}$ for the other.

This carbon atom would have a valence of zero.

Two Electrons, Coupled	One Electron, Uncoupled	One Electron, Uncoupled
$n = 2$	$n = 2$	$n = 2$
$l = 0$	$l = 1$	$l = 1$
$m_l = 0$	$m_l = 1$	$m_l = 0$
$m_s = \frac{1}{2}$ for one electron and $-\frac{1}{2}$ for the other	$m_s = \frac{1}{2}$	$m_s = \frac{1}{2}$

This carbon atom would have a valence of two.

One Electron	One Electron	One Electron	One Electron
	(All electrons uncoupled)		
$n = 2$	$n = 2$	$n = 2$	$n = 2$
$l = 0$	$l = 1$	$l = 1$	$l = 1$
$m_l = 0$	$m_l = 1$	$m_l = 0$	$m_l = -1$
$m_s = \frac{1}{2}$	$m_s = \frac{1}{2}$	$m_s = \frac{1}{2}$	$m_s = \frac{1}{2}$

This carbon atom would have a valence of four.

London and Heitler have attempted to account for the valences of the lighter elements in the manner that we have illustrated for carbon. The scheme works very well for many elements. Thus, the different valences of sulfur are explained by the following distribution of quantum numbers for the electrons of the third quantum group:

$n =$	3								
$l =$	0		1				2		
$m_l =$	0	1	0	-1	2	1	0	-1	-2
Number of electrons for each state.	2	2	2	(Valence 0)					
	2	2	1	1	(Valence 2)				
	2	1	1	1	1	(Valence 4)			
	1	1	1	1	1	1	(Valence 6)		

Although London and Heitler's theory appears to predict the valences of many of the elements in a satisfactory manner, it also predicts valences that appear very improbable. It predicts valences of two, four, six, and eight for argon, but none of these is

displayed by this element. These valences of argon must depend upon an increase in the values of l from one to two. Thus, an electron of the argon atom may be promoted from the state for which $n = 3$, $l = 1$, $m_l = -1$ to another state for which $n = 3$, $l = 2$, $m_l = 2$. The increase in energy attending such a change may be greater than the decrease resulting from the coupling of the promoted electron with an electron in another atom, and consequently the predicted valence may be one that is not likely to be encountered. The predicted valences of argon are shown below.

n =	3								
l =	0		1				2		
m_l =	0	1	0	−1	2	1	0	−1	−2
Number of electrons in each state.	2	2	2	2	(Valence 0)				
	2	2	2	1	1	(Valence 2)			
	2	2	1	1	1	1	(Valence 4)		
	2	1	1	1	1	1	1	(Valence 6)	
	1	1	1	1	1	1	1	1	(Valence 8)

The limitations of the valences of the first elements in the periodic system are accounted for with a fair degree of satisfaction. In fluorine, for example, n for the valence electrons is two. For two of the seven electrons $l = 0$; and for five of them, $l = 1$ Of the latter, two have values of $m_l = 1$; for two others, $m_l = 0$; and for one, $m_l = -1$. It is impossible, therefore, for the fluorine atom to possess more than one electron capable of coupling to form a valence bond, without promoting an electron to a state for which $n = 3$. For chlorine, however, the following distributions of electrons of the valence shell are possible with the corresponding valences:

n =	3								
l =	0		1				2		
m_l =	0	1	0	−1	2	1	0	−1	−2
Number of electrons for each state.	2	2	2	1	(Valence 1)				
	2	2	1	1	1	(Valence 3)			
	2	1	1	1	1	1	(Valence 5)		
	1	1	1	1	1	1	1	(Valence 7)	

Similarly, oxygen can have valences of only zero or two, although sulfur in the same group can have valences of zero, two, four, and six.

A great deal remains to be explained. The scheme of valences suggested by London and Heitler must be extended until the structural formulas of organic chemistry are successfully treated by the new theory. The problem offering the greatest difficulty in this connection is the directed chemical bond. Pauling has recently demonstrated that the geometrical symmetry of different atoms (such as the tetrahedral symmetry of the carbon atom) may be produced by the linear combinations of wave functions in such a manner as to produce regions of high-charge densities extending in definite directions from the nucleus. Thus, in the carbon atom, these regions of high density may extend in the directions of the corners of a tetrahedron. Combinations of carbon with other atoms will occur, therefore, in these directions by the coupling of electrons, provided, of course, that none of the four electrons of the carbon atom is already paired. This condition is possible if one of these electrons has a value of $l = 0$ and three have values of $l = 1$.

Conclusion

And at the end, as at the beginning, we ask, "What is matter?" We have learned something concerning certain divisions of matter and how they behave. But the complete answer is yet far beyond our reach. We came nearest to learning what matter is when we learned of the relation between matter and energy. But even that relation is not an ultimate truth, nor does it closely approach one. To relate matter to energy is only to tie it to another part of nature which we understand even less clearly than we do matter itself. The relation means only that we must attempt to explain the two together.

As we have delved deeper and deeper into the behavior of certain forms of matter, we have been forced to adopt strange methods of dealing with the problems that were presented. These methods have denied the validity of the use of physical models, such as we have been accustomed to construct as we have studied machines or examined other objects of scientific

interest. Many of the problems have proved to be outside the scope of our usual principles of reasoning. We have seen, for example, the principle of causality—the relation between causes and their effects—give way to the principle of indeterminism. We have found that energy during propagation appears to act as wave motions but that upon arriving at a given point, it may act in much the same manner as do particles of matter. We have learned that particles of matter, on the other hand, appear to act as waves or as if they were associated with undulatory motion during their flights through space. Most significant of all, perhaps, is the realization that neither energy nor matter has any real interpretation as waves and that the theory of waves is only a convenient method of expressing certain observable facts, such as intensities of light or the probabilities of the occurrence of electrons. Finally, in dealing with the atom, we have learned that we must discard the definite electronic positions, orbits, and velocities of the Bohr model for the statistical calculations of the probability of different positions and possible states of electrons. The new mechanics enables us only to *calculate* effects which we had hoped to *explain* by means of the mechanism suggested by the older theories. And, although it may have been apparent at all times, it is somewhat disconcerting to know that we can never hope to visualize the operation of the mechanism by which certain effects are produced.

Because of the lack of tangible quantities and properties upon which to base its conclusions, science appears to be in somewhat of a dilemma in dealing further with the structure of matter. One hears more and more frequently the expression that science can lead no further toward the ultimate truth in this direction and that for future developments new points of view must be accepted and new methods of treating the problem must be formulated and put into practice. In fact, the principle of indeterminism or lack of causality appears to be the beginning of a new and very different venture in man's study of nature. We feel almost as if the solid earth of our earlier concepts and physical models had been left behind, although these, perhaps, were not so solid as we thought, and that we have entered a strange realm, where our minds must reason mathematically concerning the world around us, but where our hands can no longer tell us any-

thing new concerning our surroundings by their touch, nor our eyes by their sight.

One cannot foretell what all this may mean for the future of science. There are those who say that science has reached its peak. From now on, they say, the world will turn from science, as we have known it, to metaphysics. Perhaps these persons are unduly agitated, having suffered, no doubt, considerable shock from the undesirable yet inevitable conviction that a new point of view and a different *modus operandi* are necessary. Such changes are not occurring for the first time in the history of science. They have come sometimes very slowly and sometimes in rapid succession. On the whole, they have appeared most frequently at times when advance has been most rapid. The history of chemistry and physics is a history of conflicts of ideas. We need only to recall the conflict of the principles of Aristotle as opposed to those of Democritus; Boyle's conception of the elements as opposed to the ideas of the alchemists; the conflict of the corpuscular and wave theories of light; the phlogiston theory as opposed to Lavoisier's explanation of combustion; the atomic concept as opposed to the continuous theory of the nature of matter; radioactivity as opposed to the concept of the elements as stable forms of matter; and the quantum theory as opposed to the theory of radiation as continuous wave motions. It is contrary to the very nature of science that its methods should remain unchanged as knowledge increases.

Will the methods that are slowly evolving in the search for truth prove successful? Or must they, too, sometime give way to something else? If science, as we know it, fails, it does so because it offers no further possibilities of satisfying man's innate curiosity and desire to explore. This and this alone will be the test of the new philosophy of science. Perhaps man may never know the ultimate truth. What manner of man would the creature be from whom nature holds no secrets? No more puzzles to solve, no more obstacles to overcome, no more use for a brain except for remembering! And yet we go on striving to reach the end of puzzles. Is there any reason for our hoping that we may sometime be successful in reaching the end? Man is little and nature is very, very big. "Specks of carbon," as some one has said, "on one of the countless grains of sand on the

shore of a boundless sea," why should we think that we are important enough in this great experiment of eternity to master the understanding of it all? Why should we try to match our intelligence against something so big, when our minds cannot grasp the meaning of one tiny atom of the universe in which we live and which we long to explore and rob of its mysteries? Nothing could express more adequately the shallow depths to which we have penetrated thus far than our own dissatisfaction with the answers that we have been able to propose to the questions "What is matter, and what is energy?"

Yet, as far as we are aware, we alone of all the animate and inanimate portions of the universe are equipped with a means of interpreting the world in which we live. We are distinguished from other forms of life by our intellect. This intelligence, urged on by our desire to come in contact with the ultimate realities of the universe and to learn ultimate truths, is always leading us on to seek answers to the questions of *what* and *why* which nature continually throws in our paths. These guides and masters of our minds know no impassable barriers. Although not always victorious, they cause us to renew the attack after every defeat with a more indomitable purpose. Baffled in one line of attack, we seize upon another. Our greatest danger lies within ourselves—the danger that lies either in extreme, dogmatic conservatism or in rash radicalism. For there are always among us those who scoff—some at the ideas of the past, others at the ideas of the present. There are others who know no prejudices and who are interested only in finding reasonable explanations of the universe and the happenings that occur within it. Sometimes it *does* become necessary to adopt a different point of view, to take up a new line of attack, just as we are now finding that the attack through mathematics serves most completely and naturally to explain the facts that are observed concerning the nature of matter and energy.

But whatever the methods of the attack may be, this much is certain. We shall continue to collect facts, to classify them, to organize knowledge, to interpret observations, and to reason as experience permits concerning the world and ourselves. In this respect, at least, science cannot change.

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