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All becoming has two causes, of which the most ancient theologians and poets chose to turn their attention to the stronger only, pronouncing over all things the universal refrain: "Zeus first, Zeus middle, all things Zeus," while they never approached the necessary or physical causes. Their successors, called *Physikoi*, did the very reverse; they strayed away from the beautiful and divine principle and refer all things to bodies, and impacts, and changes, and combinations.—PLUTARCH.

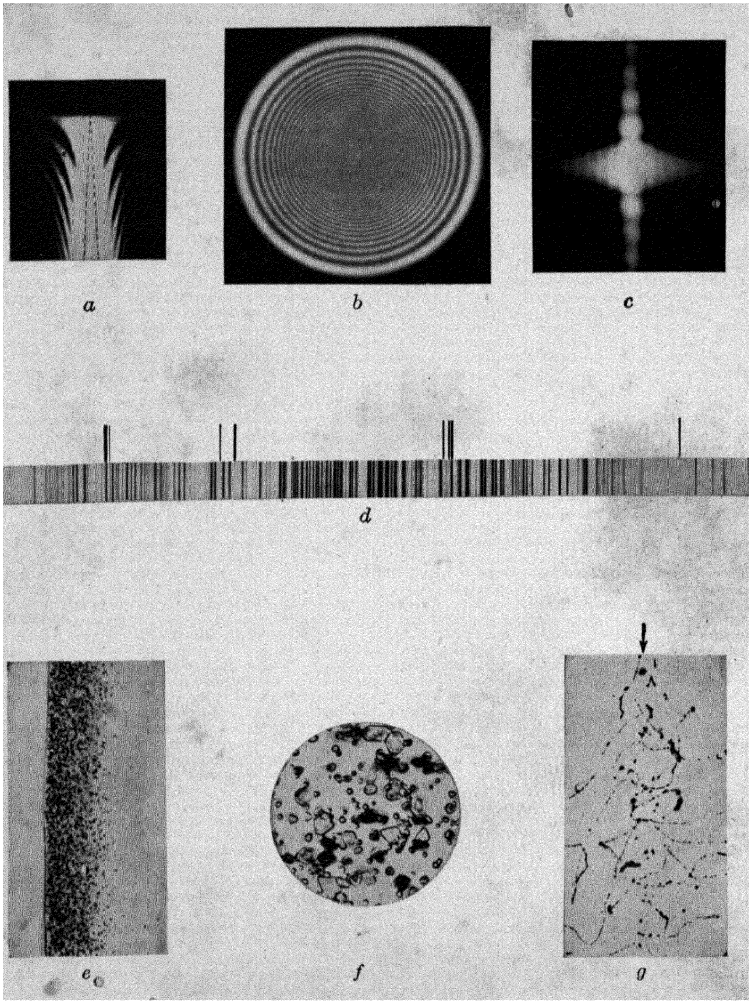


Fig. 1.—Light: Wave or particle?

a, b, c. **Diffraction of light: (*a*) through wedge opening (*Arkadief*); (*b*) through circular opening (*Hufford*); (*c*) through rectangular opening (*Thiow*)**

d Spectra: **mercury** and iron in visible region.

e, f Photographic emulsion after exposure, **showing granular development.** (*Ross and Sheppard.*)

g. Photoelectrons expelled **by x-rays.** (***Wilson.***)

(Frontispiece.)

THE PHYSICAL BASIS OF THINGS

By

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FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK AND LONDON

1934

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PRINTED IN THE UNITED STATES OF AMERICA

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THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

In introducing the fourteenth edition of the Encyclopaedia Britannica J. L. Garvin, the editor in chief, surveys the transformation of life in the last generation. "The map of the intellectual world," he says, "more than that of the political, is changed beyond recognition. On every side we see new mechanisms and agencies with consequent new social activities and habits; in many ways we are farther from the youth of our grandparents, even from the youth of our parents, than were they from the middle ages. This is ordinary evidence to the physical eye. But let the eye of the mind turn to inward views. In every direction new prospects and vistas stretch out. . . . In all the physical sciences, interacting more and more, the marches of experiment and perception during the last couple of decades are known even by the layman to be very wonderful. Many authorities pronounce that ideas in this sphere have been more profoundly altered than ever before in any equal period."

Dr. Garvin, continuing, opines that Einstein's theory of relativity is apt to have as profound an influence on the thought of this century as did the work of Darwin in the last or that of Newton in the eighteenth or of Bacon in the seventeenth. And now the New Mechanics in its implications seems almost to dwarf the theory of relativity.

We cite Dr. Garvin as a detached observer. In physics the years of this century have seen one monumental discovery rapidly succeeding another—no other science can show anything comparable. The physicist presents a superb view of nature. His discoveries are a most recent, dramatic episode in human culture. The discovery of the atom is one of the proudest achievements of intellectual man. It should not be necessary to give a brief for a course in modern physics as a part of a liberal education. Primarily this book is written not for the physics specialist but for the student of general interests. It does not aim primarily to give information but to give appreciation of the meaning of modern physics.

If it is to have a meaning, something of this story must be lived through by the student. In giving form to the book it has been assumed that in addition to reading these pages, the student will pursue some collateral reading, will work out illustrative problems, and will occasionally express himself orally or on paper. Frequent references have been made to the Encyclopaedia Britannica—because this is sure to be available. But such articles are rather too concentrated for a steady diet and other books should be at hand. And among other references I would mention the excellent summaries of current scientific developments appearing each Sunday in the New York Times. This subject is a live one and current developments should be followed.

This book is intended for students who have had a course in general physics. It is the author's belief that, because of the interest which is inherent in general physics, from any elementary course which has been sympathetically taught a large proportion of those students who are free to elect another science course will wish to elect one in modern physics. Therefore it has been intended that the subject should be within the grasp of the average sophomore with this preparation. Obviously from the first two chapters no real grasp of the theory of relativity will be obtained. But since this is somewhat aside from the story of the atom, no more than this cursory treatment has seemed justified. These two chapters throw the reader precipitately into modern physics and should cause some disturbance to complacency.

Similarly cursory are the last two chapters. For the rest of the book it is believed that the physical ideas as presented will be comprehended. It may appear that the latter half of the book is of considerably greater difficulty than the first. In reality this is not the case. The logical connections in the latter half are perhaps more intricately woven and the pace more rapid but from the earlier chapters (on kinetic theory) it is necessary to derive a vivid realization of the kinetic world of molecules. In my teaching I have found that to give this latter is no mean task. Given this, it is not too serious a matter to develop the picture of the individual atom. The story of spectroscopy and energy levels within energy levels may seem at times a little complicated but it takes only an occasional review and repeated examples to grasp the whole. It is probable

that before taking up Chap. XVIII the concepts of magnetic shell and magnetic moment and energy must be elucidated.

A *sine qua non* for any such subject as this is a questioning attitude toward the world about; for those with this attitude a course in modern physics holds a great deal. And it is for them that this book is written—for those who will look into nature with curiosity.

J. A. E.

IOWA CITY,
August, 1934.

ACKNOWLEDGMENTS

It is understood that a book of this kind is built upon the achievements of uncounted numbers of research workers. Without being able to particularize, the author must feel a general sense of obligation toward these fellow physicists and their predecessors who have made this story possible. The halftone reproductions have, for the most part, been made from prints furnished by the authors of the original papers; I wish to express my appreciation for their kindness. I also appreciate the courtesy of the publishers who have given permission to use various figures: The Royal Society for various cloud-track photographs (Figs. 1*g*, 108, 110, 115, 116); Julius Springer (Figs. 29, 72, 88, 91, 104, 108); S. Hirzel (Fig. 1*a*); The Chemical Catalog Company (Fig. 85); J. and A. Churchill, Ltd. (Fig. 121, taken from Brown's "History of Chemistry"); McGraw-Hill Book Company, Inc. (Figs. 69 and 133). Figures 30 *d*, *e*, *f* are reproduced by permission of Underwood and Underwood, owners of the copyright.

For Fig. 50 I am indebted to the observatory of the University of Michigan. The portrait of Einstein (page 69) is reproduced through the courtesy of the artist (S. J. Woolf); the other portraits have been drawn for this book by Mr. Richard Gates.

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THE PHYSICAL BASIS OF THINGS

CHAPTER I

YOUR POINT OF VIEW AND MINE

How Michelson and Morley performed an experiment and where it led; does a moving body shrink? A great thinker explains the paradox and upsets our ideas of space and time—and of philosophy. Your right and left, your future and past, and mine; but we must not go too fast or else we shall make the egg to lay the hen. Is now now or is it earlier? Pythagoras's theorem in three dimensions and in four. And how 900 quintillion ergs make a gram.

Are We in Motion?—Michelson and Morley wanted to know whether they were moving. This really started it all. They wanted to know whether they were moving and so they performed an experiment. In some ways this was the most remarkable experiment ever performed. Imagine yourself alone in space, you alone with nothing else in sight in any direction, perhaps nothing else existing in all space; and you wish to know whether or not you are in motion. An experiment which would detect such motion is surely a remarkable experiment. Or you and I are alone in space and we approach each other—is it you that is moving or I? Or, in this real universe of ours, does the sun rise and set because the sun itself is in motion or because the earth is? Ptolemy taught that the sun went about the earth and Copernicus that the earth, traveling some 20 miles a second, goes about the sun; and the astronomers tell us that earth and sun together—our whole solar system—are moving through space toward the star Vega at a rate of some 13 miles per second. But perhaps rather we are at rest and Vega is moving toward us. Michelson and Morley wanted to know whether, in an absolute sense, the earth was in motion through the ether. And hence the famous Michelson-Morley experiment.

The Michelson-Morley Experiment.—In this experiment Michelson and Morley determined the velocity of light propagated in different directions on the earth. Light is a wave motion traveling through the ether with a speed of about 187,000 miles a second (300,000 km. per second). Thus the time required for the light to reach us should be somewhat decreased if we ourselves were traveling through the ether toward the source of light and be somewhat increased if we were traveling away. If we were traveling away at the rate of 187,000 miles a second, the light should never reach us; if we were traveling away faster than this we should overtake the light and would see things happening backwards, presently coming to a place where we could see into yesterday. The apparent speed of light should depend on the speed of the observer. By observing any such difference in light speed Michelson and Morley hoped to measure the velocity of the earth through the ether. If we were on a train moving forward, light should (relative to us) have a greater velocity as it went from the engine to the rear platform than when it went in the reverse direction. This should give a means of detecting the velocity of the train.

A sensitive Michelson interferometer was used; it was mounted upon a large marble slab floating in mercury. With this arrangement the interferometer could be rotated into any direction without disturbing the instrument. In the interferometer, light from a source S falls upon a glass plate C. Here part of the beam is reflected toward the mirror B and part is transmitted through C to the mirror A. The beam returning from B is in part transmitted at C; that returning from A is in part reflected at C and the two beams fall together on the eye. If the distances from A to C and from B to C are so adjusted that it takes exactly the same time and the same number of wave lengths to go and return by the two paths, then the two rays will combine at C and give light (constructive interference); in case there is a half wave-length difference in the two beams, the result will be darkness (destructive interference). This gives a most sensitive method of comparing the speeds of light in the two directions.

If the earth is traveling in the direction from C to A with a speed of 20 miles a second (this is the velocity of the earth about the sun), it would seem that the time required to reach A would be about 20 parts out of 187,000 greater than normal; much of this time, but not all, would be recovered in the greater velocity

of the light traveling from A to C. The light reflected from C travels at right angles to the supposed motion of the earth and its apparent velocity would be not greatly affected.[1] If now the apparatus be turned to put CB into the direction of the earth's motion and CA transverse to it, then the case will be reversed. As the apparatus is rotated on its marble slab, there should be a variation in the interference pattern observed which would betray the velocity of the earth through the ether.

Actually no such result was found. The apparatus acted as if at rest in the ether; the result was the same no matter in what direction the apparatus was oriented, no matter at what time,

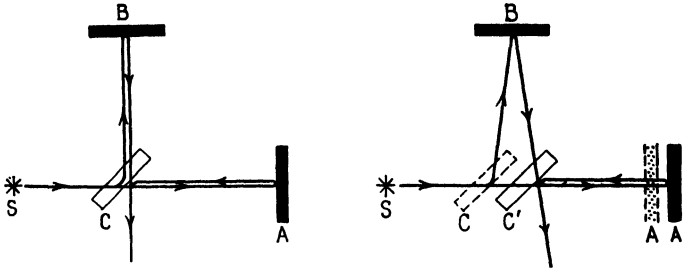


FIG. 2.—Michelson interferometer. At rest and in motion.

night or day, the experiment was performed. The experiment has been repeated in many parts of the earth with similar results.[2] The velocity of light is invariant.

Tentative Explanations.—Such result was really very difficult to understand. Light was supposed to travel through ether as sound does through air. It was as if sound, which travels with a normal velocity of 1100 ft. per second, should approach a person with the same speed, no matter how fast he ran toward it, and no matter how fast he ran away. It was suggested that perhaps light was thrown off like particles into space from the source and so would partake of the speed of the source. This theory was tested by measuring the speed of light from moving mirrors or moving stars and it was found to be false. (Some of the Greek philosophers believed that sight was something thrown off from

[1] The computed retardation in the CBC beam is exactly half of that in the CAC beam.

[2] In recent years D. C. Miller has repeated the experiment and has claimed to find a significant positive effect. However, others have not been able to confirm his results and it is generally accepted that absolute velocity cannot be measured and indeed has no meaning.

and related to the observer; some such theory might account for the result.) Some claimed that the ether was carried around with the earth (and hence the Fresnel "dragging coefficient" in optics) and therefore anyone at rest on the earth was at rest in the ether; but this view was hardly in accord with the other properties which had to be ascribed to the ether. Whatever the ether is doing here it must be doing throughout all space. It almost seemed that each man had his own ether, an ether extending throughout space, at rest for him. And indeed so strange became the properties of this medium through which light was said to be carried that the idea of an ether was gradually dropped; the "ether" is seldom referred to today.

The Fitzgerald Contraction.—So paradoxical a result would seem to throw suspicion upon the measuring devices of the observer. Fitzgerald advanced the theory that whenever a long body was turned into the direction of its motion it automatically contracted. Hence the apparatus which Michelson and Morley had so carefully tried to make rigid contracted in the very act of turning, contracted just sufficiently to conceal exactly the looked for result. Of course, no such contraction could ever be measured since any meter stick used to measure it would suffer a similar contraction. Lorentz, who was working with the theory of electrons, pointed out that such a contraction was not unreasonable. Electrical forces are propagated like light and a charge in motion would have a weakened field in the direction of this motion; matter, held in shape by electric forces between atoms, would then naturally shrink if in motion. Cubes would lose their symmetry, spheres become flattened ellipsoids. Although this concept of an absolute motion which could never conceivably be detected was very strange, no one doubted its existence—no one before Albert Einstein.

In one of Andersen's "Fairy Tales" two tailors make for the Prince a suit of clothes of cloth so fine that no one save one entirely virtuous could see it or feel it or detect it; and apparently no one was full of virtue. Nevertheless, all believed that the clothes were there, until a little child exclaimed to its mother: "Mother, the Prince doesn't have anything on." Einstein maintained that what could not conceivably be observed or measured had no existence. Physical reality consisted of measurable quantities. He held that velocity was only a relative concept.

Relativity in Newton's Mechanics.—Many of the quantities of physics quite obviously have relative rather than absolute meanings. A *large* object, a *brilliant* light, a *distant* hill—what absolute meanings have these adjectives? The object which seems large to the boy may seem small to the man; the brilliance of the lamp may pale in the sunlight. Is a hill 10 miles away a distant hill? An elephant is large, an ant is small; yes, relative to myself. In every measurement there is an element of comparison. By length I mean the number of times a meter stick will go into a distance; by mass is implied a comparison with a standard gram. Relative to some undetectable absolute, all distances in our universe might shrink a hundred fold over night and we should never be the wiser; for us all lengths would be unchanged and length has not the slightest meaning except as it refers to the measures which we can make.

In ordinary mechanics, motion is relative. Is the book on my table in motion? Relative to the table and myself, no; relative to the sun, yes. Looking from a train I see the fields and houses moving backward; and relative to the ground I am moving forward. Which is *really* in motion? Does the earth go around the sun or the sun around the earth?[1] If you are on one star and I on another and we are approaching each other, is it you or I that is moving? Meaningless questions, as meaningless as to ask whether the comparative size of the man and the elephant is due to the smallness of man or the largeness of elephant. As meaningless as to ask whether what I call left and you call right is *really* in an absolute sense left or *really* in an absolute sense right.

Mechanics (as founded on the laws of Newton) recognizes the relativity of motion. Newton's first law states that a body not acted on by a force continues in its state of rest (if you wish to consider it at rest) or of uniform motion in a straight line (if from your point of view it is moving). Were we in a uniformly moving train all mechanical systems would behave exactly as they do on the ground. A penny dropped to the floor would fall directly at my feet. A pendulum would swing, a top would spin, a ball would roll quite as though the train were stationary. In physical museums a spring pistol is pointed vertically upward

[1] Until we come to the theory of *general relativity* (Chap. II), we must recognize *change* in motion as detectable. When the train starts or stops or goes around a curve, I detect the acceleration readily enough.

from a car. When a projectile is fired it falls back upon the pistol—quite the same whether the car is at rest or in steady motion. Motion if it exists cannot be detected by any mechanical device; any observer has the right to consider himself at rest.

Electrical Phenomena.—The case would seem to be different when we consider electrical rather than mechanical phenomena. Like charges at rest exert purely electrostatic forces; the repulsive force is given by $f = q_1q_2/r^2$. When the charges are moving along together, another force, called magnetic attraction, comes into play between (what have now become) like currents. It would seem possible to detect whether I in the train or you on the ground are moving by finding which of us will experience this magnetic force between our electric charges.

Similarly light, which is an electromagnetic wave, was supposed to behave differently in a moving and in a stationary system. We have seen that the attempt to detect absolute velocity by its influence on the speed of light failed. After the Michelson and Morley experiment, other experiments with light and with electricity were tried. As a result of the magnetic field between moving charges, a strongly charged condenser, delicately suspended, should turn until the plates are perpendicular to the line of motion. The experiment (Trouton and Noble's experiment) was tried in order to detect the motion of the earth and again the result was negative. Apparently absolute motion was always to elude discovery.

The Theory of Relativity.—Michelson and Morley's original experiment was performed in 1889. In 1905 Einstein announced the theory of relativity. Einstein had approached the matter by asking himself the most fundamental questions: What do I mean by space and by time? What do I mean by two events occurring simultaneously? Can there be a meaning to a natural length, a normal length, alterations from which will occur but are in the nature of things undetectable? Does an unmeasurable physical quantity have meaning? If the question of absolute motion is forever unanswerable, is it not probably a meaningless question?

Einstein concluded that the Fitzgerald contraction was not fortuitous but was associated with the very meaning of size. Indeed this contraction appeared to be much the same as the foreshortening of an object when perceived in oblique perspective. Such foreshortening cannot change one dimension

without also changing another. If after looking at one face of a box I move to another point of view, I bring slightly into view another face of the box and the original face appears to be shorter. In just the same way Einstein as a result of his mathematical reasoning proposed that not only was the measurement of *distance* altered when a body was in motion but also, as if to compensate for this, there was a different evaluation of *time*. Not only the centimeter but also the second was altered for the moving observer.

The exact relations which Einstein developed were shown by Minkowski to be interpretable as meaning that time behaved as a fourth dimension—be it remarked as a dimension with some notable differences from the three others.

Let Us Look at a Map.—It is not possible to represent four or even three dimensions on the page but we can readily present two at a time. First let us take a horizontal plane of space. Figure 3 is a map. Four *points* are represented 1, 2, 3, 4. I have chosen one direction (*ON*) which I call north, and at right angles a direction (*OE*) which I call east. Now you may choose any direction for your north and a corresponding perpendicular direction for your east.[1] These are marked as N' and E'. Clearly such directions are purely relative.

Points 2, 3, 4 on the circle we may suppose are 1000 cm. from point 1. Point 2 is, from my point of view, due north 1000 cm. from 1. From your point of view 2 is 300 cm. to the west of 1 and therefore somewhat less than 1000 cm. north of 1 (954 cm.). But upon the *distance* between the points we agree. For you (as for me) the distance between 1 and 2 is $\sqrt{N^2 + E^2} = 1000$ cm. The point 3 is due north and 4 is due east for you, but for me 3 is somewhat east and 4 somewhat south. But in every case when the distance from the origin is computed (as the root of the sum of the squares) it is found to be "invariant." Such a map could be drawn for the vertical-north plane or for the vertical-east plane.

Nearly two thousand five hundred years ago Pythagoras enunciated the principle that the distance between two points

[1] N may represent geographic north, N' magnetic north—but it would not be necessary to restrict ourselves to these. Perhaps it would be better to let N represent the direction which is "front" for me and E represent my "right," N' and E' your front and right which may be greatly different—even exactly opposite to mine. O (not shown on figures) represents the the center of coordinates; it is the same as point 1.

was equal to the square root of the sums of the squares of its orthogonal components. Representing these as E (east), N (north), U (up), the Pythagorean theorem is that distance = $\sqrt{E^2 + N^2 + U^2}$ or, better, in terms of any orthogonal coordinates x, y, z,

$$\text{Distance} = \sqrt{x^2 + y^2 + z^2} \qquad (1)$$

And at a Time-space Chart.—Figure 4 is a diagram representing the time and place of certain *events*. The line *P-F* represents the position "here" (where I am) at successive time intervals from the past to the future. The line *W-E* represents different positions in space from west to east at the present instant. Other

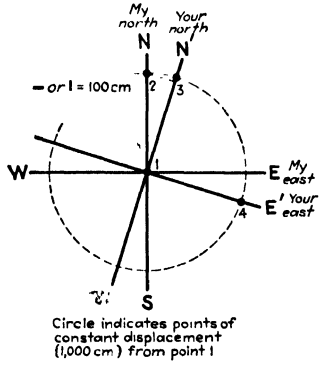


FIG. 3.—My axes and yours.

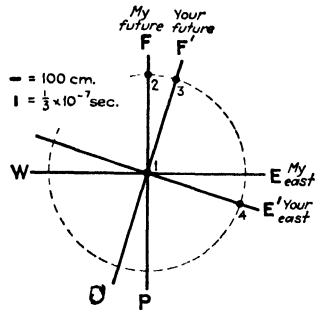


FIG. 4.—If time were merely another dimension.

directions we may forget for the present. (Suitable time-north or time-vertical diagrams can be drawn.) The scale along the *W-E* line is 2 cm. equals 1000 cm.; along *P-F*, 2 cm. equals a thirty-millionth part of a second. Four *events* are represented: (1) taking place here and now; (2) taking place here a thirty-millionth of a second later; it is almost simultaneous with (3) which takes place 3 meters farther east; event (4) took place a short time in the past and nearly 10 meters to the east of (1). These events may have been four explosions or any occurrences which had definite positions at definite times.

The line *OF'* represents a very rapidly moving body, one which travels eastward past me at the rate of 3 meters in a thirty-millionth part of a second (60,000 miles per second!). Let us call this a train—your train. You are moving eastward. Of

course, from your point of view you are at rest; OF' is your "here" line pointing directly into your future and, relative to you, I (represented by OF) am moving rapidly westward. We celebrated the start of your train from O by the event (1) and a little later another event (2) transpired at the same place (from my viewpoint) and the event (3) occurred in the train. As you saw it, (1) and (3) occurred at the same place; (2) occurred to the west.

If Time Were a Simple Fourth Dimension.—To all this there can be no objection since this is no more than making a diagram of events. But suppose time were really a dimension like north-south, east-west, up-down. Then since you certainly have a "here" line which differs from mine, you must likewise have a different "now" line. Since your sense of things which are *present* with you at different times is different from mine, correspondingly your sense of the things *simultaneous* with you at different places must differ from mine. Your now line should be OE'. From your moving[1] point of view the event (4) takes place at exactly the same time as (1). For me it appears to have occurred earlier. You and I will however agree upon the "separation" of events, where by separation we mean their difference in combined space and time as given by $\sqrt{E^2 + T^2}$.

If time were such a fourth dimension like unto the other three dimensions, our relative velocities might be so great that what I considered east you would consider tomorrow and what I considered the future you would consider west. And even, if our points of view could be exactly reversed, what I considered the future you might consider the past. This would indeed have strange consequences. If you and I perceived the same train of events, what I considered the cause you would consider the effect!

As Time Is.—Time is no such thing. The fundamental fact is, as Minkowski pointed out, that the *separation* between two *events* (which corresponds to the *distance* between two *points*) is given by $\sqrt{E^2 - T^2}$ (where E represents the distance and T the time). When we compare this relation with the Pythagoras theorem for space (distance $= \sqrt{E^2 + N^2}$), we see that time and space are indeed related, but that the relation is (speaking roughly) opposite to that holding between two components of space. In Fig. 5 are shown how your "here" line and mine, your

[1] As I see it.

"now" line and mine, are actually related. In the space-time planes we have a hyperbolic instead of a spherical geometry. The differences introduced are the following:

1. The constant separation is represented by a hyberbola instead of a circle.

2. Your "now" line is deviated in the opposite sense from before, bent toward your "here" line.

3. The greatest possible relative velocity between you and me is the velocity of light; *i.e.*, the greatest possible angle for a "World line" is 45°.

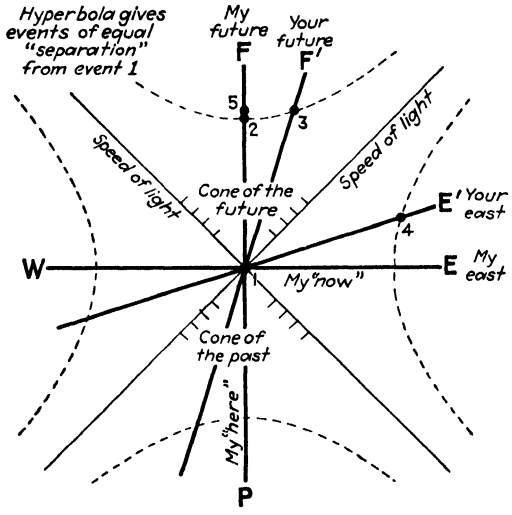


FIG. 5.—Two-dimensional section of the "The World" (in future-east plane).

4. It is impossible to turn pure time into pure distance—we cannot measure seconds with a meter stick, because a meter stick cannot travel so fast that its length will extend directly into the future.

5. We cannot turn the future into the past.

The Natural Unit of Time.—In mapping events in Figs. 4 and 5 we have chosen to express time not in seconds or minutes or hours but in a very small unit, the thirty-billionth part of a second.[1] This is the time required for light to travel 1 cm. In a geographical map there would be distortion if northerly distances were measured in one system of units, say miles, and

[1] That is, the $1/c$th part of a second where c is the velocity of light, 3×10^{10} cm. per second.

easterly distances in another, say inches.[1] So, before attempting to represent time as a dimension, it is necessary to determine a time unit which will be comparable with the centimeter. We have chosen the appropriate unit. Perhaps we could call it a centimeter (of time) but instead we have given it an independent name and in our discussion shall call it an "einstein."[2] The velocity of light in these units is *unity* (1 cm. per einstein); the velocities of all else, atoms and electrons and protons, are smaller (*i.e.*, proper fractions). Our usual velocities are very small fractions indeed. They are so small that the "foreshortening" of space and time is not obvious.

Separation.—By using this consistent system of units, the separation between two events differing (as 1 and 3 in Fig. 5) by t einsteins in time and d cm. in space is given by $\sqrt{d^2 - t^2}$ or, if the components x, y, z of the displacement d are taken,

$$\text{Separation} = \sqrt{x^2 + y^2 + z^2 - t^2}. \qquad (2)$$

It is not true, as was supposed before the time of Einstein, that the *distance* between two events is an invariant as seen by different observers in relative motion. The moving body is shorter. The *separation* between events is truly invariant. Length is only one projection, differently made by different observers, of this invariant quantity.

World Lines.—This theory of Einstein makes time a dimension, although not exactly the same kind of dimension as the other three. These four dimensions (future-past, north-south, east-west, up-down) make up what is known technically as the World (with a capital W)—the setting for all that is. The World consists of Space (*N-S*, *E-W*, up-down) and Time (future-past). The-World-at-the-present-moment is a cross section of this four-dimensional world. The World-at-1800 A.D. is another "lower" section; the World-at-2000 A.D. is another "higher" section. Each of us, each three-dimensional object about us, as it exists in time, at rest or in motion, forms a tube. Each particle in the object forms its own "World line" in this four-dimensional World. A point in the World represents a particle-at-a-given-instant or in other words an *event*; the World line represents the

[1] Such distortion is often used to exaggerate heights on relief maps.

[2] There is no name in conventional use for this fundamental time unit. There is no sanction in general usage for the name which we are using.

particle existing through time. We have attempted to portray a three-dimensional representation of the World in Fig. 6.

In space we change our reference axes by a *rotation.* A twist of the head alters "front"; a rotation of axes changes geographic north to magnetic north. Corresponding to this rotation in space, a change of *velocity* changes our time axis—it alters what we mean by "here." A change of my velocity means a bending of my World line.

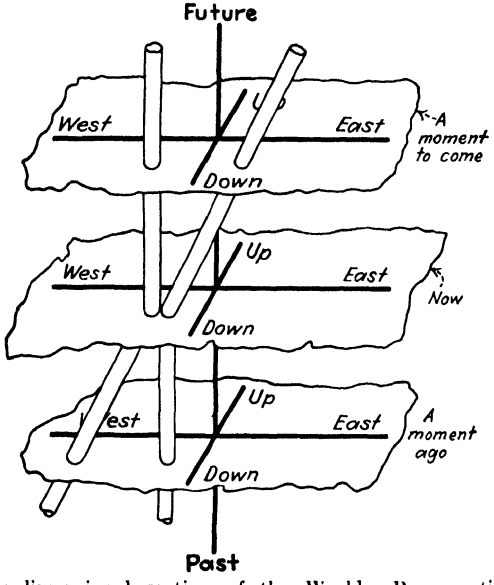


FIG. 6.—Three-dimensional section of the World. Representing an elastic collision between a moving ball and a stationary one.

It is a commonplace experience, that my "here," my neighborhood, depends on my motion. These trees and stones all remain near, adjacent to me as I sit in the field; the train moves past. As I sit in the train, the objects in the train remain adjacent; it is the trees and stones that move. This difference in "hereness" of things is occasioned by the change in my own motion, the rotation of my World line. This is commonplace. It is not commonplace or readily apparent that *pari passu* occurs a change in the "nowness" of things. As I stand in the field, I can imagine some distant event as taking place exactly at the present moment —it is contemporary. Were I instead traveling through the field (in the train), a different, say earlier, event would be contem-

porary with me. My "here" axis (very obviously) rotates with my motion—my "now" axis (remarkably) rotates through the same angle. This is the first rather bizarre result of the new theory.)

The different points of view of the observer at rest and in motion will be made clearer by a mythical news story of the making of a speed record some centuries hence.

From the *New York Flash*, January 27, 2934

Chicago, Jan. 26: The long-expected trial run of the New Thirtieth Century Limited occurred today between New York and Chicago, establishing a speed record which will probably remain long unbroken. The distance between these cities is exactly 1000 km.[1] (100 million centimeters) and the trip was made in 300 million einsteins (hundredth of a second), giving the remarkable velocity of one-third (*i.e.*, 60,000 miles per second). The train left New York City (1) at noon sharp and pulled into the union station here (3) at exactly 300 million einsteins past noon (eastern time).

New York City, Jan. 26: In anticipation of the record-breaking trip of the new Thirtieth Century Limited a celebration had been planned here. It was expected that the train would reach Chicago (3) at exactly 300 million einsteins after noon and at that instant a signal (5) was given and the local festivities began. The affair had been well planned. By many interchanges of radiograms, clocks in the two cities had been exactly synchronized. A radio message sent at the moment of arrival in Chicago (3) reached here 100 million einsteins later, indicating that the train's arrival had indeed been simultaneous with the local signal.

The *Flash* had a correspondent on the train whose account of the trip is given below.

On board the Thirtieth Century Limited, Jan. 26: New York City passed out of sight (1) promptly at noon. In spite of the fact that the citizens of the metropolis were moving at the hitherto unheard of speed of one-third the velocity of light they seemed quite insensible of the experience. Chicago arrived here (3) at exactly 283 million einsteins after noon.[2] During the trip the local observers carefully measured the distance of the territory which was passing by and determined that the distance between the two cities was 95

[1] This distance is shortened for simplicity. These events as numbered in the report can be followed in Fig. 5.

[2] Notice that the separation here between events (1) and (2) is 283 million. This observation on the train agrees with the observations as made from New York and Chicago for which places the events differed in time by 300 million einsteins and in space by 100 million centimeters giving for separation $\sqrt{300^2 - 100^2} = 283$.

million centimeters. This gives for the speed attained by the earth in this run exactly $\frac{1}{3}$.[1]

In New York it had been planned to celebrate the arrival of Chicago at our train. Plans seemed to have miscarried since the signal starting festivities was given (5) some 35 million einsteins after the arrival of the train. The attempts to synchronize the clocks had resulted in all clocks in Chicago being this amount in advance of those in New York.

The striking differences in the points of view of the two relatively moving observers in this illustration are:

1. As time goes on there is a difference in the location of events as related to the train and as related to the ground. x (or y or z) differs from x' (or y' or z'). The "here" for the New Yorker means New York—the train moves away. The "here" for the traveler means the train—New York moves away. This is the difference in the "here" axis and is the very obvious difference.

2. When events at different places (New York and Chicago) are compared, they differ as to events which are simultaneous. t (for the ground) differs from t' (for the train). Events which the New Yorker and the Chicagoan called simultaneous appeared to the traveler separated by 35 million einsteins (1.2 thousandths of a second). This is the difference in the "now" axis. It is by no means obvious.[2]

3. They measure distances differently: what for one is a pure displacement is for the other a combination of a displacement and a "distimement." Again this is not obvious.

This illustration seems rather fanciful since such very great speeds are involved; the high speeds are necessary to introduce significant difference in the descriptions. Actually the fastest nebula observed moves with a velocity of about 20,000 miles a second, in relativity units a velocity of $\frac{1}{15}$. There are, however, electrons from radioactive substances which move with extremely high velocities of more than 95 per cent of the limiting speed. Foreshortening must now be observed in the electron dimension. The erstwhile spherical electron must appear as a very much

[1] 95 million ÷ 283 million.

[2] The reason that the "here"-axis deflection is obvious and the equally large "now"-axis deflection is not is that in most of our experience we deal with things billions of einsteins apart in time but only a few centimeters apart in space. The displacement of even a very slow motion can be observed by observing over many minutes (trillions of einsteins) the distimement would be equally large if we could conveniently compare times at large distances—trillions of centimeters apart (p. 16).

flattened ellipsoid and doubtless you and I are equally flattened from its point of view.

The Development of the Concept of Relativity in Space-time.—What we call space is of three dimensions. There is front-back, right-left, up-down. One may imagine some precocious, philosophically minded infant reflecting upon the world into which he is born and mapping out the world in his self-centered fashion —as long as he is confined to his crib he may believe his front and his right and his up each have *absolute* meaning. But, as he reaches years of greater discretion and moves about, he finds that he cannot force these ideas on his fellows, each of whom has his own front and his own right, though everyone in his vicinity agrees about "up." And here is a first step in relativity. Perhaps he now chooses a better system of coordinates as north-south, east-west. He can choose any arbitrary direction as north: toward the earth's pole (as we usually actually do) or toward the magnetic pole or toward Greenwich or Paris. North-south and east-west are not essentially different; away from the sun and stars and compasses and they cannot readily be distinguished.

But this slowly developing man of ours still maintains a unique direction: up-down. This is about the stage of relativity which the world had reached before the time of Copernicus. But when it was known that the world was round and but a small part of a universe, it was realized that this up-down direction had a unique meaning only relative to this earth. In the larger sense all three directions of space become interchangeable. One cannot too much emphasize the importance of this new and broader point of view, this realization of the relative place of the earth in the universe, introduced by Copernicus, emphasized by Galileo, and interpreted by Newton. It was revolutionary, affecting religion, morals, literature, politics, as well as science.

But always hitherto the future-past has been considered as a unique thing called time, a thing different from north-south, east-west, up-down. No one would think of measuring it with a meter stick. It is but the next and final stage in the growth of our perception of relativity to recognize that that which we call the "due future" may by others be differently regarded. As a rotation of my head alters my "front" and my "right," so a velocity alters my sense of "here" (obviously) and my "now" (less obviously). One must proceed with caution, however.

Time is not exactly the same kind of dimension as the others. The difference is seen in the Pythagorean theorem in four dimensions:

$$\text{Separation} = \sqrt{x^2 + y^2 + z^2 - t^2}$$

Einstein's influence on twentieth century thought is comparable to that of Copernicus four centuries ago.

Why Is Relativity Not Intuitively Obvious?—It is to be remarked that in terms of einsteins and centimeters we are all

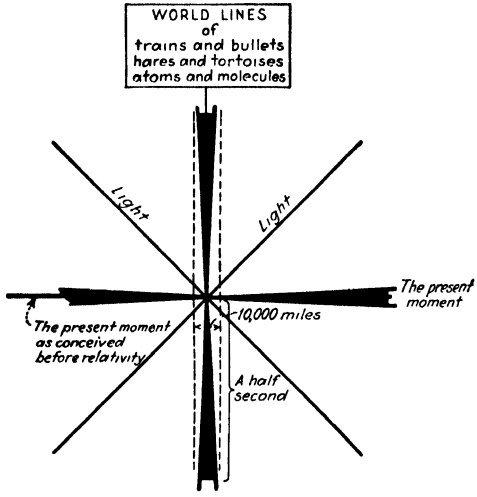


FIG. 7.—Our World lines. Dotted lines enclosing 10,000 miles of space and only 1 sec. of time show how much longer temporally than spacially is our World of daily experience. The vertical wedges include all World lines except very high speed corpuscles (as electrons, protons, and photons). The horizontal wedge contrasts the prerelativity concept of simultaneity (the same line for all observers) with that introduced by Einstein.

very slim creatures in the four-dimensional world. I am some 180 cm. tall and some 40 cm. broad and some 20 cm. thick and have lasted, as far as my memory goes, some 30 billion billion einsteins. I can easily perceive a tenth of a centimeter but cannot distinguish events separated in time by less than a billion einsteins. You, I, all of us, exist in lines almost parallel to my time axis. Even a rifle bullet moves only about 1 cm. in a million einsteins. Its world line in Fig. 4 would be inclined at an angle of about a fifth of a second of arc. Not much chance of detecting foreshortening here; all our points of view are nearly the same.

If you and I were creatures extending miles to the north and inches to the east and west, I dare say that we would adopt different units and instruments to measure "northness" and "eastness." And probably we should never perceive the foreshortening in the "northness" due to our slightly different directions.

In Fig. 7 it is intended to show how nearly parallel are most world lines. Actually few things about us go as fast as a mile a second—the blackened wedge of world lines could be ten thousand times thinner and yet include all such. Taken in connection with the fact that most of our experiences are limited to much less than a thousand miles but include many seconds, it should be obvious why we so inevitably recognize the difference in our respective "here" things but not in our respective "now" events.

Here and Now.—It is quite obvious that the meaning of "here" is purely relative. Is New York at the same place now that it was a year ago? Does the seat in a railway coach remain in the same place from minute to minute? What is meant by "the same place" or "here" at different times depends on the observer.

But what is meant by the same time, "now"? What is meant by the same time at different places in the universe? Certain unknown things we may say are happening on certain stars at the present instant; the radio message (light) will tell us of it years later. What does this "present instant" mean? Einstein asked: How do we determine simultaneity? To make my clock in San Francisco synchronous with one in Washington, I listen for a time signal; I allow for the time required for the radio wave to travel 3000 miles ($\frac{1}{60}$ sec.) and set my clock accordingly. But another observer may disagree as to this distance; if moving rapidly he may call it 1500 miles *and will make a different correction.* I may consider event A in Washington and B in San Francisco as simultaneous; you moving east consider A the earlier event and another observer moving west considers it the later. "Here" and "now" and our measurements of time intervals and space intervals are relative to the observer.

Modification of Mechanics.—The mechanical principles of Newton are not exactly valid. It has been pointed out that the usual mechanics was relativistic and the new theory introduces no modification which is significant at small speeds. But when the speed of a body approaches that of light, the mass increases. In mechanics an unbalanced force always produces a change in

momentum (mv); at low velocities the mass of a body stays (practically) constant and the *velocity* is increased by an accelerating force. At very high velocities the velocity stays (practically) constant and in this case the momentum is changed by the force because the *mass* of the body is increased. The velocity cannot exceed the velocity of light. All the mechanical laws must be restated in terms of relativity if they are to hold for the highest velocities.

One of the most important consequences of relativity is that mass and energy are one. If we use relativistic units (einsteins), the unit of energy is the gram. In ordinary units the energy unit is the erg; 9×10^{20} (*i.e.*, c^2) *ergs are equivalent to* 1 *gm.*

$$M \text{ (in grams)} = \frac{\text{energy (in ergs)}}{c^2} \tag{3}$$

Therefore if m_0 is the *rest mass*, the mass of a body in motion is

$$m = m_0 + \frac{1}{2} m_0 \frac{v^2}{c^2} \tag{3''}$$

This is approximate. The exact expression is (page 27)

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{3'}$$

Indeed $\frac{1}{2}m_0v^2$ represents kinetic energy only for small values of v.

The Mass of the Electron.—Bucherer has measured the mass of high-speed electrons and has found the expected increase as the velocity of light was approached. Table 1 gives the theoretical values of the electronic mass.

As the kinetic energy increases, this energy (in relativity units) is simply added to the rest mass. The fastest electrons from radioactive substances are the beta rays of thorium C′; their velocity is 95 per cent that of light and their masses are 30×10^{-28} gm. Even faster electrons are found in cosmic rays. Their masses may be thousands of times as great as the rest mass.

Further Examples of Energy as Mass.—When a body is heated, the additional energy of thermal agitation must increase the mass of the body. 1 calorie equals 42 million ergs. Dividing

by 9×10^{20}: 1 cal. equals 4.7×10^{-14} gm. Such a minute quantity cannot be measured.

When energy is given out in a chemical combination, the resultant compound should weigh slightly less than the original constituents. The chemical energy of formation of compounds amounts to only a few thousand calories and the effect on the mass cannot be detected. It must be true, however, that a molecule of water weighs slightly less than the sum of the original weights of the hydrogen and oxygen atoms of which it is composed.

TABLE 1.—ENERGIES AND MASSES OF HIGH-SPEED ELECTRONS

Speed, centimeters per second	Kinetic energy, ergs	Kinetic energy, grams	Mass, grams
Rest	0	0	9.0×10^{-28}
0.5×10^{10}	$0\ 12 \times 10^{-7}$	0.13×10^{-28}	9.1×10^{-28}
1.0×10^{10}	$0\ 51 \times 10^{-7}$	0.6×10^{-28}	9.5×10^{-28}
$1\ 5 \times 10^{10}$	$1\ 38 \times 10^{-7}$	1.4×10^{-28}	10.4×10^{-28}
$2\ 0 \times 10^{10}$	2.8×10^{-7}	3.1×10^{-28}	12.1×10^{-28}
2.5×10^{10}	6.6×10^{-7}	7.3×10^{-28}	16.3×10^{-28}
2.7×10^{10}	10.4×10^{-7}	11.6×10^{-28}	20.6×10^{-28}
2.8×10^{10}	$14\ 4 \times 10^{-7}$	16.0×10^{-28}	$25\ 0 \times 10^{-28}$
2.9×10^{10}	23.8×10^{-7}	26.4×10^{-28}	35.4×10^{-28}
$(3.0 \times 10^{10}$	∞	∞	∞)

It is generally recognized that all of the more complex atoms are themselves composed of hydrogen atoms, united with enormous emission of energy. The energies involved in these cases of atomic synthesis are so great that even when measured in grams they are not inconsiderable. In consequence, the helium atom does not weigh exactly four times as much as a hydrogen atom—there has been a loss of some 30 mg. of energy and of mass in the process (Table 14).

Four-vectors.—In the four-dimensioned world, the physicist recognizes vectors with four components: four-vectors. The familiar three-vectors of ordinary mechanics are the space projections of these. Examples of four-vectors are:

1. Displacement-time; components x, y, z, and t. The "length" of the four-vector is $\sqrt{x^2 + y^2 + z^2 - t^2}$.

2. Momentum-energy (or mass); components mv_x, mv_y, mv_z, and m (or energy). "Length" of the four-vector is $\sqrt{(mv_x)^2 + (mv_y)^2 + (mv_z)^2 - m^2}$.

3. Force-power; components F_x, F_y, F_z, power, each corrected by the factor $\sqrt{1 - v^2/c^2}$.

Relativity and Electromagnetism.—Does there still remain for us something of unreality in all of this? If so, it is probably because we do not recognize relativity in practical things. The astronomer and the physicist can read relativity from their experiments, but even in their laboratories it is usually found only in the last decimal place. Is there no place where the relativity correction makes a practical difference?

As a matter of fact there is. Two unlike charges attract in accordance with Coulomb's law (page 6). If we should now move relatively to them, we should observe this mutual attraction to be lessened. The electric force is evidently one of those things which appear differently to the moving observer. The decrease is not large; it involves the factor v^2/c^2.

But the electric locomotive could not wait to be born for the theory of relativity. It was Oersted and Henry and Faraday and Maxwell who first observed this effect and they named it magnetism. For it turns out that, in a conductor, there are such enormously large numbers of charges, positive and negative, that the decrease term (despite the factor v^2/c^2) is not small after all; and, more pertinently, it turns out that the Coulomb forces among all of these positive and negative charges cancel, so as to leave only the correction! So it is that it is the "trivial" relativity correction which does in America the work of 30 million horses, and it is the "electrostatic force" which is trivial. But still there remains the factor v^2/c^2 to betray the origin of the magnetic force.

There was little in mechanics left unchanged by the theory of relativity; the theory left Maxwell's equations unaltered as the basic law of electromagnetism. To be sure, the motors ran as well before Einstein—the more useful laws of Nature cannot await a full understanding before they are used. But the scientist must have some difficulty interpreting electricity without relativity, and as a matter of fact it was electrical theory which guided Lorentz to his early derivation of what later became the basic relativity transformation.

Influence of Relativity on Modern Thought.—One cannot doubt this special theory of relativity which we have been portraying. It agrees so well with the known facts and is fundamentally so simple that it is regarded as scientifically certain. Yet it introduces concepts bizarre to our usual way of thinking and the corrections which it introduces into Newtonian mechanics are usually of transcending smallness. Its fundamentals cannot be portrayed in a single chapter. We can but remark that here in relativity a great new chapter of science was written. It was a chapter which has had little contact with practical science, with inventions and patents, but one which has revolutionized thought. It has again given man a broader outlook upon things, much as did the discoveries of Copernicus, Columbus, Galileo, and Newton at the dawn of the modern age.

However, it was not in giving us this particular picture of space and time that Einstein most fundamentally modified

modern thought. Einstein's critical analysis of these concepts introduced the modern era in physics in which all the fundamental concepts have been subjected to careful scrutiny. There is a tendency for men to worship words. The physicist today refuses to grant meaning to any concept which is not measurable. Does light travel through an ether or through empty space? The question was once hotly debated; today we assert that an "ether" which allows light to travel and an "empty space" which allows it to travel are synonymous. Is time *really* a fourth dimension, is there something smaller than the electron, what would happen to the earth if the moon suddenly ceased to exist? Physicists consider these as meaningless questions unless experiments are at least conceivable by which they can be answered.[1]

"Things are as they behave." This pragmatic philosophy is the creed of the physicist. Speculation about "ultimate realities" deeper than these results of measurement if not meaningless are at least outside the scope of science. The whole of physics is an attempt to describe as simply as possible what things do, not what they "really, really are."

Space and time are concepts with meanings only relative to our yardsticks and clocks. So did Einstein begin his search into the nature of things. Einstein's theory is not a mere trimming of the idols of thought set up by our intuition but is a closely knit fabric woven from observable events. New ideas are scarce. Because the theory of relativity is not, like most theories, a mere recasting of an idea that runs at large, it is at first hard to "believe in."

Development of Relativity Transformations.—We have chosen to describe the facts of the special theory of relativity in geometrical terms, using the concept of time as a quasi-fourth dimension. The justification of this interpretation is the close analogy existing between the ordinary equations of transformation which correspond to a rotation in space and those corresponding to a velocity of the axes of reference. The derivation of these transformation relations (discovered by Lorentz[2] and derived from relativity considerations by Einstein) is not difficult. The "Lorentz transformation," as these relations are called, is the heart of the special relativity theory.

The fundamental fact with which the theory of relativity must reckon is that the velocity of light c has the same value for any observer.

[1] The reader will be interested in the early pages of Bridgman's "Logic of Modern Physics," where he gives examples of meaningless questions.

[2] H. A. Lorentz (in Leyden) was our most renowned theoretical physicist in the early years of this century.

The Newtonian Transformation.—Let there be two reference systems of Cartesian coordinates, S and S', in relative motion one to the other. Suppose that the x, y, z and x', y', z' axes in the two systems coincide at a certain moment. Suppose that the relative motion of the S' system is to the right, along the x axis. If x, y, z and x', y', z' are the coordinates of a certain point at a time $t(t')$, then by Newton's mechanics

$$\begin{aligned} y' &= y \text{ and } z' = z \\ x' &= x - vt \end{aligned} \qquad (A)$$

According to Newtonian mechanics, the clocks in one system read the same as those in the other.

$$t' = t \qquad (B)$$

To illustrate this Newtonian transformation concretely, suppose that S represents a reference system fixed on the ground, that S' represents one on a moving train—the track extends along the x (and x') axes and at a certain moment (when t and t' equal zero) the x and x', y and y', z and z' axes all coincide. At this moment a point (say $x = 3$, $y = 0$, $z = 0$) will have identical coordinates in each system. But as time goes on, the origin fixed in the train moves along, and, at time t, the S' system of coordinates is displaced a distance vt to the right with respect to the S system. A point having coordinates of x, y, z at this time (with respect to the ground) will evidently have coordinates $x' = x - vt$, $y' = y$, and $z' = z$ with respect to the train.

The y and z coordinates, perpendicular to the motion, are unchanged and do not enter into the argument. It will be simpler to neglect them and consider only distance $x(x')$, *i.e.*, along the track (train), and time (t, t').

Now this simple transformation (A and B) cannot be strictly true. For, according to this Newtonian mechanics, if any velocity has a value u along the x axis (the track) in the one system, it will have a value $u - v$ in the other. If the value of the velocity of light is c as measured from the ground, its speed relative to the train would be $c - v$ and this contradicts the fundamental postulate established by Michelson and Morley that c is an invariant. Einstein undertook to find the true transformation which would leave the velocity of light invariant. He was led to the transformation of Lorentz.

The Lorentz Transformation.—Consider again this S system which is fixed on the ground and the S' system fixed on the train. Let us consider both the x coordinates and the times t and the x' coordinates and times t' of two events. Let us take for the two events (I) the sending of a light beam from one point $O(O')$ and (II) the reception of this light beam at another point (A, A') shortly later. Suppose that the signal is sent from the origin ($x = 0$) at the time $t = 0$. It will travel with velocity c and at a time t sec. later will be received at a point along the track a distance ct. The coordinates of this second event (II) in the S system are $x = ct$, and the time is t. (Also if we were considering the other dimensions, we should have $y = 0$ and $z = 0$.) Now if the axes are chosen for simplicity so that the origins in S and S' coincide and the clocks at the origin are set so that $t = t'$ at the instant that the signal is emitted (event I), then the coordinates

of event I in the primed system are $x' = 0$ and $t' = 0$. This primed system moves to the right (relative to S) and Fig. 8*A* represents the two systems at the moment t, when the light signal is received (II). S' has moved a distance vt. Its origin ($x' = 0$) is opposite the point $x = vt$. It might seem that the coordinate x' of the second event (II) would be $x' = x - vt$. But since we remember that measuring sticks and clocks have a habit of changing their lengths and rates in the relativity theory, distorting the scale of things, it will be better to write

$$x' = \alpha(x - vt) \tag{C}$$

where the constant will allow for any possible contraction in scale. (α equals unity in the Newtonian transformation.)

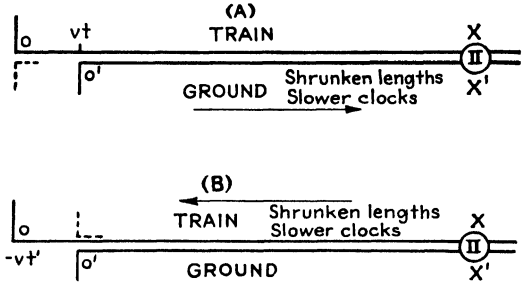


FIG. 8.

It is quite evident that t' cannot equal t. For we must have the relation

$$\alpha(x - vt) = ct' \tag{D}$$

since light velocity is c in both systems. Hence combining Eqs. (*C*) and (*D*)

$$t' = \alpha\left(t - \frac{vx}{c^2}\right) \tag{F}$$

Now consider the state of affairs as it appears from the train. Figure 8*B* shows the situation at the time t', when the light arrives at x'. Of course, x and x', the points in the two systems at which II occurs, coincide at this moment. The point on the ground (*O*), from which, shortly before, the signal was sent, has now moved to the left (passed beyond the rear of our train) a distance vt'. Hence by the same argument as before, in the S system the coordinate (x) of event II is

$$x = \alpha(x' + vt') \tag{E}$$

Now by using Eqs. (*C*) and (*D*) the primed terms may be eliminated

$$x = \alpha^2\left(x - vt + vt - \frac{v^2x}{c^2}\right)$$

$$1 = \alpha^2\left(1 - \frac{v^2}{c^2}\right)$$

giving for the contraction constant:

$$\alpha = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad (G)$$

To illustrate this numerically: the fastest observed nebulae move with a velocity about one-tenth the velocity of light. For such a system $\alpha = 1/\sqrt{1 - 0.01} = 1.005$. Measuring lengths would appear contracted, clocks retarded in this system by ½ per cent.

It has here been assumed that the relative velocity of S to S' and S' to S is, except for sign, the same. Also that the contraction constant α of either system, as seen from the other, is the same. These assumptions are rational and follow from the very concept of relativity. Absolute direction has no meaning and the contraction constant must be the same for the train as seen from the ground or for ground as seen from the train.

Summarizing then: Instead of

$$x' = x - vt$$
$$t' = t$$

we have for the Lorentz transformation

$$x' = \alpha(x - vt) \qquad (E)$$
$$t' = \alpha\left(t - \frac{vx}{c^2}\right) \qquad (F)$$

where

$$\alpha = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad (G)$$

and for coordinates y and z perpendicular to the motion

$$y' = y \text{ and } z' = z$$

This net result is (a) that the Newtonian transformation for x is preserved except for the factor which allows for a contraction of the unit of length in a moving system; and (b) time (t') in the one system is different from that in the other (t) at any instant at different places, depending on x; and (c) also there is a progressively greater discrepancy in the value of the time as t increases.

If t is expressed in "einsteins," the equations become somewhat more symmetrical. This makes c equal to unity and

$$x' = \alpha(x - vt) \qquad (E')$$
$$t' = \alpha(t - vx) \qquad (F')$$

Let us illustrate this fundamental transformation of the relativity theory by using numerical values. We shall use the same events which were employed in the foregoing derivation—the transmittal and reception of a light beam as viewed in two different systems. Instead of train and earth let us consider two meter sticks in relative motion. The upper stick we may suppose is your standard of measure. It is at rest relative to you. The

lower one is mine. I and my stick are moving to the right (relative to you) with a speed equal to half the velocity of light, c. In relativity units $v = \frac{1}{2}$ and $\alpha = 1.16$. Figure 9 represents the instantaneous positions of the two sticks from *your* point of view (a) when the light signal leaves the zero division and (b) when it reaches the 100-division mark on your stick (and

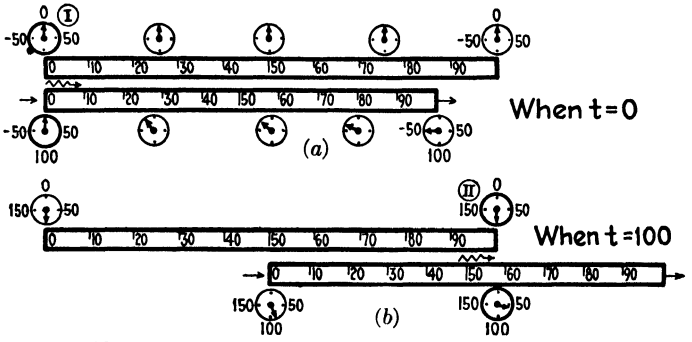


FIG. 9.—"Your simultaneity." (a) Signal is sent. (b) Signal is received.

the 57-division on mine). There is a 100-einstein time interval and in this interval my stick has moved 50 cm. (since $v = \frac{1}{2}$). My stick appears to you as shrunken. At the beginning ($t = 0$) your 86-cm. mark and my 100-cm. mark coincide. For

$$x' = \alpha(x + vt) = 1.16 \times 86 = 100$$

Clocks are represented along the two sticks. Since these pictures represent

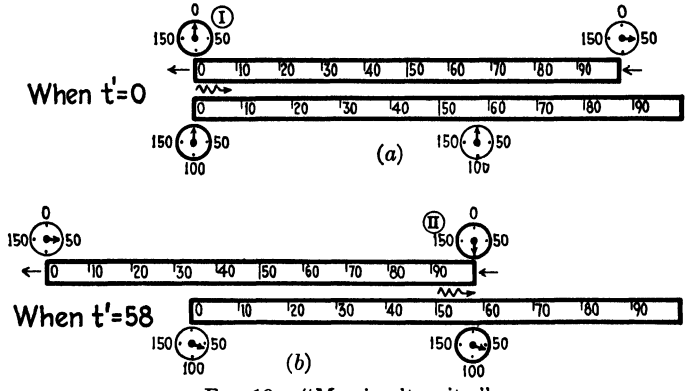


FIG. 10.—"My simultaneity."

simultaneity (your simultaneity), your clocks, of course, all read alike, zero time in (a) and 100 einsteins in (b). But my clocks at your zero instant all read differently—indeed the coincidence between my 100 and your 86 occurred 50 einsteins (according to my time reckoning) before the left-hand ends coincided ($t' = -50$)

$$t' = \alpha(t - vx) = 1.16(\tfrac{1}{2} \times 86) = -50$$

For me Fig. 9*a* does not represent simultaneity. Also the interval between (*a*) and (*b*) is by my reckoning less than 100 einsteins (notice my left-hand clock or my 57-cm. clock which is represented in both figures).

Figure 10 represents the situation from *my* point of view (*a*) when the light was sent and (*b*) when received.

I see various coincidences in Fig. 10*a* (such as 0 with 0, 20 with 23, 70 with 80, etc.). These coincidences are a number of "events"—these events, of course, are observed in each system. For me (in the lower system) these events are all simultaneous; they are not so considered in another—relative to me—moving system.

It can be readily shown that the Lorentz transformation [Eqs. (*E'*) and (*F'*)] gives an invariant value for the separation.

$$\sqrt{x^2 + y^2 + z^2 - t^2} = \sqrt{x'^2 + y'^2 + z'^2 - t'^2}$$

This in itself suggests the geometrical interpretation.

The Lorentz Transformation as a Rotation.—The role of time as a fourth dimension with imaginary values can be seen when these equations are compared with the transformation of coordinates corresponding to a rotation of coordinates. Suppose that we have two Cartesian coordinate systems S and S', and that the x', y' axes are rotated from the x, y axes by an angle θ. Let w represent $\tan \theta$. Then if x', y' and x, y are the corresponding coordinates of some definite point in the two systems, we have by analytic geometry

$$x' = x \cos \theta + y \sin \theta$$
$$y' = y \cos \theta - x \sin \theta$$

or

$$x' = \cos \theta (x + wy)$$
$$y' = \cos \theta (y - wx)$$

where

$$\cos \theta = \frac{1}{\sqrt{1 + w^2}}$$

These equations resemble Eqs. (*E'*) and (*F'*) except for signs. But if we let y and y' have imaginary values, say it and it', and let the angle of rotation be an imaginary angle so that w equals iv, we have for the rotation of this complex coordinate system through the imaginary angle

$$x' = \frac{1}{\sqrt{1 - v^2}} (x - vt)$$
$$t' = \frac{1}{\sqrt{1 - v^2}} (t - vx)$$

exactly as in Eqs. (E') and (F'). Here the contraction constant α corresponds to $\cos \theta$.

If the reader is familiar with hyperbolic functions, he will recognize that these equations are just the relations for transforming coordinates after a rotation through a hyperbolic angle θ such that $\tanh \theta = v$, and that the contraction factor $\left(\alpha = \frac{1}{\sqrt{1 - v^2}}\right)$ is $\cosh \theta$.

x, y, z, and t can be considered as defining a four-dimensional vector—a position-time vector. The Lorentz transformation is the characteristic transformation for any relativity four-vector between relatively moving reference systems. Another such four-vector is the momentum-energy vector whose components are mu_x, mu_y, mu_z and (the time component) the mass or energy m. Hence if v is the velocity of the moving system, parallel to the x axis we have

$$m'v'_x = \alpha(mu_x - vt)$$

and

$$m' = \alpha(m - vm'u_x)$$

Or for a particle at rest in S, (u_x, u_y, $u_z = 0$) m is the rest mass m_0 and

$$m' = \alpha m_0 = \text{(in c.g.s. units)} \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

which is Eq. (3′).

PROGRESS OF SCIENCE

YESTERDAY *Newton, Einstein today, tomorrow? I hear it said that the proud science is as frail, evanescent, fickle, insecure, impermanent as any philosophy of the past which has come and gone. Do not believe it. Newton took from Galileo a rare pearl of truth and cleansed it and polished it until it had beauty to light the world for two hundred years. And Einstein found within this truth a greater truth; it is as the pearl collector may peal from an imperfect pearl a thin shell with its blemishes and lo! this far lovelier gem appears. Newton's theory is not lost but lives in this greater theory.*

Such is scientific progress—not drifting, not fickle, but firmly founded in nature's facts. It grows, advances, improves on the old and stakes claims on eternal truth. For the most part science is not lost—an early scientist invented the digging stick and the stick will still dig. It may be improved—we may have digging stones or digging bronzes or picks and shovels and steam shovels and dynamite. But the digging stick can still dig.

Newton wrong? Is a man wrong who seizes on a truth fit to last without a change for two centuries and then to be in error by less than one part in a million when the velocity is a million feet per second? Is he in error when his theory builds bridges and locomotives and sciences and forms the start for a new and better theory?

Newton's theory is not overthrown but supplemented. So the theory of relativity, founded upon experimental fact, is truth—not, we hope, an ultimate truth, but a truth waiting to be further refined through the mind of some future master scientist.

CHAPTER II

WRINKLES IN THE MAP

In which a mouse and a flatman and Einstein collaborate to elucidate the curvature of space-time. How light has mass and weight; and how the universe has a radius of 20 *sextillion miles—more or less.*

Once there was a mouse that lived in a freight car. This was an unusually thoughtful mouse and it was certainly an unusual car. Instead of just learning to jump and run and eat cheese and raise a family like other mice, this mouse devoted himself to observation and meditation. And he noticed that whenever he dropped an object from his paws the object did not fall directly to the floor but rather tended to fall somewhat toward the rear of the car; it fell exactly as if, while it was in the air, the car had speeded up. And whenever the mouse jumped upward from the floor instead of falling down again in the same place he would fall back somewhat toward the rear of the car. And the mouse thought about these things and decided that there was a force pulling him to the rear. And he called this force gravity and published a book.

And then there was another mouse even more thoughtful and observant. And he noticed that not only some things but all things alike had this tendency to fall toward the rear. And partly because there was already a book on gravity and partly because he thought his new idea was good anyway, he asserted that the force notion was all wrong. Actually (said he in his book) there is no such tendency of a body to move toward the rear but rather to remain in position while the rear of the car moves up to strike the body. The car (according to the new theory) was constantly being accelerated! But the first mouse said, "Who ever heard of a car constantly going faster and faster?" And the second mouse said, "Who ever heard of a car ever doing anything else?"

Which mouse was right?

* * *

Accelerated Motion and the General Theory of Relativity.—Einstein advanced the theory of restricted relativity in 1905, the general theory in 1915. In the restricted theory which has been described in the last chapter, it was asserted that *uniform* velocity was not to be detected; but any change of velocity would be observed, as when we observe the acceleration of a train as it goes about a curve or starts or stops, or as we may detect the rotation of the earth (by a Foucault pendulum, by a gyroscope, or in other ways). Any straight World line could be used for the time axis in the restricted theory but not one which was bent.

The general theory went further than this. It asserted that a force field (like gravity) which acted alike on all bodies was not to be distinguished from acceleration. So accelerated motion as well as steady motion was a relative concept and the value of the acceleration depended upon the viewpoint of the observer. The force of gravity could be explained away by assuming a continual upward acceleration of the surface of the earth. Why not suppose the earth to rise up to hit the apple instead of the apple to fall to hit the ground? In the restricted theory it had been assumed that the World line of a free body, a body not acted on by any force, was straight (corresponding to a constant velocity). The restricted theory adopted the conventional viewpoint that a falling body was not, in this sense, free—it was in a force field. The general theory did not recognize gravity as a force. Instead this theory supposed space near matter to be "curved" and the natural paths of bodies to be "straight" only in the sense that great circles on a spherical surface are straight. The World line of the free body represents the shortest distance between two points in the curved space. Like great circles on a sphere, the World lines of two free bodies can intersect more than once. A ball thrown upward from the earth later strikes the earth. The World lines of the free ball and of the free earth are in this relativistic sense straight, yet they certainly intersect twice. Before examining this theory let us look to its experimental tests.

Tests of the General Theory.—In general, this theory of Einstein's had the same consequences as the older theory of Newtonian gravitation. In three respects it led to slightly different results and in each case these predictions of the relativity theory have been verified.

1. Light, as well as "material bodies," should be affected by gravity. Hence, as light from a star travels to us past the rim

of the sun, the light will be bent inward. The actual acceleration, indeed, will be twice that of a simply falling body near the sun; while a stone would fall with an acceleration of 270 meters per second per second on the sun, light passing very close to the sun experiences an acceleration of 540 meters per second per second. The result is to change slightly the apparent positions of such stars as appear close to the sun. The maximum deflection is only 1.7″. The stars can be viewed only at the time of an eclipse of the sun and at each eclipse since 1919 observations on such deviations have been made and the results are in agreement with the theory.

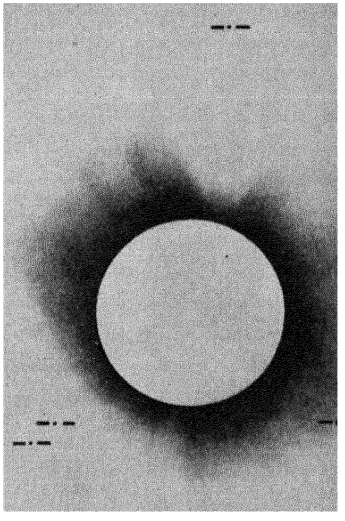


FIG. 11.—Solar eclipse (1919) (British Expedition). Showing positions of four stars. The nearer of these star images are displaced 1″ radially from the sun; the solar disk subtends about 30′. (The faint star tracks have been greatly strengthened in this reproduction.)

2. The unit of time as well as that of distance is altered at points near the sun. Hence the frequencies observed in the absorption lines of the solar spectrum should be altered slightly. The sodium line from the sun should have a wave length of 5895.943 angstroms instead of 5895.931. This shift toward the red of 0.012 angstrom is hardly to be separated from other effects. The observations at Mount Wilson solar observatory would, however, seem to show that the shift actually exists.

There are in the heavens certain stars of very high temperatures and with almost unbelievable densities. So the small companion star to Sirius has a density more than sixty thousand times as great as that of water.[1] The gravitational force is very great here and a relativity shift of wave length some thirty times greater than in solar lines is expected. Such a shift is observed and confirms the theory.

3. In (1) it was remarked that the attraction of gravity is doubled for light. For a body moving comparatively slowly,

[1] These densities are probably due to the stripping of the electrons from the atoms in these stars (p. 212).

as the planets do about the sun, the effective acceleration of gravity is not doubled but it is increased slightly. The result is that the ellipse in which each planet goes precesses slowly. (Compare Fig. 58.) The effect is greatest in the case of the innermost, fastest planet, Mercury; in this case the planet in going from one perihelion to the next should pass through 360.00003°; the orbit has a precession of 40 sec. per century.[1] The existence of such a precession has been recognized by the astronomers for some years. No explanation for it had been advanced before the theory of Einstein appeared. The general theory of relativity gave a quantitatively correct explanation.

Curvature of Space—Non-Euclidean Geometry.—The special theory of relativity introduces us to a space of four dimensions. But the question now arises in the general theory of relativity of what kind of a four-dimensional space is this? Are its fundamental properties exactly those described in the geometry of Euclid, where parallel lines never meet, where the sum of the angles of a triangle are 360°—or does the World have a slightly non-Euclidean character? Einstein hypothesizes that Euclidean geometry is not exactly valid near heavy bodies such as the sun and earth. A free body originally at rest (leaving at first its trace along my "here" line) is known to acquire a speed, and fall 4.9 meters in 1 sec. near the earth. Only 490 cm. of variation in 30 billion einsteins of time! This is a measure of the departure (in the up-time plane) from Euclid's theory—surely a small difference.

Einstein assumes that every free body travels (in the World) in a "straight line."[2] Suppose two projectiles are directed from a single point in space to opposite sides of the earth. Owing to gravitational attraction their paths will be altered and it may be that the projectiles come together again on the other side of the earth. Einstein does not recognize a gravitational "force" and calls each of these paths a straight line. Two straight lines may intersect in two points!

This non-Euclidean geometry of general relativity resembl very much what "plane" geometry would be li if the "plane were really the surface of a sphere. such a rved surfac

[1] This is in addition to the precession caused by the disturbing influence of the planets.

[2] "Geodesic" is a better term—the shortest distance between two points. Naturally, what line I call straight and what curved depends entirely on how I measure distance.

the angles of a triangle are more than 360°; if a circle is drawn on the sphere its circumference is less than 2π times the radius; the shortest lines between points are great circles and two such "straight lines" clearly meet at two points. If a "square" with 1 foot sides is drawn on the spherical surface its area will be more than 144 sq. in.

Exploring Flatland.—As illustration of the way in which an alteration in the character of space (a matter of pure geometry) may appear as a force (a matter of physics), consider a flat world of peculiar properties.[1] Suppose the space to consist of a large circular disk (Fig. 12). Suppose in this world there is a peculiar "law of force" tending to make all things contract as they approach the center. This is *a flat land with a force field.* As I (a flatman) walk toward the center from *e*, my paces become half as great when I am halfway to the center of the disk and continue to diminish proportionately as I approach the center nearer and nearer. Clearly it is an infinite number of paces to the center. (Query: Do these paces measure the "true" radius of the disk? See the note on meaning of truth on page 21.)

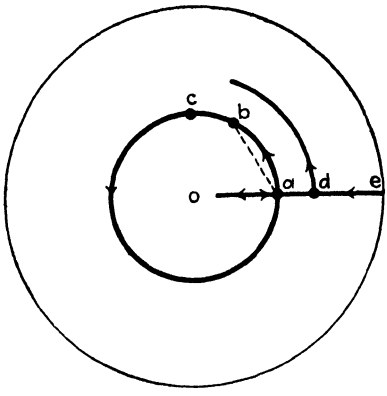


FIG. 12.—Explorations of a flatman.

Now stopping at *a* I turn through 90° and proceed to walk to *b*. My path (along the full line) is "straight," for it is the smallest number of paces between the two points. The dotted line (which the reader from his superior three-dimensional viewpoint sees to be "really" straight) would be longer for me, since ng it my paces are slightly smaller. Similarly, a beam of ght would travel along the full line. The light is refracted he reader w' say) because of the decreasing wave lengths toward the center, but of this the flatlander knows nothing. Sighting along them, he finds that the points *a*, *b*, *c* are exactly in line; this sighting method is our usual way of determining a

[1] The little booklet "Flatland, by A²" (Little, Brown) is an entertaining exposition of adventures in a two-dimensional space. The space there considered does not have the peculiar contractive properties of our example.

straight line. But ultimately following this straight line I will come to where I started at *a*! A straight line reenters itself!

Now if I go to point *d* and repeat the experiment, I find it takes the same number of paces to walk around my flat world here. A strange world this! After cogitating the matter, I, the flatman explorer, analyze my world: infinitely long from *e* to *o*; at right angles to this my space is finite—the same number of paces in every case. And so I discover that I live on *an infinite cylinder!* This completely explains my world without any mention of the law of force, without any suspicion of the contraction. A flatland with a contractive force or a cylinder without force. My physical law disappears into the laws of geometry. Einstein drops the law of gravity but assumes that space is curved.

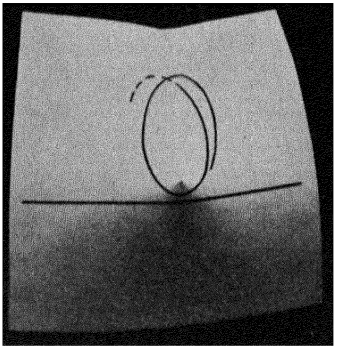


FIG. 13.—Curvature in a conical flatland.

A Closer Analogy.—This illustration is rather extreme. Suppose now that as we approach the center of this flatland there is a contraction but this time only a small one. Now the distance through the center is increased by the contraction but is not an infinite number of paces. In this case the world appears not as a cylinder but as a cone or, if the contraction takes place by a slightly different law, as a rounded hummock. In any case, however, a straight line not passing through the center will in virtue of the curvature change its direction.

By drawing a straight line and an ellipse (Fig. 13) on a piece of paper and then cutting the paper to the center and slipping the cut edges slightly over one another to form a slight cone one can see readily how a straight line receives a curvature and an ellipse is made to "precess." Similarly the sun or any heavy body produces a hummock in four-dimensional space-time. The curvature of the straight line illustrates the behavior of a falling body or of light as it is deflected near the sun; the precession of the planet Mercury is illustrated by the ellipse.

This warping of space can be illustrated by the hummocks produced by placing some drops of water on a piece of paper.

Figure 14 represents stars in space. A geodesic line is curved as it rides the side of one of these hummocks.

(This represents the space section of the World. In a time section the stars are lines, not points. The warping of the World would produce wrinkles extending almost parallel to the time axis rather than hummocks.)

Newton's Law of Gravity and Modified Geometry.—Space-time is shrunken near material bodies or, in other words, the four-dimensional space of the World is curved. In so far as this affects the xt, yt, zt planes, the wrinkles give the mechanics of gravitation. The curvature of the World line in these planes amounts to Newton's law of gravitation. The curvature is slight but a body proceeding billions of einsteins along time may well be deflected a few centimeters along x. (The acceleration of gravity on the earth is 980 cm. per 30 billion einsteins^2.) Because of this, the planets go in ellipses.

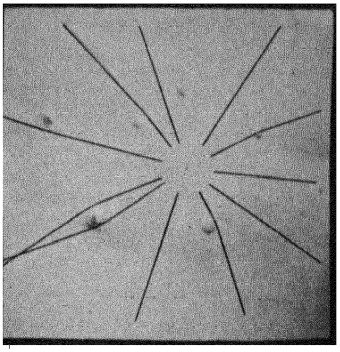


FIG. 14.—Warping of space near stars in two-dimensional space. This illustrates curvature of light near heavy bodies and shows how a pair of "straight" lines may intersect twice.

We must grant a like distortion to the xy, yz, and xz planes. This distortion in space affects *geometry*. But only slightly. Our ordinary bodies, our ordinary straight lines, do not extend the billions of centimeters necessary to get a significant difference. The circumference of the sun is not (according to this theory) exactly 2π times its radius. Only in the case of Mercury in its accumulated effect over a century has this distortion of geometry made an observable difference among planetary orbits. But in the case of light which, traveling by the sun, travels just as many centimeters as it does einsteins, the effect of the xy curvature equals that of the xt; the acceleration of gravity for light (or for a body traveling nearly as fast as light) is twice the normal value for slowly moving objects.

Is Light Material?—What is matter? Presumably anything which (*a*) gives us a reactive push when we stop it or start it, *i.e.*, has inertia, and (*b*) falls to the ground, *i.e.*, has weight. We have just seen that light is affected by gravity, that it falls as

other particles do. The property of inertia was demonstrated by Lebedew and by Nichols and Hull (1901). If light strikes a vane very delicately suspended in a vacuum,[1] the vane will be given an impulse. This demonstrates that light has pressure. If there are 9×10^{20} ergs of energy in a given volume of a light beam, its mass is 1 gm. (page 18) and its momentum (mv) is 3×10^{10}. The effect of this radiation pressure is evident in its effect on the tails of comets which are always directed away from the sun. The tenuous matter of the comet's tail is pushed away by the sunlight.[2] When the sun is overhead, about 500 cal. or 2 kilojoules of heat are received per square meter of earth's surface per second. How many grams is this?

Energy is radiated from the sun at the rate of 140,000 hp. per square yard[3] or from the whole sun 7×10^{32} ergs per second Reduced to grams, this means a loss of mass from the sun of 10^{12} gm. or a million tons per second.

Undoubtedly, if we mean by a material body anything with weight and anything which has inertia, light must be classed as a material body. Furthermore, light is, surprisingly enough, corpuscular in structure. Just as other matter is made up of small particles (atoms, or electrons and nuclei) so also light is made of small particles called photons (Chap. XIII). Yet this radiant energy is absolutely different from those other bodies which are composed of electrons and nuclei. Such other material bodies have a *rest mass* and an increment in mass as their velocity increases, the mass approaching infinity as the velocity approaches that of light. The photon, on the other hand, always moves with this limiting velocity c and yet its mass is small. It has no rest mass, and one electron if it moved with the velocity of light would have more energy than all the photons in the universe.

Refraction of Light Waves and Attraction of Photons.—Near the sun the speed of the light wave is *decreased.* This is a consequence of the general theory of relativity and we have seen the evidence for it in the bending of a light beam passing near the sun. However, aside from any consideration of relativity, bend-

[1] This is not to be confused with the radiometer which is not highly evacuated.

[2] Another instance of the pressure exerted by radiant energy (x-rays) is given on p. 337.

[3] If this enormous energy were furnished by chemical action such as burning of coal, it would mean the consumption of a coal layer 25 ft. deep hourly.

ing of the light ray is to be expected if the photons are acted on by gravity. Indeed Newton considered the possibility of such an effect. (But according to the Newtonian law of gravitation, the bending of a beam of photons is only half that predicted by relativity and confirmed by astronomical observation. This is because the warping of space is neglected.)

But, if light is considered as a shower of photons and these photons are attracted to the sun, their velocity is *increased*, not decreased, near the sun. This seems like a fundamental discrepancy between the two points of view. Actually it is a very significant difference and is typical of a difference which always exists between the wave and particle aspects of things.

Are all these photons alike; do they have equal masses? This question we shall defer.

The Fundamental Tensor.—Mathematically the attack of general relativity centers around the nature of the "fundamental tensor." The Pythagoras theorem gives for the distance between two points in a plane $\Delta s^2 = \Delta x^2 + \Delta y^2$. But by using another coordinate system or in a spherical geometry or in a non-Euclidean geometry, the interval is given by the more general quadratic expression.

$$\Delta s^2 = g_{11}\Delta x^2 + g_{12}\Delta x \Delta y + g_{22}\Delta y^2$$

(In polar coordinates $\Delta s^2 = \Delta r^2 + r^2\Delta\theta^2$. Here g_{22} is equal to r^2.)

The values g_{11}, g_{12}, g_{22} form the fundamental tensor which defines the geometrical properties of the space. It is with the nature of this fundamental tensor (of 10 members when dealing with the four-dimensional space) that general relativity concerns itself. Out of this fundamental tensor comes the law of gravitation, the result of a slightly non-Euclidean property of the four-dimensional space-time, or, if one prefers, of a curvature of this four-dimensional "World surface" in a 10-dimensioned superspace.

Cosmology.—The theory of special relativity is almost certainly true; it is demanded as an explanation of the phenomena of electricity and magnetism. It underlies all considerations of physics today. The general theory is more complicated and less rigorously developed and, although it has met with no contradictions, one can hardly regard it with the same complete confidence that one has in the restricted theory.

The theory has been applied to the nature of the universe as a whole. This is called cosmology and theories in this field must be regarded by all as rather speculative. The question arises as

to whether the universe is limited in time and space. Shall we, following down the time line into the future, ultimately come again upon the present? May we by extending a straight line far enough in space finally come again to the solar system and the earth? Until recently Einstein has considered that the first question was to be answered negatively and the second affirmatively. The cumulative effects of curvature due to all the bodies in the universe cause ultimately a complete reversal of the straight line in space though not of the time line. Einstein pictured the universe as very much like our elementary example of the flat-contractive or cylinder world (page 33, though, of course, in four rather than two dimensions), extending indefinitely along time but not indefinitely in space. The radius of this universe is estimated as about three billion light years or some ten or twenty times as far as the strongest telescope can reach. (Hence it is not possible that some one of the distant stars seen by the telescope is ourselves.)

DeSitter has had a somewhat different picture from this one of a universe with constant radius. The distant nebulae in general appear to be receding at very great speeds and this leads to the belief that the whole universe is expanding.[1] Einstein has recently adopted this same view. It is a conelike rather than a cylinder-like World.

The "exploding universe"—this is the way it looks to us. But in view of relativity would it not be equally correct to say that it is *we* who are *contracting?* From the viewpoint of a cosmic spectator we are contracting in space and time. "We walk the stage of life," says Eddington, "performers of a drama for the benefit of the cosmic spectator. As the scenes of life proceed, he notices that the actors are growing smaller and the action growing quicker. When the last act opens, the curtain rises on midget actors rushing through their parts at frantic speed. Smaller and smaller. Faster and faster. One last microscopic blur of intense agitation. And then nothing."

Well, that is a point of view. But in terms of heartbeats of time and paces of distance, we, the actors on this stage, shall still live our lives. Time and space are only rather artificial props for thought—make them as you will. We, the midget actors, shall still dream our midget dreams—this is all that counts.

[1] The recession is proportional to the distance—about 1 km. per second at a distance of 5000 light years.

Summary.—It is easy to see the dilemma in which the demonstrated constancy of the velocity of light for all observers places us. It is impossible in a few pages to get more than a few half-true, half-false ideas of the doctrine of relativity. The most important aspect of the theory is that distance and time and many of the fundamental concepts of physics are relative, appearing to us as they do only because we are where we are and what we are. This is one of the most fundamental lessons to be learned of physics. When we say that time is a fourth dimension, we say but a half truth; if we say so much, it must be with the reservation that it is a dimension with quite unique properties. The theorem of Pythagoras in these four dimensions becomes: separation equals $\sqrt{x^2 + y^2 + z^2 - t^2}$, (if we use as rational unit for time, the thirty-billionth of a second). The discovery that mass is a form of energy is very important. Mass (energy) is indeed the time component of a four-vector. The space components of this same vector are momenta.

General relativity would seem to show that, near heavy bodies, four-dimensional space is not the simple kind of space in which Euclidean geometry holds. However, the geometrical discrepancies introduced affect us in only one very important aspect: they give us our force of gravity. (They also give us, near the sun, bending of light, changing of light wave lengths, precession of orbits—tests of our theory.)

We can think of the universe and all that has happened or will happen as represented in a four-dimensional space-time continuum (the World). The present moment is a section in the World. We can remember in our minds a few of the World lines as they extend near our own lines into the past; the future comes to us with an element of surprise. The universe we can imagine as spread out as a (four-dimensional) map with, here and there, the suns and planets and stars tracing their World lines. These stars indeed are slight warpings in the map or wrinkles, usually running along, except for some very high-speed nebulae, nearly parallel to the time axis. The courses of the wrinkles are not always straight; they tend to run into one another. This is the gravitational attraction between bodies. Does the cumulative effect of these local wrinkles cause a general curvature of the space as a whole? Probably, but we do not know. This is the problem of cosmology.

And now we have in a few strokes indicated the canvas, the space-time background, into which will be painted the picture of the physical world. Into this space-time we now fill in some details. We have just been looking a thousand times above the range of the strongest telescope; let us now look a thousand times beneath the range of the strongest microscope, into the world of the molecule.

CHAPTER III

THE DANCE OF THE MOLECULES

How the Greeks talked of an atomic theory and how Dalton proved it; and how Avogadro found the molecule. The molecules are restless—particularly when warm. How energy is divided equitably among the molecules—but there are here no traffic laws. Producing and measuring a vacuum.

Historical: The Birth of the Atomic Theory.—Some of the Greek philosophers held that the world was made of very small indivisible parts, the atoms (*atemnos*, uncuttable). The theory was proposed by Democritus (consult Democritus, "Encyclopaedia Britannica," 11th ed.). He attributed round molecules to water and jagged ones to iron and particularly mobile ones to fire and to the soul; he supposed them in constant motion. But such ideas of the Greeks were pure unfounded speculation. A Greek philosopher would put his heels on his desk and think up a pretty theory unhampered by experiment. It was the armchair school of science. Aristotle's theory of the four elementary substances, earth, air, fire, and water, supplanted the theories of the early atomists.

The modern atomic theory followed as a result of three fundamental laws of chemistry: the law of definite proportions, the law of interproportionality, the law of multiple proportions. (1) The French aristocrat Lavoisier, known as the founder of modern chemistry, discovered the first law late in the eighteenth century. Hydrogen unites with oxygen in the ratio of 1:8, a definite invariable ratio. Why? (2) Richter, a German saturated in alchemy, discovered interproportionality. Hydrogen unites with nitrogen in the ratio of 1:4⅔, therefore nitrogen unites with oxygen in the ratio 4⅔:8. What could this mean? (3) And finally the natural philosopher Dalton discovered the law of multiple proportions early in 1803. Hydrogen combines with oxygen not always in the ratio of 1:8 but at times in the ratio of 1:16 (hydrogen peroxide). And Dalton announced the atomic theory.

The chemical elements appeared to be found in "small packages." The relative weights of these atoms are hydrogen 1,

oxygen 16, nitrogen 14, and these atoms combine together 1:1 or perhaps 1:2 or in other simple ratio. This was Dalton's interpretation of the three fundamental chemical laws.

The actual relative weights assumed by Dalton were somewhat different from these. He always used for atomic weight the most common combining weight of an element. He supposed the formula for water to be HO and the atomic weight of oxygen to be 8 rather than 16. It was only later that the law of Dulong and Petit, the molecular theory of Avogadro, the discovery of the periodic law of Mendeleef combined with other relations of physical chemistry to point to the exact numbers, multiples of the combining weights, which are taken as atomic weights (see Chap. VII). But in the main the ideas of Dalton were sound and the atomic theory was born.

Avogadro's Hypothesis.—The Italian physicist Avogadro was first to distinguish clearly between the atom and the molecule (1811). Dalton had supposed that in elementary gases the atom existed in the free state. Avogadro showed that in most cases these atoms usually combined into pairs. His famous hypothesis is that *for any gases under similar conditions of pressure and temperature equal volumes contain equal numbers of molecules.* More specifically 1 gm. molecule (or "mole") of any gas under standard conditions (S.C. = 1 megabar pressure,[1] 0°C. temperature) occupies 22.7 liters; 22.7 liters of hydrogen weigh (approximately) 2 gm., of helium 4 gm., of oxygen 32 gm., of chlorine 71 gm., and so on. In each of these cases except helium the molecular weight is twice the atomic weight.

TABLE 2

Monatomic Molecules	Diatomic Molecules
Helium	Hydrogen
Neon	Nitrogen
Argon	Oxygen
Krypton	Fluorine
Xenon	Chlorine
and	Bromine
metal vapors	Iodine

[1] This differs slightly from the usual standard pressure of 76 cm. of mercury. One million bars is almost exactly the pressure of 75 cm. of mercury.

$$p = 75 \times 13.6 \times 980 = 999{,}000$$

This "75-cm. atmosphere" is coming into use and its equivalence to a million c.g.s. units makes it convenient. At 76 cm. pressure a gram molecule occupies 22.4 liters.

Oxygen sometimes forms ozone which is triatomic. Sulphur vapor has 8 atoms in the molecule at 100°C. but, as the temperature is raised, the molecule is broken up. All molecules are broken into single atoms at very high temperatures.

The hypothesis of Avogadro has been abundantly justified. The molecules do not fill the space occupied by them, of course. They occupy it in the sense that a country is occupied by its population. And there is always the tendency to expand into new territory. This tendency to expand is the pressure of the gas. We might suppose that in this struggle for territory the lighter molecules would be at a disadvantage but this is not so; what they lack in mass these lighter molecules make up in speed. A given number of molecules occupy the same volume (at the same temperature and pressure) regardless of their nature. Avogadro did not know how large the individual molecule was or how many molecules it was which occupied 22.7 liters. Today we know this number. The number of molecules in a gram molecule is 6.06×10^{23} and this is called *Avogadro's number* (N_o).

Combination of Boyle's and Charles's Law and Avogadro's Hypothesis.—The pressure, volume, and temperature of a gas are related. The approximate relation is given in the *general gas law.*

$$pV = RT \tag{4'}$$

This is a combination of Boyle's (p, V) law and Charles's (p, T) law. The value of the constant R will evidently depend upon the quantity of gas considered.

If we consider a gram molecule of any gas, R is a universal constant (called the *gas constant* R_o). Its value in c.g.s. units is (approximately) 83,000,000. This follows from Avogadro's hypothesis. For under standard conditions p = 1,000,000 bars, T = 273, and the volume is 22,700 cc. R_o may then be found from Eq. (4):

$$R_o = \frac{pV}{T} = \frac{1{,}000{,}000 \times 22{,}700}{273} = 83{,}000{,}000 \text{ ergs per mole}$$

For a gram molecule of any gas

$$pV = R_oT \tag{4}$$

Molecular Motion and Pressure.—Bernoulli as early as 1750 explained the simplest properties of gases in terms of a molecular theory. The firm foundations of the theory were laid during the

latter half of the nineteenth century by Clausius and by Clerk Maxwell and by Boltzmann. The actual measurement of the sizes of the molecules and atoms and hence the final demonstration of their reality did not come until the end of the century.

The molecules are moving hither and thither in a gas with a velocity usually somewhat less than a mile a second. Pounding against the walls, they produce the pressure of the gas. The force which they exert is by Newton's second law equal to the rate of change of momentum.

Suppose we have the molecules in a vessel with rectangular walls, of dimensions a by b by c. Let the mass of the molecule be m and their number per cubic centimeter be N_1. For simplicity we suppose that one-third of them are traveling in each direction in the vessel. Then $\frac{1}{3}N_1$ per cubic centimeter (or $\frac{1}{3}N_1 \cdot abc$ in all) will be traveling parallel to c and, after striking the face ab, will reverse and go a distance $2c$ before striking the front face again. Suppose their average speed is v. Then the average molecule has a change of momentum $2mv$ at this wall, and (since a time $2c/v$ elapses between collisions) this average molecule will make $v/2c$ collisions with the wall per second. There are $\frac{1}{3}N_1$ abc molecules traveling in this direction. Hence the total momentum change per second is $\frac{1}{3}N_1\, abc2mv \cdot v/2c$ or $\frac{1}{3}N_1 \cdot ab \cdot mv^2$ and this equals the force exerted against the face. The force per unit area is the pressure p; this is (dividing by ab)

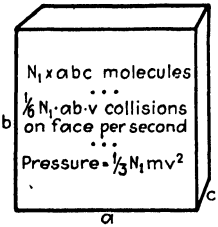


FIG. 15.

$$p = \tfrac{1}{3}N_1 mv^2 \tag{5}$$

$N_1 m$ is the density of the gas ρ and hence

$$p = \tfrac{1}{3}\rho v^2 \tag{5'}$$

(We have here neglected collisions between molecules because such collisions are really irrelevant. If a collision deflects one molecule moving toward the wall from its path, it is as apt to deflect another molecule so as to strike the wall.)

This is a very remarkable result. By the most elementary reasoning the speeds of the molecules have been computed here in terms of such things as density and pressure of the gas. It almost seems to justify the "armchair school" of science.

Velocity of the Molecules.—A number of simple relations are evident from this result.

a. The pressure in Eq. (5) is clearly proportional to the square of the molecular speeds. For indeed, as we have seen in the proof, if the velocity of the molecule is increased, it will strike the wall not only harder but also more often. $p \propto v^2$.

b. At the same pressure and temperature Avogadro's hypothesis is that the number of molecules per cubic centimeter (N_1) is constant. Hence from Eq. (5) it follows that as between different gases the velocity will be inversely proportional to the square root of the mass of the molecule.

A further relation will perhaps make Eq. (5′) somewhat easier to remember. Since $\frac{1}{2}\rho v^2$ is the kinetic energy of a unit volume of the gas, *the pressure equals two-thirds of the kinetic energy per unit volume.*

Let us compute the speed of hydrogen molecules at 0°C. 22.7 liters of hydrogen weighs (approximately) 2 gm. (S.C.); hence the density ρ of hydrogen is 1/11,300. The pressure (1 atmosphere) is 1 million dynes per square centimeter. Putting these values in Eq. (5′) we have

$$v = \sqrt{\frac{3p}{\rho}} \qquad (5'')$$

$$= 184{,}000 \text{ cm. per second or } 1.8+ \text{ km. per second}$$

This is approximately 1 mile a second. The speeds for other gases can be obtained from this by proportion. (Check the inverse square proportionality in Table 3.)

TABLE 3

	Molecular weight	Velocity, miles per second
H_2	2	1
O_2	32	¼
Cl_2	71	⅙
Br_2	160	⅛
Hg vapor	200	1/10

The air about us consists chiefly of nitrogen molecules and oxygen molecules and about 1 per cent each of argon molecules and water molecules. These race back and forth; their average speed is about a quarter of a mile a second—not so fast in terms of

centimeters and einsteins but rather fast as most familiar things about us go—about the speed of a rifle bullet. They go a little faster in summer, slower in winter. They bombard my hand, billions upon billions of them every second and produce upon it "atmospheric pressure."

Velocity and Temperature.—Simple compression at constant temperature does not affect the speed of the molecules but only their number per unit volume. The speed of the molecules depends on the temperature.

We can find the relation from the general gas law of Eq. (4)

$$pV = R_o T$$

We may write $\rho = M_o/V$ and Eq. (5′) becomes

$$pV = \tfrac{1}{3} M_o V^2 = R_o T$$

where M_o is the molecular weight.

Or the kinetic energy of a gram molecule of the gas is

$$\tfrac{1}{2} M_o v^2 = \tfrac{3}{2} R_o T \qquad (6)$$

This relation shows that *the kinetic energy of a gram molecule is proportional to the temperature,* or that the velocity is proportional to the square root of the temperature.

We have found that the speed of hydrogen molecules at 0°C. (273° abs.) is about a mile a second. At four times this temperature (819°C.) the speed would be about 2 miles per second.

Boltzmann's Constant.—So far it has been quite unnecessary to know the number of molecules in a gram molecule, or the actual mass of the individual molecule. It will be interesting, however, to consider now the average kinetic energy of the individual molecule. We must then introduce "Avogadro's number," the number of molecules in a gram molecule. This is (as has already been remarked and as we shall later show, Chap. X) $N_o = 6.06 \times 10^{23}$. Dividing both sides of Eq. (6) by this and putting $M_o/N_o = m$, the mass of the molecule, we have

$$\frac{1}{2} m v^2 = \frac{3}{2} \frac{R_o}{N_o} T \text{ or } \frac{3}{2} \kappa T$$

The gas constant per single molecule R_o/N_o (or κ as it is generally expressed) is called *Boltzmann's constant.* Its value is $83{,}000{,}000/6.06 \times 10^{23}$ or 1.37×10^{-16}. Multiplied by $\frac{3}{2}T$ it gives the average kinetic energy of a single molecule.

Temperature is often considered as an essentially non-mechanical quantity. In measuring it we leave the c.g.s. system of mechanical units and introduce a new unit: the degree. This is really unnecessary. The mechanical interpretation of temperature has just been given. It is that which is proportional to the kinetic energy of the molecule.[1] This interpretation is quite general.[2] Even in the cases where the molecule is constrained, as in a solid or liquid, and the motion can result only in the molecule's chattering back and forth about its equilibrium positions, the average speeds of the molecule are the same as in the gas and the average kinetic energy is $\frac{3}{2}\kappa T$.

Equipartition of Energy.—The molecular picture which we are painting resembles very much a perfect chaos. Molecules, moving with all speeds, are continually colliding one with another. (There are no traffic laws in the molecular world.) With such random motion it might be supposed that there would be no such thing as law—everything happening as a matter of chance. Yet laws exist, which are statistical in nature, like the laws of the insurance actuary. It is quite impossible to predict the path of any individual molecule. The average conduct of the molecules can be definitely predicted.

The most important such statistical law is the law of equipartition of energy. In equilibrium the kinetic energy of translation is, on the average, shared equally between the respective molecules. The gas seems to form a perfect socialistic community, sharing kinetic energy equally among its members. In a mixture of hydrogen and oxygen each molecule will have, on the average, an equal energy, the hydrogen making up for its smaller mass by its greater speed.[3] The law follows from the relation between the average kinetic energy and temperature.

$$\text{K.E.}_{(\text{mol})} = \tfrac{3}{2}\kappa T \qquad (6')$$

Since each molecule tends to assume the same temperature, it has on the average the same kinetic energy. In this communistic régime Boltzmann's constant is of supreme importance. It is a measure of the kinetic energy which each molecule can claim at any temperature.

[1] Strictly, the kinetic energy associated with translation.

[2] Except for limitations introduced by the quantum theory (p. 283).

[3] This recalls its equal space possessing property which was noted by Avogadro.

Kinetic Theory and the Gas Laws—Flow of Heat.—Why is pressure inversely proportional to volume at constant temperature? (Boyle's law.) Because, from Eq. (5), if the velocity is unchanged, the number of impacts of molecules with the walls, and therefore the pressure, will depend on the number of molecules per unit volume. This will be greater when the volume is made smaller.

Why is the pressure (at constant volume) proportional to the temperature? (Charles's law.) Because if the number of molecules per unit volume is unchanged, the pressure must by Eq. (5) be proportional to v^2 and to m; *i.e.*, the pressure is proportional to the kinetic energy of the individual molecule.

Why does heat always flow from a hotter to a colder body? This is the endeavor of the bodies to establish equipartition, the energy being given from the richer to the poorer molecules, in accordance with this inevitable law of statistical equilibrium. Gas molecules, as they strike and rebound, cool a relatively hot surface and warm a cold one. Therefore the thermos bottle is evacuated. This conduction of heat is especially great in the case of hydrogen in which, because of their greater mobility, the molecules make many more collisions in a given time than do molecules of another type. A beaker of liquid air surrounded by hydrogen will boil violently.

Hydrogen molecules move from high pressure to low more quickly than do other molecules. A vacuum can be obtained more quickly with hydrogen than another gas. It has already been shown (page 44) that the number of molecules striking per second on a unit area of surface is $\frac{1}{6}N_1v$. This is the number which at low pressures (when collisions and bulk motion can be neglected) will pass through an orifice of unit area. Since N_1 is the same for all gases at the same pressure, the number of molecules that can pass out from a vessel into a pump in a second will be proportional to v. However, in practice, the speed of pumping is limited by the capacity of the pump to handle the influx.

Vacuum Pumps.—The first step in much of the work of the physicist in studying the nature of matter is to eliminate most of it, *i.e.*, to get a vacuum. An ordinary water aspirator will produce a vacuum of 1 or 2 cm. of mercury; this is just about the pressure at which the Geissler tube discharge begins to occur. A good oil pump will carry the evacuation some ten thousand

times farther, down to a pressure of about 1 bar (or about a thousandth of a millimeter). This pressure is so low that the mean free path of the molecules between collisions is several centimeters long. To get a better vacuum than this we usually resort to the mercury-vapor pump.

In the vapor pump a stream of mercury vapor issuing through a nozzle moves downward and is condensed on the walls of the pump (which are water cooled). The air molecules from the chamber above (which is connected to the vessel to be evacuated) wander into this vapor stream and are driven downward by it. Here the large mass of the mercury molecule is important. Its larger momentum insures that the gas molecule will be driven downward rather than the vapor molecule be driven upward into the evacuated chamber. The speed of the pump depends upon the size of the inlet opening around the nozzle. Even the smaller sizes of vapor pumps are extremely fast, exhausting at the rate of perhaps a liter per second and the larger iron pumps may exhaust at a rate of 20 liters per second or even faster. Such high pumping speeds are necessary in many experiments being performed today with atomic beams (page 368). The vacuum which can be obtained with the mercury-vapor pump is better than can be read on any gage (10^{-5} bar). These pumps will not pump against atmospheric pressure; they require an oil pump to produce a forevacuum.

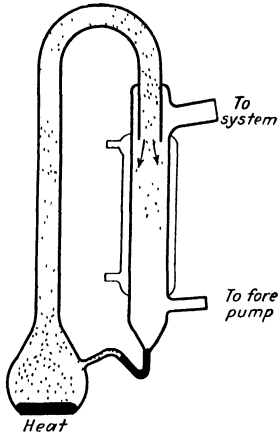


FIG. 16.

The so-called molecular pump operates upon an interesting principle. A metal disk rotates with a high peripheral speed (about 100 ft. per second) between two static disks. In the stator a spiral groove is cut in such a way as to force the rotating gas to the center and out to the fore pump. Every molecule which strikes the rotor is given by it a component of speed in its direction of motion and, since the speed of the rotor, particularly near the periphery, is comparable with the normal speed of thermal agitation, the gas molecules are given the necessary rotational motion to run around the spiral and out into the forevacuum.

Measurement of Vacua.—The McLeod gage is the gage most commonly used for measuring low pressures. Its operation depends upon Boyle's law. *c* communicates with the evacuated vessel. If the mercury well is raised, the gas in the bulb is cut off and compressed, ultimately being confined in a very small volume in the capillary tube *b*. The volume of the entrapped gas may by this compression have been reduced some thousands of times and its pressure correspondingly increased (Boyle's law). This increased pressure is read by noting the difference in level between the mercury in the capillaries *a* and *b*. The gage is calibrated so that the pressure can be given directly in terms of this height. The McLeod gage will measure pressures down to about 1 millibar.

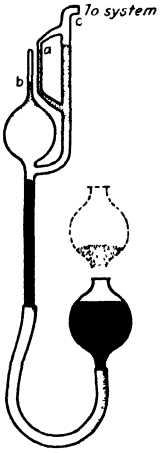


FIG. 17.—McLeod gage.

For measuring smaller pressures or for more readily recording pressures, the ionization gage or Pirani gage is often used. An ionization gage may be made from an ordinary radio tube. The electrical connections are so arranged (by keeping the plate at lower potential than the filament) that only positive charges can reach the plate. These are produced by the electrons from the filament when they strike and ionize the gas molecules which may be present. This ionization current then gives a measure of the gas pressure.

The Pirani gage consists of a single filament—an ordinary light bulb can be connected to the evacuated system and used. A small current heats the filament slightly and the resistance is determined as a measure of temperature. If gas is present, the filament will be slightly cooled and the resistance lowered. The Pirani or the ionization gage can be used to measure vacua down to about a hundredth of a millibar, the lowest vacua which have been measured.

Note on the Compound-interest Law—Exponential Function.—The pumping out of a system is a good example of the "negative compound-interest law." The pressure after *t* strokes of an oil pump is given by

$$P = P_0 e^{-rt}$$

where *r* is the ratio of the volume of the pump to that of the system.

The reader is perhaps not familiar with the base of natural logarithms (*e*). This quantity (whose value is 2.71+) has an importance in mechanics and

elsewhere in mathematics quite analogous to that of the familiar quantity π (3.14+) in geometry. (Indeed the quantities e and π have a close fundamental relationship.) The simplest illustration of the meaning of this natural base is obtained from a consideration of interest.

If \$1.00 is deposited at 5 per cent (*i.e.*, $\frac{1}{20}$) simple interest, it will be worth \$1.05 after 1 year and \$2.00 after 20 years. If, however, the interest is compounded yearly, the dollar will be worth \$1.05 in 1 year, $\$1.05^2$ in 2 years, $\$1.05^3$ in 3 years, and $\$1.05^{20}$ or \$2.65 in 20 years. The interest may however be compounded more often. In the ideal case where it is compounded *continually*, the account is worth \$2.718+ after 20 years. This number 2.718+ is represented by e. If N_0 dollars are deposited, if r is the rate of interest, then the value of the account after t years is

$$N = N_0 e^{rt}$$

This is called compound-interest law. N equals 2.71 N_0 after $1/r$ years; it equals 7.39 N_0 (*i.e.*, $e^2 N_0$) in twice that time, and so on. The nature of this exponential function is shown in Fig. 18.

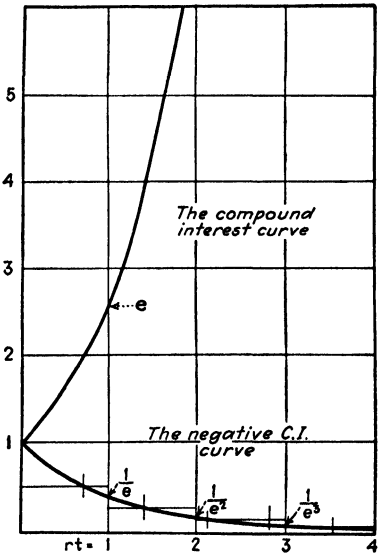


FIG. 18.—Compound-interest curves. Note the doubling or halving at rt = 0.7, 1.4, 2.1, etc.

Nature sometimes gives compound interest. (The rate of increase of guinea pigs is proportional to the number of pigs.) But we shall find more instances where she charges interest. If the banker charges me 5 per cent for guarding my money, then after a year I will have but 95 cts. of my dollar, in another year 5 per cent less than that, and so on, but compounded continually, N_0 dollars become after t years

$$N = N_0 e^{-rt} \qquad (7)$$

(In 20 years at 5 per cent the principal has shrunk to 1/2.7th, in 40 years to 1/7.4th, etc.) This is the negative compound-interest law, holding wherever the rate of loss is proportional to the principal. The decomposition of radium is proportional to the radium present; the decrease in electrical oscillations due to resistance damping is proportional to the amplitude of the oscillations.

Suppose that a pump is 10 per cent as large as the whole system which is to be evacuated. Then in each stroke 10 per cent of the gas is removed. For the pressure in this case there is a 10 per cent "negative interest rate." After one stroke the pressure falls to 90 per cent, then to 81 per cent (90 per cent of 90 per cent), then to 72 per cent. In 10 strokes the pressure drops (approximately) to 1/2.7th of its original value.

Very often the rate of change of a quantity is proportional to the quantity. In such cases we always have the compound-interest law.[1]

The Law of the Atmosphere.—As we go upward, the atmosphere about us decreases in density by the negative compound-interest law. The decrease in density is proportional to the density. For the atmosphere the "interest rate" is $-\frac{1}{5}$ per mile. The pressure equals $P_0 e^{-\frac{h}{5}}$ (where P_0 is the pressure at the surface of the earth and h is the height). This means that the pressure divides by 2.7 for every 5 miles or is halved for every $3\frac{1}{2}$ miles as we ascend.

Molecular Collisions.—Molecules are continually colliding with each other. Figure 21 might well represent the path of a molecule. (It actually represents the motion of a much larger particle.) In the air the average distance between collisions is a ten-thousandth part of a millimeter. This average distance of free travel is called the *mean free path* (λ). Naturally as the number of molecules per cubic centimeter decreases the mean free path increases; indeed the mean free path is inversely proportional to the pressure (at constant temperature).

Collisions in the molecular chaos are, of course, a matter of pure chance and a molecule may go much farther than the mean free path without colliding. Indeed a moment's consideration will show that the collisions must obey the negative compound-interest law. Out of 100 air molecules half of them will collide in seven hundred-thousandths of a millimeter (compare Fig. 18). The other 50 have the same chance to collide and 25 will probably do so in 0.00007 mm. more. Half of these (12) should collide in another equal distance; in the next interval 6 will probably collide; and then after a total distance of 0.00035 mm. 3 molecules out of the original hundred will probably remain which have not made collision. Of course it is a matter of chance; but these are the probabilities. Out of an original number (N_0) the number (N) which have not collided after going any distance x is given by

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

$-1/\lambda$ is the "interest rate."

[1] It is the negative compound-interest law which usually appears. Only occasionally, temporarily, can the positive compound-interest law operate. This function, e^{rt}, increasing ever more rapidly, gets larger and larger and larger. It must always end in catastrophe. Only in human affairs, in economics, do we deceive ourselves into believing in compound interest—with the resulting depressions and wars.

The mean free path of several types of molecules is given in the table.

TABLE 4

	Mean speed at 0°C., meters/sec.	M.F.P. standard conditions, millimeters	Molecular diameter, 10^{-8} cm. or angstroms
Hydrogen (H_2)	1,839	0.00018	2.47
Helium (He)	1,311	0.00028	2.18
Nitrogen (N_2)	493	0.00009	3.50
Oxygen (O_2)	461	0 00010	3.39
Neon (Ne)	561	0.00019	2.44
Argon (A)	413	0.00010	3.36
Electron	100,000		

Effective Size of Molecule.—If the molecule is considered as a simple sphere, clearly the larger this sphere the more the chance of collision. The theory is not difficult. If the radius of the molecule is taken as r, then when the centers of two molecules approach within a distance $2r$ there will be a collision. Hence we may consider that as a molecule goes 1 cm. of its path there will be an imaginary cylinder of radius $2r$ and volume $4\pi r^2$ about this path and there will be a collision with any molecule which lies in this cylinder. If there are N_1 molecules per cubic centimeter there will be in this imaginary cylinder $4\pi N_1 r^2$ molecules.[1] This is the number of collisions per centimeter. The mean free path (λ) equals $1/4\pi N_1 r^2$ (approximately).

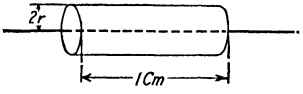


FIG. 19.

In this way the size of the molecule can be obtained from the mean free path. The values so obtained are given in the table. The smallest molecule (helium) has an effective diameter of about 2 angstroms. There is no upper limit; long-chain hydrocarbon compounds have spheres of influence many times greater than this.

It must not be supposed that a molecule completely fills the volume of this sphere of influence. The molecule is made of atoms and each atom in turn is made of a nucleus and electrons

[1] A small correction has to be made for the motion of the other molecule.

which of themselves occupy very little volume. But when molecules get rather close, they repel one another, and it is the distance from the molecular center at which strong repulsion begins which is here measured. At greater distances there is a slight attraction between molecules (Chap. VI).

Viscosity, Heat Conductivity, and Diffusion.—How are these free paths measured? When two species of gas molecules are in the same vessel, each molecule tends to wander from its original position; gases tend to mix. This is *diffusion.* When the pressure is very low so that collisions are infrequent, this diffusion is very rapid indeed. But in the hit or miss motion of molecules at ordinary pressure, the velocity of each molecule is constantly being reversed and the diffusion is much slower. Evidently the rate of diffusion will depend on the mean free paths; in a liquid, where the molecules have almost no freedom of motion, the diffusion is very slow.

Not only may the molecules of different species mix but also molecules of the same species of greater and smaller energies will do likewise or will at any rate pass on the energy from one molecule to the next; and also if the momenta of molecules are different in different parts of a vessel there tends to be a similar equalization of momentum. The equalization of energy causes *heat conductivity* from a hot body to a cold. If one of two parallel plates is moving, the gas between will tend to drag the other plate along. This effect is called *viscosity* and the viscosity of the gas is due to the transfer of momentum from one plate to the other.

The heat conductivity and the viscosity of a gas are independent of pressure (except at very low pressures). Surely a remarkable fact; but it is a fact which can be understood in the light of what has been said. One probably expects an increase in number of molecules to increase the viscosity or heat transfer but when the gas is compressed the free path is decreased just enough to compensate for the added number of molecules. A relatively small amount of gas will completely destroy the thermal insulation of a thermos bottle. Only at pressures so low that the free paths are terminated by the walls of the vessel rather than by collisions with other molecules is a decrease in gas pressure accompanied by a decrease in conductivity or viscosity. Diffusion, heat conductivity, and viscosity depend, respectively, upon the transfer of molecules, of energy, and of momentum.

Each such transfer process is impeded by a short mean free path. Each of these phenomena then gives a measure of the free path.

All of these methods for determination of the mean free path and of molecular size have given consistent results. The size of the molecule can also be determined in other ways. For instance, by noting the departure at higher pressures from Boyle's law (which assumes the molecules to be without size), the effective molecular diameters (and hence the mean free path) can be determined (see Chap. VI).

Atomic Beams and Wave Motion.—All of this assumes that the molecules act as spheres. There is much reason to doubt this. With the aid of modern pumps beams of atoms can be obtained. The mean free path, effective cross section, and angle of scattering of the atoms in such beams as they pass through another gas have been studied. The mean free path found is several times less than that deduced by the indirect methods above; there are a great many more small angle deflections than would be expected between rigid spheres. In fact the observed scattering closely resembles the scattering of water waves as the waves pass through a number of piles. When a long wave strikes the pile, most of it sweeps around and goes on with little deflection. Slow moving molecules appear to act similarly.

Summary.—We have in this chapter opened the first door and barely entered the fairyland of the atomic world. What do we find? Enormously large numbers, excessively small individuals, motion everywhere. The gas is somewhat like a hive of bees, but the molecules are going pell mell, aimlessly, with the speed of bullets.

Pounding on the walls they produce a pressure equal to $\frac{1}{3}N_1mv^2$ (or $\frac{1}{3}\rho v^2$), *i.e.*, to two-thirds of their kinetic energy per unit volume. κT equals two-thirds the kinetic energy per molecule where κ (Boltzmann's constant) is the gas constant per molecule. Out of this comes the concept of the equipartition of energy. Also the actual speeds of the molecules are derived—about a mile a second for hydrogen at ordinary temperature. For other molecules and other temperatures the speed depends (inversely or directly) upon the square root of the mass and the temperature.

Moving at high speeds, molecules are continually colliding. The mean free path is obtained from transfer experiments. For the common gases at ordinary pressure the mean free path is about a ten-thousandth of a millimeter. The diameters of the spheres of influence are 2 or 3 angstroms.

HERE *detail by detail we see the world of the molecule taking form. It looks surprisingly like the see-hear-touch world about us. In these sophisticated times when every student of high school physics knows about the motion of the molecules, perhaps all this seems a bit commonplace. But what a marvel in the sixties and seventies and eighties when the first explorers entered this molecular world! Gases have always been mysterious. (Gas means* GEIST *or ghost or spirit.) And it is only within the century that the significance of heat has been understood.*

Not long ago the very concepts of force and of energy were confused (and the young student still confuses the dyne and the erg). Newton had emphasized momentum and impulse (force times time) and Leibnitz had emphasized energy and work (force times distance). Two schools of mechanics developed. Newton's disciples attempted to solve all problems by the conservation of momentum, Leibnitz's followers all problems by conservation of energy. Ideas were confused—kinetic energy is still sometimes known as VIS VIVA *("living force").*

Count Rumford first realized the true nature of heat. Mayer and Joule in the eighteen forties established the law of conservation of energy. And then Clerk Maxwell and Boltzmann unraveled this kinetic interpretation of molecular energy, giving us the first real glimpse of the microcosmus about us. The first absolute determination of a molecular magnitude was made in 1851 *when Joule determined the average speed of the gas molecule (page* 45*). The second molecular magnitude to be found was the mean free path in the gas (Maxwell,* 1860*).*

Maxwell died in 1879 *at the age of forty-eight. His first scientific paper he published at the age of fifteen. Maxwell followed Faraday and gave to his discoveries their strict interpretation. Much of this electrical research was done while still a student in Cambridge. "Maxwell's laws" are the basic electrical principles. He suggested the electromagnetic nature of light; he established the basic principles of kinetic gas theory.*

A prince of theoretical physicists. But in influence he was more than this. In his book "Matter and Motion" he preached to the people the new doctrine of energy. In 1870 *he was appointed to the newly founded professorship of experimental physics at Cambridge, the first director of the famous Cavendish Laboratory.*

CHAPTER IV

THE HEAT CAPACITY OF THE MOLECULE

But diatomic molecules have more energy than monatomic ones. It takes heat to move the molecule—and then some to make it rotate. We become tired of watching the decimal point and choose some new units. The moment of inertia of a dumbbell and how fast the molecules rotate. The atoms in solids get their due share of energy.

Specific Heat and Rotation of Molecules.—We have developed our picture of molecules rushing hither and thither at great speeds, continually colliding and changing their courses. Out of the chaos has arisen one fundamental statistical law: the equipartition of energy. But should not these molecules, particularly the molecules with two or more atoms, be rotating?

Diatomic molecules, like H_2 and O_2, may be supposed to be composed of two atoms joined together, somewhat like a dumbbell. Table 4 shows that such molecules are usually larger than monatomic molecules (compare H_2 and He). Should not this dumbbell be set tumbling as it strikes another? Should there not be energy of rotation as well as of translation in such a gas? Indeed so. It is in the specific heats of gases that the effect of this rotation is most clearly seen.

Molecular Heats of Gases.—By specific heat is meant the heat required to raise the temperature of 1 gm. 1°; molar heat is the heat required to raise a gram molecule 1°. Since a gram molecule always contains the same number (6.06×10^{23}) of molecules, the molar heat is the more significant quantity. It is proportional to the heat capacity of the individual molecule. In Table 5 are given the molar heats (in calories) of several gases.

The specific heats are not especially significant. But when these are multiplied by the molecular weight to give the molar heat it is seen that all monatomic gases have (at constant volume) a molar heat of 3, diatomic gases of 5, and triatomic gases 6 or more.

Table 5 is not very extensive. We could have added the monatomic gases; argon, krypton, xenon, and several metal

vapors—all these monatomic gases have a molar heat of 3. The diatomic gases (except as explained in Chap. XXIII) have a molar heat of 5. The molar heats at constant pressure are always 2 cal. greater. A remarkable simplicity in nature.

TABLE 5

Gas	Molecular weight	Specific heat (constant volume)	Molar heat (constant volume)	Molar heat (constant pressure)
H_2	2	2.5	5	7
He	4	0.75	3	5
N_2	28	0.18	5	7
O_2	32	0.15	5	7
Ne	20	0.15	3	5
CO	28	0.18	5	7
H_2O	18	0.34	6	8
CO_2	44	0.16	7	9
C_5H_{12}	72	0.38	27+	29+
Hg (vapor)	200	0.015	3	5

Energy of Translation—Monatomic Heats.—Now the explanation. It has been shown by Eq. (6) that the average energy of translation of a gram molecule of any gas is

$$\text{K.E.} = \tfrac{3}{2}R_0T$$

For a single molecule

$$\text{K.E.} = \tfrac{3}{2}\kappa T$$

The value of R_0 is about 83,000,000 ergs or about 2 cal.; the kinetic energy of translation of a gram molecule of any gas at room temperature (300° abs.) is $\tfrac{3}{2} \times 2 \times 300 = 900$ cal. But the most significant fact is that this energy of the gram molecule increases by $\tfrac{3}{2}R_0$ or 3 cal. for an increase of temperature of 1°. For a monatomic gas this is the energy to be added to heat the gas 1°—it is the molar heat. Hence the kinetic theory agrees exactly with the result found above. For diatomic gases rotation must be considered.

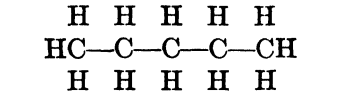
Degree of Freedom.—These monatomic gas molecules must at present be considered as mass points, incapable of rotation; they can move in translation in three different directions (the x, y, z axes or north-south, east-west, up-down). They are

said to have three degrees of freedom. A block confined to run in one direction along a track would have but one degree of freedom. A ball which can move in three directions and can also rotate in any direction (*i.e.*, about any one of its three principal axes) has six degrees of freedom.

Our law of equipartition has not yet been stated in proper form since the consideration has been limited to translational energy. *In equilibrium the* KINETIC *energy (on the average) is equally partitioned between each degree of freedom*[1] *and the share for each degree of freedom is* $\frac{1}{2}\kappa T$. For a monatomic gas, with three degrees of freedom, the energy is $\frac{3}{2}\kappa T$.

Rotational Energy.—Diatomic molecules must be considered as having no rotation about the line joining the atoms, but (in general) as being able to rotate about the two other axes. The molecular dumbbell can "tumble" but apparently does not "spin." Such a molecule has therefore two degrees of rotational as well as three degrees of translational freedom and it follows that the energy of the molecule at any temperature should be $\frac{3}{2}\kappa T$ (in translation) + $\frac{2}{2}\kappa T$ (in rotation) or $\frac{5}{2}\kappa T$. Multiplying by N_0 we get the energy of a gram molecule to be $\frac{5}{2}R_0T$ or an energy per Centigrade degree of $\frac{5}{2}R_0 = 5$ cal.

This explains the molar heat of diatomic gases. These diatomic-gas molecules "hold more heat" than monatomic molecules; they store energy in their rotary motion as well as in their translation. There is kinetic energy in translation and kinetic energy in the tumbling but no energy of spin. In general, we may say that for any gas the kinetic energy per gram molecule equals $\frac{1}{2}R_0$ (or 1 cal.) for each degree of freedom of the gas molecule. More complicated molecules—the long-chain carbon compounds such as pentane



can rotate in three dimensions and can usually vibrate as well, giving very large values of the molar heat.

[1] For instance, on a billiard table if the balls moved with perfect elasticity, we should expect each ball on the average to have the same kinetic energy as another. But if they were perfectly free to spin (unretarded by the felt), they would average as much energy of rotation as of translation.

Atomic Units.—In the atomic world we shall be continually dealing with very small masses, distances, and times, and it will be convenient to adopt a special system of units appropriate to these quantities in order to avoid very small fractions.

For a unit of distance we take the angstrom, 10^{-8} cm. The molecular diameters in Table 4 are given in these units. Helium has the smallest sphere of influence; its diameter is 2.18 angstroms. The carbon atoms in a long-chain molecule are about $1\frac{1}{4}$ angstroms apart. The effective cross section of such carbon chains is about 5 square angstroms.

For the mass unit it is convenient to take $1/N_o$ gm. (*i.e.*, 1.65×10^{-24} gm.). The weight of any atom then is simply its conventional atomic weight. Since this unit of weight is practically the weight of a proton (the nucleus of hydrogen), we may call the mass unit a "protol." The weight of the hydrogen atom is 1.008 protols, of oxygen 16 protols, and of the oxygen molecule 32 protols.

For time, 10^{-13} sec. will be taken as the unit and will be called the subsecond.

Other units can be derived from these to take the place of centimeter per second of velocity, of the dyne of force, of the erg of energy, etc. The unit of velocity is, of course, 1 angstrom per subsecond but this is 10^{-8} cm./10^{-13} sec. = 10^5 cm. per second or 1 km. per second. So the mean speed of hydrogen molecules (at 0°C.) is 1.8 atomic units.

The Unit of Energy.—Kinetic energy is $\frac{1}{2}mv^2$ and hence the energy unit (the atomic erg) will be protols × (velocity units)^2 or $1.65 \times 10^{-24} \times 10^{10}$ or 1.65×10^{-14} erg. Boltzmann's constant in these units is $\frac{1}{120}$. The kinetic energy per degree of freedom ($\frac{1}{2}\kappa T$) at 300° abs. is 1.25 atomic ergs.

This system of units is quite unconventional but will be convenient. Such units as will be immediately needed are given

TABLE 6.—ATOMIC UNITS

Mass	1.65×10^{-24} gm.	"protol"
Distance	10^{-8} cm.	angstrom
Time	10^{-13} sec.	"subsecond"
Velocity	10^5 cm./sec.	kilometer per second
Energy	1.65×10^{-14} erg	"atomic erg"
Moment of inertia	1.65×10^{-40}	

Boltzmann's constant = $\frac{1}{120}$

Velocity of light = 300,000 km. per second

in Table 6. A larger table of the new units is given in the Appendix (Table 57).

TABLE 7.—ENERGIES

Atomic ergs per atom; or kilojoules per gram atom, or per gram molecule

K. E. of monatomic molecule, 27°C	3.75
K. E. of diatomic molecule, 27°C	6.25
Heats of vaporization:	
Water	40
Nitrogen	3
Hydrogen	0.5
Helium	0.1
Iodine	13
Electron from tungsten	450
Heats of chemical action:	
Combustion of hydrogen	290
Dissociation of hydrogen molecule	420
Dissociation of oxygen molecule	680
Dissociation of chlorine molecule	240
Dissociation of iodine molecule	150
Electron in hydrogen atom	−1300
Average alpha particle	500 million
Average beta particle	50 million
Four protons in helium	-3×10^8
Total mass equivalent of a proton	9×10^{10}

Angular Velocity of Molecules.—Using these convenient units, we shall now describe the rotation of the molecules more precisely. In hydrogen it is known (Chap. XXIII) that the atomic centers are 0.76 angstrom apart. Each atom is 0.38 angstrom from the center of mass. Hence since the weight of each is 1.008, the moment of inertia I of the "dumbbell" about its center can be found.

$$I = mr^2 = 2.016 \times 0.38^2 = 0.290 \text{ atomic unit.}$$

At room temperature (300°abs.) the average rotational energy is

$$\text{K.E.}_{\text{rot}} = 2/2\kappa T = 2.5 \text{ atomic ergs}$$

But rotational kinetic energy is given by

$$\text{K.E.}_{\text{rot}} = \tfrac{1}{2} I\omega^2$$

This gives

$$2.5 = \tfrac{1}{2}\, 0.290\omega^2$$

$$\omega = \sqrt{14.5} = 3.7 \text{ radians per subsecond or}$$

0.6 revolution per subsecond

This means that the average hydrogen molecule is rotating almost 10^{13} (10 million million) times per second.

At this temperature any molecule with two degrees of rotational freedom has this same kinetic energy of rotation. In other words, the angular velocity varies as the inverse square root of the moment of inertia. The oxygen atoms in the oxygen molecule are rather farther apart (1.2 angstroms) than these hydrogen atoms and have much greater masses; the O_2 molecule has a moment of inertia of 11.6, about forty times that of hydrogen. In consequence its mean angular velocity is some six or seven times less than that of the H_2 molecule.

Angular velocities and the periods of rotation for several other molecules are given in the table.

TABLE 8

	Separation	Moment of inertia	Revolutions per subsection	Period
H_2	0.76	0.290	0.6	1.6
O_2	1.2	11.6	0.10	10
CO	1.15	9.0	0.11	9
HCl	1.28	1.60	0.26	4
I_2	2.66	450	0.015	60

Diatomic molecules containing a hydrogen atom are the ones with the largest angular speeds. Because of its lightness the hydrogen atom in HCl rotates about the heavy chlorine very rapidly, with about half the angular velocity of the H_2 molecule itself. Other diatomic molecules take several subseconds to rotate; the heavy iodine molecule takes sixty subseconds.

But in every case, for heavy molecules and light, the mean rotational energy is exactly the same, *i.e.*, $\frac{2}{2}\kappa T$. We know exactly the average rotational speed of every molecule as well as its translation. We know just how many turns it is apt to make per second as well as we know its linear speed.

For the most part these diatomic molecules are quite rigid under the impacts which they are apt to receive from other molecules at ordinary temperatures. However, in some cases, for very heavy molecules (like I_2) or long-chain molecules, vibrations are set up among the atoms of the molecule (Chap.

XXIII). The best example of vibrational motion however is found in solids.

Atomic Heats of Solids.—In 1819 Dulong and Petit discovered the law of atomic heats of solids. If the specific heat of an element is multiplied by the atomic weight, the product is the *atomic heat*, the heat capacity of a gram atom. Dulong and Petit found that for solid elements this atomic heat was nearly always close to 6 cal. per degree centigrade. What validity the law has can be seen in the table. In general, the law holds for the heavier elements but not for the lighter.

TABLE 9.—ATOMIC HEATS AT ROOM TEMPERATURE

	Atomic weight	Specific heat	Atomic heat
Carbon	12	0.125	1.5
Sodium	23	0.297	6.8
Aluminum	27	0.168	5.8
Iron	56	0.119	6.6
Copper	64	0.094	6.0
Silver	108	0.056	6.0
Lead	207	0.030	6.2

Energy of an Oscillator.—This atomic heat of 6 is exactly $3R_o$. This is for the gram atom; the heat required to raise by 1° the temperature of a single atom in a metal is 3κ. The fundamental reason for this law of Dulong and Petit is to be found in equipartition of energy.

In a solid neither simple translation nor rotation of the atoms can occur; instead, the atoms vibrate about their equilibrium positions. Since vibration in any direction may occur, each oscillating molecule will have three degrees of freedom and on the average will have then $\frac{3}{2}\kappa T$ of kinetic energy. But it is characteristic of an oscillator that its energy is potential (at the end of the swing) as often as it is kinetic and hence it must in its three degrees of freedom have $\frac{3}{2}\kappa T$ of potential energy as well as $\frac{3}{2}\kappa T$ of kinetic energy. In general, *an oscillator has κT total energy for each degree of freedom.* In this case of the solid the total energy of an atom is $3\kappa T$ and the energy for each degree of temperature is 3κ and the atomic heat $3R_o$ or 6. The exceptional cases will be studied later.

Brownian Movement.—How far can this law of equipartition of energy be carried? We turn to one of the most beautiful of experiments. In 1827 the botanist Brown noticed that minute particles suspended in a liquid were in ceaseless motion. Momentary fluctuations in pressure occur upon the surface of these particles, and each acts like some minute pushball as it is jostled about by the molecules. Or, better, these particles act exactly like gigantic molecules. Quite aside from any rotation of the particle and from any vibration of the atoms within it, these particles may be expected to have translational energy equal to $\frac{3}{2}\kappa T$. These particles each must get as a whole the same quota of translational energy as any one molecule. Or perhaps we should say "as any other molecule," for it is difficult to draw a distinction here,[1] even though the smallest of such colloidal particles is millions of times as large as the usual gas molecules. When a cork is floated in a dish of water and after the wavelets on the water surface have become ripples and the ripples have become imperceptible and all conditions have become those of the steadiest equilibrium, the cork is actually not at rest. Why should the rain of molecules on the opposite sides of the cork exactly cancel in their pressures? The cork acts as a single particle and moves with kinetic energy $\frac{3}{2}\kappa T$. But we are going too far; what would this energy, the energy of a single molecule, mean to a cork? The ultramicroscope is usually necessary to perceive the particles in which the Brownian movement is large enough to be perceptible.[2]

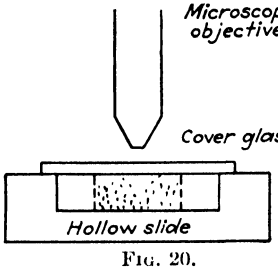


FIG. 20.

Quantitative Observations of Perrin.—Now if the motion of these minute particles can be measured, their kinetic energies can be computed. Not that it is easy to deduce the velocity from the completely irregular motion of one of these particles. (As well try to find the total distance covered by a peregrinating dog by noting merely his distance from his home.) But Einstein and Smoluchowski, using probabilities and statistics

[1] A molecule is a group of closely associated atoms. In referring to the motion of the particle, we refer to the motion of the center of mass. Each molecule or atom within the particle has its own quota of energy.

[2] Since K.E. $= \frac{1}{2}mv^2$, the velocity gets smaller as the mass increases.

and means and averages, had worked out the theory. The French physicist Perrin in a famous series of experiments undretook to make accurate measurements of the Brownian movement. He made suspensions of resin precipitated in water. The grains were spherical and of very uniform size. Although they were usually too small to be seen in the ordinary microscope, he was able to count the number and measure the size of these grains. By long, patient observation he measured the average change in position of these particles in a second; using the Einstein-Smoluchowski theory, he computed their average velocity. And by comparison with these gigantic "supermolecules," which he could see in his ultramicroscope, he deduced the mass of the ordinary molecule and the mass of the atom.[1]

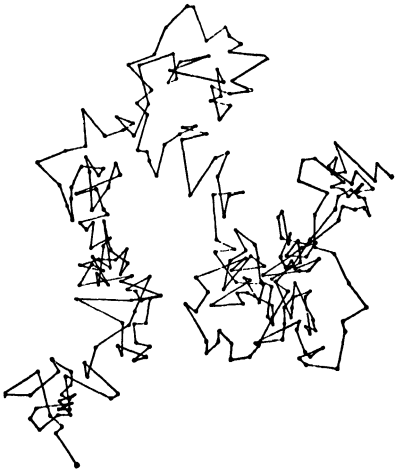


FIG. 21.—Observation of colloid particle at 10-sec. intervals. (*Perrin.*)

Figure 21 shows observations of Perrin of a typical particle as it was observed after successive intervals of time. The motion is absolutely random. It gives us a picture with greatly reduced velocities of what the planless dance of the molecules must be. If the velocities of these particles are small, it is because their masses are large—the average translational energy of the resin particle is just equal to that of a single one of the water molecules which bombards it ($\frac{3}{2}\kappa T$). The speeds of the particles must evidently be to the speeds of the molecules inversely as the square roots of the masses

$$(\tfrac{1}{2}mv^2)_{\text{particle}} = (\tfrac{1}{2}mv^2)_{\text{molecule}}$$

Clearly, when Perrin measured the mass and speed of his giant "molecules," it was but a matter of proportion to find the masses of the molecules of the water or of any other molecule in terms of its velocity which was already known (page 45). The smallest particles which Perrin used weighed about a ten-

[1] In 1921 Perrin received the Nobel prize (in chemistry) for this work. A table of Noble prize winners is given on p. 397.

millionth billionth (10^{-16}) gm. Their mean speed (computed from the Brownian movement) was the one twenty-thousandth part of that of one of the water molecules about it; hence the mass of such particles was computed as 400 million times greater than that of the water molecule, or 3.6 billion times the mass of the hydrogen molecule.

Rotational Brownian Movement.—The rotational motion of some of the larger particles could be observed. These particles can, of course, rotate about all three principal axes; their mean energy of rotation should be as great as their translational energy. So Perrin found it. Again a verification of the equipartition law and another independent measurement of the size of the molecule.

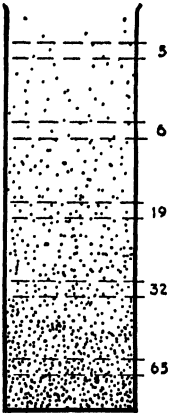


FIG. 22.—The colloid atmosphere. Observe that the number of particles is approximately halved in each half inch of ascent in the illustration.

The "Colloid Atmosphere."—Finally, and perhaps most interesting of all, Perrin found the particles to become fewer and fewer in number as he went higher into the liquid, much as the molecules in the air become rarer at increasing altitudes. Indeed these resin particles decreased in number in a few hundredths of a millimeter by the same negative compound-interest law that holds for the density of our atmosphere as we go up a few miles. His colloidal particles formed an "atmosphere" on a minute scale within the suspending liquid. In their random motions these particles tended to diffuse upward away from the bottom of the observing vessel by the breadth of a hair or two just as on the larger scale the nitrogen and oxygen molecules of the air wander upward from the earth several miles. Gravity pulls millions of times harder on these gigantic "molecules." By a direct comparison of the height[1] of this atmosphere of resin particles of known size with the known height of our nitrogen-oxygen atmosphere, a third independent evaluation of the size of the molecule is obtained.

The value of Avogadro's number as deduced by Perrin by these three different methods is given below. These results are to be compared with the more precise value obtained less directly from a measurement of the charge on the electron

[1] We have not mentioned the buoyant effect of the water which helps support the particles. This acts essentially as a decrease in the gravitational force and must be allowed for.

($N_0 = 6.06 \times 10^{23}$). Considering the difficulties of the experiment it is a remarkable agreement.

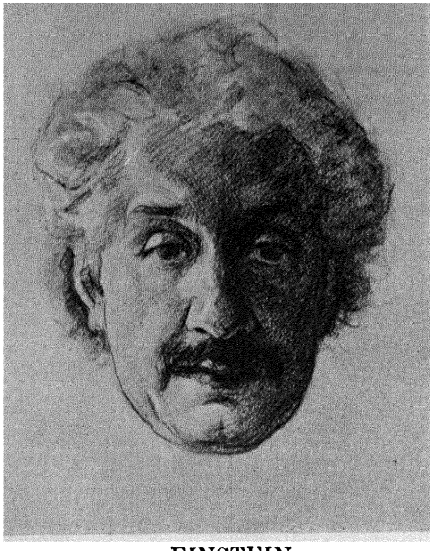
TABLE 10.—AVOGADRO'S NUMBER FROM BROWNIAN MOVEMENT

From translational velocities	6.8×10^{23}
From rotational velocities	6.4×10^{23}
From decrease of number with height	6.4×10^{23}

Never can one come closer to this molecular world of incessant motion than when he observes this Brownian movement. He sees these particles going hither, thither, up, down, right, left, always changing, never stopping; he sees this motion, quite planless, entirely unpredictable, and he can readily imagine the vastly faster motions of the water molecules themselves.

Summary.—The law of equipartition shows that the kinetic energy of any molecule is $\frac{1}{2}\kappa T$ for each degree of freedom. Boltzmann's constant κ is 1.37×10^{-16} in c.g.s. units or $\frac{1}{120}$ in atomic units. This gives an energy of translation of $\frac{3}{2}\kappa T$ to each molecule or $\frac{3}{2}R_0 T$ per gram molecule. The law holds even for the particles visible in the Brownian movement and enabled Perrin to determine Avogadro's number. Similarly $\frac{1}{2}\kappa T$ and $\frac{1}{2}R_0 T$ are the energies for the molecule and gram molecule associated with each degree of rotational freedom. Since the value of R_0 in calories is practically 2, this explains the molar heats of 3 observed for monatomic gases and 5 observed for diatomic gases at constant volume. Applied to solids, the law of equipartition of energy explains the law of Dulong and Petit. The atomic heat of solid elements is usually about 6; this follows because the energy of oscillation (in a gram atom) is $R_0 T$ for each degree of freedom.

What amazing results are these—each feature of the molecular world being explained *quantitatively* by the kinetic theory! What does this mean? Can it be that in this molecular world, the world of ultimate things, this world a million times beyond the strongest microscope, there is nothing novel? Are customs there the same as in the world of everyday perception? Does cause and effect reign there, Euclidean geometry reign there, the ordinary laws of mechanics reign there, each exactly as they do among the balls on a billiard table? Do molecules, to all intents and purposes, act as small elastic balls? It would be strange indeed if in such a recondite realm we discovered nothing novel, nothing disconcertingly strange.



EINSTEIN

(*Drawn from life by S. J. Woolf.*)

Here again in the theory of Brownian movement, we find the influence of Albert Einstein. What manner of a man is this? A German Jew, he was born some fifty odd years ago. He studied in Zurich (Switzerland) and was professor there until called to the University of Berlin in 1913. *His first papers on the relativity problem were published in* 1905 *and his general theory announced ten years later. We have mentioned his theory of Brownian movement. Einstein was one of the earliest to recognize the significance of the quantum theory of energy. In explaining the photo-electric effect* (1905) *he advanced the view that light is corpuscular in nature, a view which seemed impossibly radical at the time but which has come to be accepted. In* 1925 *he, together with the Indian physicist Bose, proposed a new atomic statistics. Since* 1932 *Einstein has been Professor of Theoretical Physics at the Institute for Advanced Study (Princeton).*

Einstein is a man of broad sympathies and simple tastes; like so many others of mathematical genius he finds his avocation in music (he plays the violin). He has had a broad interest in humanity, in his country and his race and in world peace. Usually reckoned the foremost mathematical physicist of our time.

CHAPTER V

THE LAWS OF CHANCE

We toss a coin and find the distribution of molecular velocities. Boltzmann's law of settling. The degradation of energy; it is easier to scramble an egg than to unscramble it.

The Probability Curve.—If we toss a coin, it may come heads or it may come tails—it is a matter of chance. In the long run the number of heads will nearly equal the tails. Out of this develop the laws of chance and many of the laws of physics.

If we toss two coins, the chances are one in four that we get two heads, one in two that we get one head and one tail, and one in four that we get two tails. If we have six coins and toss them, we may get anything from all heads to all tails. If we toss them repeatedly a great number of times, we can find the chances of getting different combinations from no heads to six heads; these relative chances are as given by the numbers in the table.

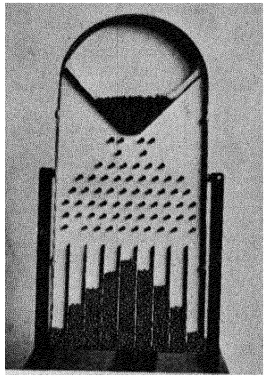


FIG. 23.—Probability board, showing random distribution of falling shot.

TABLE 11

Number heads	0	1	2	3	4	5	6
Probability	1	6	15	20	15	6	1

This is also shown in Fig. 24. The chances are 1 out of 64 of throwing all heads (or no heads) but nearly 1 in 3 of getting an even distribution of three each.

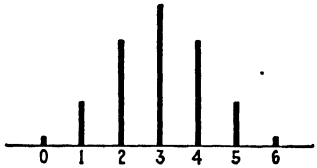


FIG. 24.

Here there were but seven different possibilities. The probability can be computed for much greater numbers. We then get what is known as the normal distribution curve (Fig. 25). The equation for this distribution curve is

$$P \propto e^{-\frac{x^2}{\alpha^2}}$$

where α is a constant determining the spread of the curve. (Compare this with the equation for the negative compound-interest curve.)

Errors in Measurement.—This curve is sometimes called the error curve and α the modulus of error or the dispersion constant. Any physical measurement, from the measuring of a stick to the measuring of an electron, is subject to errors. Positive and negative errors occur as the heads and tails of the coin. Small errors are more common than large ones and in normal cases the errors will be distributed about the true value as in the proportion above. The results of a novice as he measures a length again and again may be scattered as in the one curve; the results of a Millikan as he measures an electron may be more consistent as represented in the other; but be its dispersion great or small we each of us have, for any kind of measurement which we make, our own characteristic error curve.

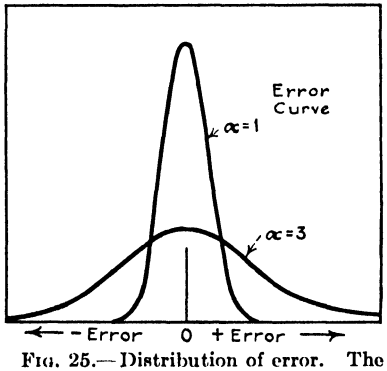


FIG. 25.—Distribution of error. The figure also illustrates distribution of a single component of velocity.

Molecular Velocities.—Clerk Maxwell it was who first analyzed molecular velocities. Already in Chap. III we have found the value of the average molecular speed; but, of course, no two molecules are moving exactly alike nor does the same molecule retain the same speed for more than the few subseconds elapsing between collisions. We are now interested in the distribution of velocities among the molecules.

To make the problem as simple as possible, one first considers not the actual velocity with its three possible directions but instead the component velocity in a given direction. For instance, the molecules in air are moving with mean speeds of about a quarter mile per second; our present question is how many are going upward with half this speed, how many moving downward with three times the average speed, and so on. It is all a matter of chance. Maxwell showed that *the components of velocity in any given direction* follow exactly the error curve.

The dispersion constant now depends on the temperature. Consider the vertical component. As many molecules go up as down. The average and most probable value of this component is zero. The two curves in Fig. 25 may be considered to represent the relative number of molecules with different speeds at two different temperatures.

Maxwell's exact expression for the probability of different values for the component of velocity is[1]

$$\frac{N^1}{N_0} = e^{-\frac{\frac{1}{2}m}{\kappa T}v^2} \qquad (8')$$

When we consider the *total* velocity (which depends on all three of the velocity components), the curve is somewhat different and gives what is called the *Maxwell distribution law* (Fig. 26). The reason for the difference is this: While the most probable value for the upward component or the northerly component or the easterly component taken alone is zero (Fig. 25), it is not probable that at the same time the upward *and* the northerly *and* the easterly components will be zero as will be necessary if we are to have zero total velocity in Fig. 26. Some molecules go fast, some slowly, on the average with a mean speed which depends upon the temperature.

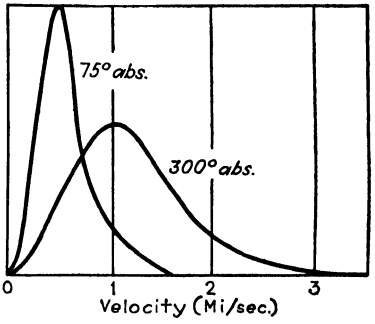


FIG. 26.—Maxwell distribution law. (Velocity scale applies to hydrogen.)

The two curves in Fig. 26 represent the distribution of velocities for hydrogen molecules (1) at ordinary temperature (300° abs.) and (2) at 75° abs. when the mean speed is half as great. Other molecules would have similar distributions with a change only in the velocity scale.

Molecular Rotation.—Some molecules rotate fast, some slowly. Naturally Maxwell supposed that these rotational motions obeyed the same law of chance as the translation and have

[1] N_1 represents the number of molecules having velocity component v; N_0 represents the number having a zero component. In each case the number within some small interval (say 1 meter per second) of the chosen value is meant.

similar probabilities. Figure 25 might well represent the number of molecules with different angular speeds about a certain axis.

Chance and Position.—Boltzmann picked up this problem of the random motions of the molecules where Maxwell left off. Maxwell had studied the probable distribution of velocities; Boltzmann studied the probable distribution in position of the molecules.

Other things being equal, the number of molecules in any given cubic centimeter is apt to be very nearly the same as that in another. But if molecules are in a force field, this will not be the case. The molecules tend to concentrate in regions where their potential energy is low. There are 2.7 times (*i.e.*, e times) as many molecules per unit volume at sea level as at the peak of Mt. Everest (5 miles high; see page 52). We know that it is possible for a bottle to contain water molecules in two very different states. In the upper portion of the bottle the water molecules may for example be some 30 angstroms apart, in the lower some 3 angstroms apart. In the densely populated lower region there are about a thousand times as many molecules per unit volume as above, and yet, at certain temperatures and pressures, these two vastly different states of "liquid" and "gas" may be in stable equilibrium.

Boltzmann, by a remarkable extension of the statistical reasoning which Maxwell had initiated, demonstrated the law of probable population densities for molecules. Given two positions between which the potential energies of a molecule differ by PE, the relative number of molecules in the two localities will be

$$\frac{N_1}{N_2} = e^{-\frac{PE}{\kappa T}} \qquad (8'')$$

(Compare page 66 and Fig. 22.) The negative curve of Fig. 18 may represent the relative population densities in localities of different potential energies.

This law of Boltzmann has the widest application. It embraces the law of the atmosphere. It embraces the laws of evaporation. A molecule loses kinetic, gains potential, energy (heat of vaporization) on evaporating—the population is small in the gas phase because of the high potential energy there. At low temperatures PE is larger than κT and the difference in populations is very

great—as T is raised evaporation occurs and the population in the gas phase increases.

Probably no law is of more general application in chemistry. H atoms or O atoms or Cl atoms usually combine into pairs, H and O atoms tend to combine into H_2O, other atoms form into the countless combinations which the chemist has discovered—why? Because these particular combinations have low potential energies.

The Maxwell-Boltzmann Distribution Law.—It is interesting to compare this distribution of positions with the law of velocity distribution. Maxwell's law for velocities in a particular direction is (page 71)

$$\frac{N_1}{N_0} = e^{-\frac{1}{2}\frac{mv^2}{\kappa T}} = e^{-\frac{KE}{\kappa T}}$$

Here the relative numbers of molecules having different velocities depend upon the ratio of the kinetic energy to the average kinetic energy ($\frac{3}{2}\kappa T$). In Boltzmann's law the relative numbers in different positions are seen to depend upon the ratio of potential energy to the average kinetic energy. The two laws are often combined. The ratio of the number of molecules in one particular position with one particular velocity to those in another position with another velocity is given by

$$\frac{N_1}{N_2} = e^{-\frac{KE+PE}{\kappa T}} \text{ or } = e^{-\frac{W}{\kappa T}} \qquad (8)$$

when W represents the total energy. This is the celebrated Maxwell-Boltzmann statistical law (M-B law).

The subject of statistical mechanics is the application of this Maxwell-Boltzmann distribution law to all problems of statistical equilibrium in physics and chemistry—from such simple problems as the distribution of molecules in the atmosphere to the evaporation of vapor from the liquid state, or the dissociation of molecules into atoms, or to the evaporation of electrons from a metal or the "evaporation of light" from a heated solid.

The Atmospheric Law.—The simplest illustration must here suffice. Quite evidently this Boltzmann law is identical with the law of the atmosphere. If a molecule is lifted above the earth's surface, the increase in its potential energy is mgh. Let us consider the oxygen molecule. We shall use ordinary c.g.s. units.

$m = 1.65 \times 10^{-24} \times 32 = 5.3 \times 10^{-23}$ gm.
$g = 980$ cm. per second
$h = 5$ miles or 8×10^5 cm.
$\kappa = 1.37 \times 10^{-16}$
$T = 300°$ abs.

The potential energy of an oxygen molecule 5 miles high is

$$mgh = 4.2 \times 10^{-14} \text{ erg}$$

This is practically equal to κT which at 300° abs. equals 4.1×10^{-14} erg.

Hence from Eq. (8″) the relative number of molecules at the two heights (assuming perfect equilibrium with no winds, no temperature difference, etc.) is as e^{-1} or as 1:2.7.

This atmosphere which bathes us is the condensation of a gas upon the earth; the earth serves as a nucleus for condensation. Without the earth this nitrogen and oxygen and argon and the carbon dioxide and hydrogen and the rest would be thinly spread throughout all space. What, we may ask, is the chance of these molecules of our atmosphere "evaporating" away from us?

Let us consider the lightest gas: hydrogen. We can compute its potential energy in a number of ways. Perhaps the simplest method will be to remember that for a projectile to leave the earth requires a speed of 7 miles a second; the average velocity of hydrogen molecules is 1 mile a second (corresponding to an average energy of $\frac{3}{2}\kappa T$). This makes its mean kinetic energy one forty-ninth of that required for escape. $PE/\frac{3}{2}\kappa T = 49$. In the Boltzmann equation it is κT rather than the mean kinetic energy ($\frac{3}{2}\kappa T$) with which the PE is to be compared. $PE/\kappa T = 74$. Hence the number of hydrogen molecules occurring in free space relative to those in our atmosphere will be as e^{-74} or 0.00000000000000000000000000000001.

The velocity of escape from the moon is only $1\frac{1}{2}$ miles per second; the energy required to leave the moon is twenty times smaller than from the earth. Hence the gases—not only hydrogen but nitrogen, oxygen, water, all gases—have in fact left its surface. No atmosphere, no twilight, no erosion from winds and rain, no possibility of animal or plant life, all because mgh on the moon is not much larger than κT.

Statistical Laws in Physics.—Here we see two laws of physics which are at the same time laws of chance. It must not be

supposed that the molecules *must* be distributed after the law of Boltzmann. Their positions are all matters of chance; this particular distribution is by far the most likely—it is practically inevitable. It must not be supposed that the molecules *must* have these particular velocities predicted by Maxwell any more than in tossing a coin the number of heads *must* equal the number of tails. Out of a thousand tosses all *may* be heads; out of a thousand persons all may have been born on the same day but the chances are against it. A thousand molecules all may be at rest rather than having speeds distributed as in the Maxwell law but the chances are against it. With the billions of billions of molecules which make up our usual systems the chances are enormously in favor of the statistical laws being observed. And yet it is important to remember that many of the laws of physics are statistical in nature and it is not certain—it is only very very probable—that in any given instance the law will be obeyed.

All of the molecules in the wood of the library shelf may by chance move upward at once and throw my book into the air, but the chances are tremendously against it. Over a very small area of surface such effects do occasionally take place. This gives fluctuations in pressure as seen in Brownian movement. A gas tends to expand into a vacuum and heat tends to flow from the hot to the cold and electrons in a conducting wire to move from low potential to high, but these are only laws of chance. Each molecule in the gas and each electron in the metal moves at random, some here, some there. Only as to the average behavior of the average molecule can we find probabilities so great that they are indistinguishable from rigid laws.

Physics today treats of the individual atom and electron; the physics of the nineteenth century, on the other hand, dealt with matter in bulk and the fundamental laws of heat and sound and electricity and even the fundamental principles of mechanics refer to the mean behavior of many molecules; these fundamental principles are usually statistical in character.

The Second Law of Thermodynamics.—*Energy is indestructible.* This is the first law of thermodynamics. However, energy tends to appear in ever less and less useful forms. This is the law of *degradation of energy*, the second law of thermodynamics. The potential energy of the pile driver is quickly turned into kinetic energy and this in a moment is dissipated in heat as the blow is

struck. The chemical energy of the gasoline-air mixture is converted into intense heat and pressure, drives the automobile, and, if we choose, will ultimately appear as a warming of the brakes. Such processes cannot be reversed; by using the heat in the brakes we cannot make gasoline from the exhaust gases. All existence consists of energy changing from one form to another and nearly always this is a one-way progression of events. This is the second law.

A red-hot iron ball is suspended above a beaker of water. The ball may drop into the beaker. It splashes and hisses as it strikes, it cools off, it evaporates a little water, and ultimately it comes to rest at the bottom. But all this cannot be reversed. The heat cannot flow into the ball, making it red hot and leaving the water colder. At least this is unlikely. Nor are the evaporated molecules apt to return to the water nor are the walls of the room apt to conspire to reproduce the hiss which they have absorbed nor is the table apt to return the kinetic energy of the splashings so that these drops will leap back into the beaker and strike the ball in such a way as to return it to its original position. We need not say that this reverse process *cannot* happen but it is certainly unlikely. This is the second law.

The sun loses energy to space, the waters of the earth wear down the continents, even the rotational motion of the earth is being reduced to heat by the action of tides. In general, other forms of energy tend to disappear and become converted into heat. And among heated bodies the hotter one tends to become colder, the colder one hotter, and all things seem to be moving toward a time when all will be in equilibrium, each body at the same temperature, each molecule having the same average kinetic energy in each degree of freedom ($\frac{1}{2}\kappa T$) and in the universe all one vast sameness. And for all things, if not exactly the same motion, at least one final all-inclusive Maxwell distribution law. This ultimate toward which we seem to be moving is called by some the "heat death" of the universe. In thermodynamics a measure of this "sameness" of things is called *entropy;* the second law says that entropy always increases.

Statistical Meaning of the Second Law.—The story of Humpty Dumpty is that of the second law. When Humpty Dumpty fell from the wall, all the king's horses and all the king's men were unable to reverse the process. It is easier to scramble eggs than to unscramble them. When the orderly motion of a falling

weight is interrupted and the kinetic energy becomes distributed among the hundreds and thousands and millions and billions of molecules of the floor the process cannot be reversed. The energy has become scrambled. Heat in a hot body is really kinetic energy in scrambled form. It is possible that the first and the second and all the other molecules may sometime by chance be moving upward together and may push the weight back whence it came. But this is infinitely unlikely. I never expect to see my inkstand jump from the table by absorbing heat.

Another example from the nursery is the man so wondrous wise who jumped into a bramble bush and scratched out both his eyes. He jumped in again and scratched them back again! Ridiculous! Even in the nursery the second law is recognized. The law of increasing entropy is true for the same reason that by shuffling one can mix a pack of cards but cannot by this means arrange them in order, not even if they are shuffled backwards! The law of increasing entropy is based on the simple fact that there are more ways of producing confusion than of producing order. There are infinitely many ways of putting things out of place and only one way to have them in place. It is easier to mix than to unmix.

Gases tend to expand; the chance is one in a thousand that in a liter vessel two given molecules will be in the same cubic centimeter, one in a million that three, one in a billion that four, and in a trillion that five will come simultaneously into this same cubic centimeter. There are 999,999,999,999 chances against it. Such a slim chance for only five molecules! What is the chance that the 20 billion billion billion molecules normally in a liter of air will condense? There is a chance. It may also be (as Eddington puts it) that a monkey romping over the keys of a typewriter will reproduce an "Encyclopædia Britannica," but it is doubtful. The chance in this latter case is, however, much greater than that a gas left to itself will spontaneously contract.

The second law of thermodynamics explains why heat flows "downhill," why gases expand rather than contract, why only a small share of heat can be reconverted into work, why an automobile cannot appropriate its running energy from the air—and the molecular picture explains the significance of the second law

Time's Arrow.—In the theory of relativity, future is inevitably distinguished from past. Placed in a closed room we should be

unable to distinguish north, south, east, and west and, except near the earth, be unable to distinguish up and down. But of the future and of the past there can never be doubt. What is the characteristic difference? Psychologically there is the difference that we can remember the past but cannot preview the future. Eddington finds that the physical difference rests in entropy. That direction in time toward which entropy increases, toward which energy dissipates, is the future. Time has a unique forward direction. As Eddington puts it, time is not to be represented by a mere line but by an arrow and it is the increasing property of entropy which gives the point to time's arrow.

Is the Universe Running Down?—Is the argument for dissipation of energy conclusive? As far as we can see entropy must increase. But for us to extrapolate our experience of a few years and a few miles or few billions of miles to all time and the whole universe is rather venturesome. It has been maintained that there must be an upbuilding as well as a degrading process in the universe. In our particular corner of the universe in this particular era of time entropy increases. But cosmic rays have been interpreted by Millikan as due to the building of helium and other atoms in the depths of space by the conjunction of a number of hydrogen atoms. How came these atoms to convene?

Is the Universe running down? And if so when did the Universe begin, when will it end? When faced by fundamental questions of such immensity our truest answer is: we do not know.

CHAPTER VI

MOLECULAR ATTRACTION

Molecules feel drawn toward each other; we modify Boyle's law. How Boltzmann's law relates the boiling point with latent heat. Crystals are like giant molecules. Free electrons.

Nothing has been said as yet about the tendency of molecules to cling together.

In a drinking glass on my desk are some water molecules. There are in this glass some twelve hundred times as many molecules as should be there by Avogadro's hypothesis. The molecules are very different from nitrogen or oxygen molecules—they have a notably stronger attraction one for the other. The water in the glass we say is in the liquid state. This tendency to form liquid or solid aggregates is concrete evidence of an attractive force which always exists in lesser or greater degree between molecules. Helium molecules are not liquefied until they have lost nearly all their motion (at 4° abs.); carbon remains a solid until nearly 4000°C.; but in every case there is an attractive force. The force is present even in the gas; in the gas it results in a decrease of the pressure exerted against the walls.

Perhaps we may liken the gas and liquid states of a substance to country and city life—the wide-open spaces where a molecule's a molecule, and the congested community where individuality is largely lost. There is a notable difference in the compressibility of one of these densely populated molecular communities and of the molecules in the wide-open spaces. Hooke's law of elasticity holds for the liquid; the volume decreases in direct proportion to the force applied; the compressibility is very small. For the gas we have Boyle's law. Boyle's law holds only in so far as intermolecular attraction can be neglected. Never exactly true, often far from true for vapors, and not applicable at all to the liquid, Boyle's law offers no explanation of condensation.

Van der Waals' Equation.—The Dutch physical chemist Van der Waals considered these attractive forces and appropriately corrected Boyle's law and the general gas law. In the general

gas law he substituted $\left(p + \frac{a}{V^2}\right)$ for p and $(V - b)$ for V. The internal pressure is, in virtue of this intermolecular attraction, somewhat greater than the pressure (p) as ordinarily measured at the surface of the gas. The term a/V^2 corrects the pressure for this intermolecular attraction. Clearly this correction is more important when the gas is compressed, the molecules close together. The correction b is made in the volume to allow for the finite size of the molecules. The volume available for molecular motion is only the space between molecules.[1] This gives Van der Waals' general equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (9)$$

What we have here is not a gas law any more than it is a liquid law; it serves fairly well to give all the elastic properties and thermal expansivity of both gas and liquid.

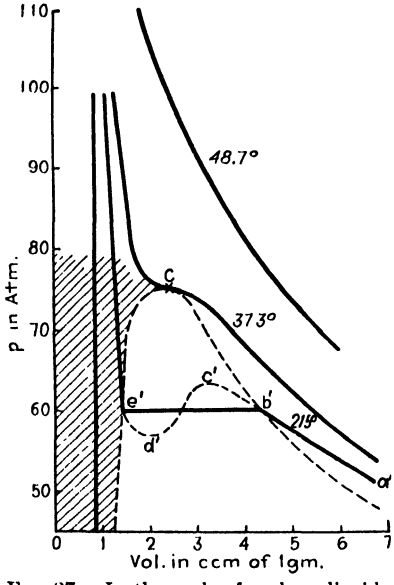


FIG. 27.—Isothermals of carbon dioxide at high pressures.

Figure 27 represents Van der Waals' equation in a special case. It shows the compressibility of carbon dioxide at constant temperature. At 48.7° the curve does not differ greatly from the familiar hyperbola which represents Boyle's law. At 21.5° the case is different. For this value of T the curve has an oscillating character between b' and c'. Before it is given a physical interpretation, a straight line must be substituted for this oscillating (dotted) portion. We shall not undertake here to justify this except for the observation that obviously a substance which increased in volume when a greater pressure is applied (as in the curve from d' to c') is unthinkable. This straight-line portion of the curve represents the formation of liquid from the gas; here the gas can be condensed to liquid with a great decrease

[1] Actually b is four times the aggregate of molecular volumes.

in volume without any increase in pressure. On the right from a' to b' the curve represents the compressibility of the gas, not departing far from Boyle's law. On the left the liquid state is represented; the liquid has slight compressibility, obeying Hooke's law. Above 31° no flat part exists; this is the *critical temperature.* Above the critical temperature no condensation into a liquid or evaporation into a vapor state can be observed. As the temperature is further raised, the correction constants a and b have less relative importance and the curve becomes practically the Boyle hyperbola. At these temperatures the attractive forces still exist but are not sufficient to hold the molecules together against the violence of their high velocities.

Evaporation.—In the case of water the critical temperature is 365°C. Below this temperature the water may be either vapor or liquid, depending on the pressure. When water evaporates, it must not be supposed that every molecule approaching the surface leaves. The attractive forces are so great that only the very fastest molecules of the liquid have sufficient energy to overcome these forces and leave. The number of these molecules which are able to escape naturally increases as the temperature is raised, nearly doubling in the case of water for every 10° rise in temperature. But in any case equilibrium will be reached when the number of molecules entering the water from the vapor above equals the number leaving. The water evaporates until this condition obtains.

Let us illustrate. At 100°C. the equilibrium vapor pressure of water is 1 atmosphere and the densities of liquid and gas are as 1700:1. There are 1700 molecules in the liquid to 1 in the gas, there are 1700 molecules striking out from the surface of the liquid into the gas to every 1 entering the liquid. But, since equilibrium obtains, only as many can leave the liquid as enter—only 1 molecule in the 1700 succeeds in escaping.[1] Ten degrees lower and the speeds of the liquid molecules are only slightly reduced; yet only half as many escape. At room temperature only 1 molecule in 50,000 breaks away. Obviously this tendency to break from the restraining force of the liquid depends very critically upon the velocity.

[1] It takes 40 atomic ergs of energy for one molecule to escape; the average molecule in the water at 100°C. has in its translation only about 5 atomic ergs of kinetic energy (Table 7).

Only the faster molecules leave and in doing so they lose kinetic energy (gaining potential); the average kinetic energy of the average molecule is the same in vapor as in liquid and consequently the temperature is the same. This emigration of the faster molecules results in cooling of the liquid and gives the heat of vaporization. The heat of vaporization measures the energy given to overcome the force of attraction of the molecules. To evaporate a gram of water (at 100°) 540 calories are required. This is 40 atomic ergs per molecule.

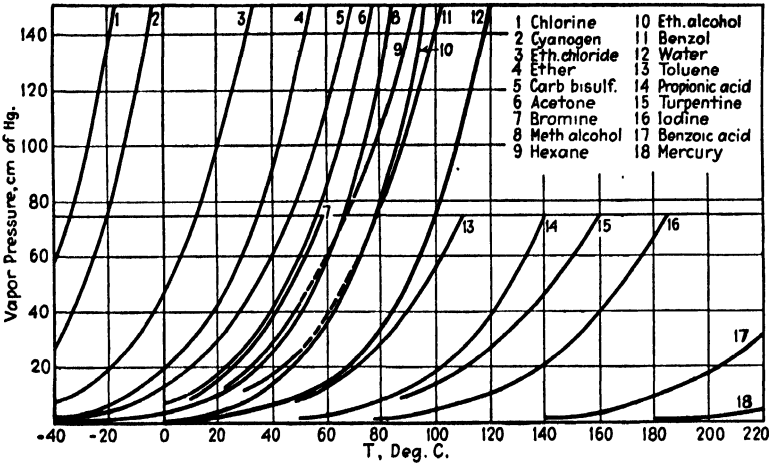


FIG. 28.—Vapor pressures of common liquids and vapors.

Boiling Points.—The most interesting portion of these isothermal curves of Van der Waals is the horizontal portion $b' - e'$ where liquid and gas states can exist together. Here a decrease in volume does not increase the pressure as it does for the gas alone and for the liquid alone; it only results in a transfer of more molecules from the gas phase into the liquid phase. The curves in Fig. 28 show at what pressure this transition occurs for different temperatures. Carbon dioxide is not shown; it would lie at low temperatures and high pressures, off the upper left-hand corner of the figure. Far beyond that would lie the curves for oxygen and nitrogen and hydrogen—and finally, a few degrees above absolute zero, the curve for helium.[1]

Now the most notable thing about these vapor-pressure curves is their marked similarity. Indeed each of these curves is but a

[1] Helium, most volatile of substances, was liquefied in 1908 by Kamerlingh Onnes and frozen by his successor Keesom in 1926.

portrayal of the Boltzmann distribution law.[1] Each curve is nearly of the form

$$P = P_0 e^{-\frac{mv^2}{2\kappa}\frac{1}{T}}$$

The curves are roughly like the compound-interest curve. Consider water. Its pressure is something less than doubled for every 10° of temperature rise. Its pressure is about ½ cm. of mercury at 0°, about 1 cm. at 10°, something under 2 cm. at 20°, just over 3 cm. at 30°, 5 cm. at 40°, and so on, up to 76 cm. at 100°C.

Potential Energies of Evaporation for the Molecule.—It takes about 7 atomic ergs to evaporate an oxygen molecule, about 26 for an ether molecule, 40 for a water molecule, and 57 for a mercury molecule; their corresponding boiling points are 90° abs. for oxygen, 308° abs. for ether, 373° abs. for water, and 630° abs. for mercury. In fact, for most elements the heat of vaporization (in atomic ergs) is about 8 or 9 per cent of the boiling point in degrees absolute (Trouton's rule).

TABLE 12.—HEATS OF VAPORIZATION

	Heat of vaporization, kilojoules per gram	Molecular weight	Heat of vaporization, kilojoules per mole or atomic ergs per molecule	Boiling point, degrees abs.
Helium	0.025	4	0.1	4
Hydrogen	0.50	2	1.0	20
Oxygen	0.21	32	7	90
Carbon dioxide	0.36	44	16	195
Ammonia	1.37	17	23	240
Ether	0.35	74	26	308
Alcohol	0.85	46	39	351
Water	2.26	18	40	373
Mercury	0.28	200	57	630
Tungsten	5.0	184	970	6000

[1] These pressures increase with temperatures chiefly because of the increased populations in the gas, although, of course, the speeds of the individual molecules also increase. In going from 0 to 100°C., the vapor pressure of water increases one hundred sixty times—the kinetic energies of the molecules by less than 40 per cent.

The M-B law, Van der Waals' equation, Trouton's rule, laws of molecular motion, and laws of chance, all are interwoven in the behavior of the liquid and its vapor. They have all been subject to the fairly exact computations of the mathematical physicist—in this case a statistician.

Comparison with Chemical Bonds.—These forces between molecules are due largely to the electric charges of which they are composed. Of course, the molecule as a whole is neutral. The theory is not simple. Essentially these forces which hold the liquid together and the solid together are not different from the "chemical bonds" which link the atoms into molecules. Two hydrogen atoms or two oxygen atoms or eight sulphur atoms unite to form single molecules; enormous numbers of atoms or molecules join together to form a liquid droplet or a solid crystal. The forces in these respective cases are sometimes distinguished as chemical forces and physical forces but they are similar except possibly as to magnitude. To break up 18 gm. of water into hydrogen atoms and oxygen atoms requires 1000 kilojoules as compared with 40 kilojoules for evaporation. The former process can occur only at very high temperature. (In the gases around the sun practically all molecules are dissociated into individual atoms.)

In the freedom of gas life, molecules are able to express their individualities as they cannot do in the congestion of either the solid or the liquid. This is well illustrated by the light which the molecule may emit. When a gas molecule is electrically excited, light with sharply defined frequencies is emitted and these frequencies are entirely characteristic of the molecule; the neon or argon or helium or mercury vapor in "neon signs" has each its own spectrum. On the other hand, when a solid or liquid is heated so that it emits light, the frequency depends primarily on the temperature rather than on the substance. An incandescent bar always presents nearly the same appearance at the same temperature, be it made of iron or silver or copper; what difference there is depends on the reflecting power (Chap. XIII).

Crystals.—Most solids are characterized by regularity of arrangement; they are crystalline. The elementary parts of the crystal may be atoms or groups of atoms or ions. The hardest crystal of all and the one with the highest of all melting points is the diamond. Here the atoms are arranged in the fashion shown in Fig. 84. Carbon is in the fourth group of the periodic table

(page 96) and its valence is 4; in the crystal each carbon is joined to four neighbors. In organic chemistry, molecules are made sometimes of long chains, sometimes of rings of carbon atoms. Here in diamond the atoms are joined not in chains but in each direction one atom is joined to others and these to others and so on into the millions and billions until we get perhaps a large diamond crystal. In a sense this crystal is but a gigantic molecule, a great number of atoms joined together by chemical forces. An alternative arrangement of carbon atoms is found in graphite (Fig. 84). A much less rigid structure this. Graphite is softer, individual atoms are more easily set into vibration, and consequently the specific heat is greater. In graphite one finds the benzene ring continually repeated like a vast mosaic in the cleavage planes.

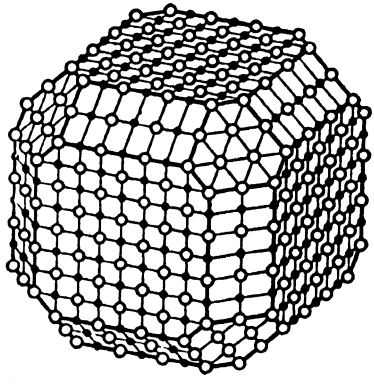


FIG. 29.—Structure in rock salt crystal.

These alternative crystal forms are called allotropic. Many other substances, elements and compounds, show such allotropic forms. We have monoclinic sulphur and rhombic sulphur, gray tin and white tin. There are seven known forms of ice.

In some cases the crystal is composed of charged rather than neutral atoms. Common salt is such an ionic crystal. The salt crystal is cubic, and the ions are equally spaced along each of the three axes. Sodium$^+$—chlorine$^-$—sodium$^+$—chlorine$^-$, so they go. Each positive sodium has six negative chlorine neighbors and each chlorine ion has six sodium neighbors. The molecule of Na^+Cl^- has here lost its identity; we cannot tell which sodium is associated with which chlorine. It is possible to refer to the whole crystal as a gigantic molecule; unless we do this, the idea of the molecule, so useful in the gaseous state, has lost its meaning. There may, however, be especially closely associated groups of atoms forming a single ion within the crystal. This is illustrated in the case of calcium carbonate (calcite) (Fig. 84).

Metals.—Usually in metals the crystals are very small. Many of the properties of the metal depend upon the character

of these crystals. As iron is hardened, its crystalline structure as seen under the microscope is greatly altered.

Most of the studies of metals have hitherto dealt with them in this polycrystalline form. Recently methods have been developed for growing large single crystals of metals by carefully regulating

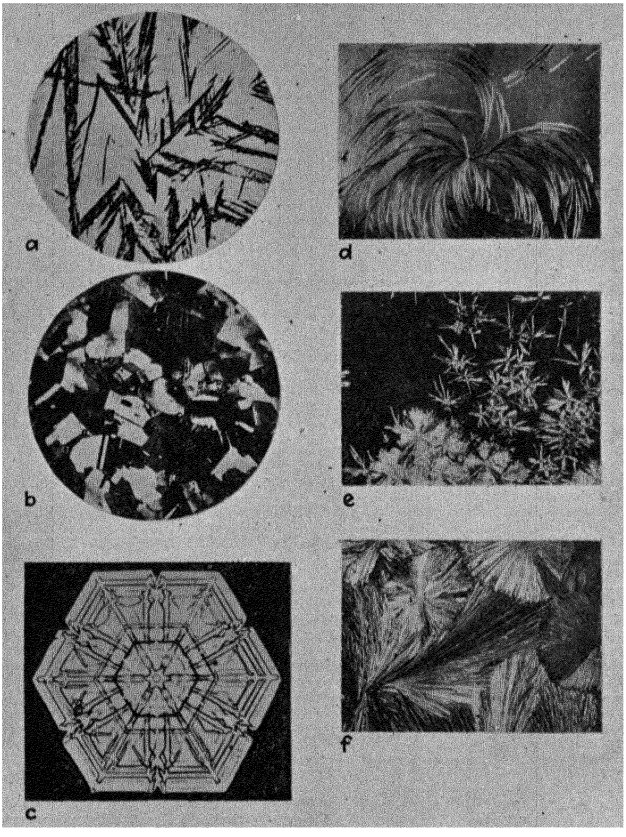


FIG. 30.—Microscopic crystals. *a*, *b*, hardened steels; *c*, snow crystal, *d*, aspirin grain; *e*, succinic acid; *f*, pyrogallic acid.

the temperature during freezing. The more fundamental properties of these individual crystals are now being studied.

Noncrystalline Solids.—Glass and sealing wax and butter—such substances get so stiff at low temperatures that they appear as truly solid as does a crystal. Yet such apparently solid substances tend to flow slowly and have no definite melting

points, merely getting softer and softer as the temperature is raised. They are usually considered as extremely viscous liquids.

Liquids.—A liquid, like a crystal, may be considered as all a single molecule. (The Atlantic Ocean forms a sizable molecule!) If we do so consider it, it is a "molecule" in which the constituent parts can change their linkages. Liquids can flow. Whatever we call them, they are assemblages of atoms bound together by forces not essentially different from chemical forces. In water two hydrogens and an oxygen join; this is the gas molecule. And then several of these attract each other and these others and so on. Physical chemists tell us that in liquid water the molecule is H_4O_2 or H_6O_3—but really it is difficult to say why some minute water droplet should not be called

$$H_{2,000,000,000}O_{1,000,000,000}.$$

It has usually been supposed that all regularity of structure is lost in liquids. Actually this does not seem to be the case. Perhaps the regularity of arrangement is not so perfect as in a crystal but it is there. This is shown by x-rays. This is more markedly the case with long molecules of many atoms. Possibly we should expect the arrangement; if a large number of matches were shaken up, great irregularities would exist but would there not be a general tendency for neighboring matches to lie parallel to each other? Sometimes the effect is so pronounced in the liquid that the liquid appears to behave as a single crystal. Indeed single crystals of bismuth have been carefully melted and on recrystallizing the same crystal form was obtained. The whole story here is not known but liquids are something more than chance arrangements of molecules.

Absorption.—This is an interesting example of attraction between molecules. When a vessel is being evacuated, its walls tend to retain molecules; to get a good vacuum these molecules should be driven off by heating. A powder with its large surface absorbs large quantities of gas. Best of all absorbers is charcoal with its many fine pores. The gas taken up by a piece of charcoal may be many times its own volume. Charcoal is often placed in evacuated systems and cooled with liquid air to absorb the last traces of gas. For those unsociable gases helium, neon, argon, krypton, xenon, the absorption is not very great; charcoal is often used to remove impurities from them.

Monomolecular Films.—A clean water surface has large surface tension. A trace of grease greatly reduces this tension. The reader has probably seen a camphor fragment cavorting wildly about on a fresh surface of water; it is pulled by these surface forces. The motion stops when the finger is dipped in the water as the trace of grease from the finger forms a film over the surface. A minute droplet of olive oil or a bit of a fatty acid will form a low-tension film of this kind over a large area. The properties of these films have been studied by Lord Rayleigh, Langmuir, and others. It appears that such surface films are only one molecule thick.

The fatty acid molecule consists of a long hydrocarbon chain with the oxygen-hydrogen acid radical on one end. This latter is adsorbed to the water, leaving the hydrocarbon chains bristling upward from the surface. These adsorbed molecules may be scattered loosely over the surface, like molecules in a gas; or with a piece of paper they may be brushed together (compressing the "gas") until they form a continuous film, carpeting the surface. Now, when each molecule covers about 5 square angstroms of the surface, further compression is more difficult. The film acts like a solid or liquid (in two dimensions). The effective cross section of the hydrocarbon chain is about 5 square angstroms. These experiments are readily shown and give a direct method for estimating molecular sizes.

Adsorbed surface layers, one molecule or one atom thick, are found also on solids. A trace of thorium, diffusing out to the surface from heated tungsten filaments, forms there a monatomic layer and lowers the heat of vaporization of electrons (page 140).

Conduction Electrons.—In a metal some of the electrons are free. Probably about one electron (or possibly more) is released from each atom and allowed to wander about the metal. These free electrons are the agents of electrical conduction. Wandering about among the atoms of the metal, they act very much as gas molecules would. These electrons exert their own pressure; they carry heat by convection as they move through the metal; they have their free paths as they move between the molecules; they are continually bumping into the molecules and changing their directions of motion.

When an electric field is applied to the metal, these free electrons tend to drift in one direction. The electron is 1840 times lighter than the hydrogen atom. According to the ordinary kinetic theory they should move about sixty times faster than hydrogen molecules. We adopt this view at present. (It will be shown in Chap. XXVII that the speeds of most of them are in fact some ten times greater than this.) Imagine a piece of copper wire. The copper atoms are 2.5 angstroms from their nearest neighbors, each vibrating but with a definite mean position in the crystal array. And between these atoms

an approximately equal number of electrons, hurrying hither and thither, 60 miles a second, bumping here, glancing there, but in general going nowhere. And now at one end of the wire some additional electrons are introduced. We say that the potential is lowered. The increased electronic pressure there drives other electrons away and, superimposed upon this thermal agitation, there is now a general drift of electrons up the field (very much as a breeze carries the molecules of air along a few feet per second while individually they are hurrying back and forth at much higher speeds). We say then that negative charge has moved from low to high potential. We say the difference of potential has produced a current. An electric current is the diffusion of electrons through the metallic ions.

Of course, in this process electrons do not actually collide; they repel one another at a distance. But, after all, is not this what molecules really do? Only in the case of electrons and ions the distances at which effective repulsion takes place are somewhat larger. So these electrons act as a very light gas. If the metal be heated, the electrons evaporate from the surface—this evaporation of electrons is used in the radio tube. If one end of a metal rod is heated, the heat is carried down the rod mostly by the electrons; their high mobility gives electrons high heat conductivity. Metals are good conductors of heat.

Yes, electrons act just like charged atoms of a very light gas traveling about among the heavier positively charged metallic atoms. But, if so, *why did we neglect the heat capacity of the electrons in computing the specific heat of a metal? And, further, what of the electrons bound in each atom? Why do they not each partake in the equipartition of energy? Why does not the electron vibrate back and forth in the hydrogen atom with energy* κT*? Why do molecules usually act as rigid particles?*

These are questions so disturbing that before 1900 the theoretical physicist hardly dared to ask them of himself. It will take the remainder of this book to formulate the answer to these questions.

We now have a fairly definite picture of the molecular world about us. We have looked as if through some supermicroscope into the drop of water and seen the molecules there in their never-ending movement, held together by intermolecular attraction. The motion in the drop of liquid is greatly restricted and amounts substantially to but a vibration of the molecule. These molecules chatter back and forth, diffusing slowly through their fellow molecules. Those on the surface try time and again to leave but for the most part they are pulled back into the liquid. Occasionally a faster molecule breaks away from the crowd into its more lonely life as a member of the atmosphere.

And we have looked at the gas molecules always darting, dodging, turning, each molecule with the same quota of kinetic energy of translation on the average, the same in gas and liquid. We have seen how this air about us exerts a pressure on the hand by a continual bombardment of those billions of tiny bullets; we have seen how the air cools or warms the hand as its molecules share their energies with the vibrating molecules of the skin.

How inconceivably small and inconceivably many these molecules are! If we had an evacuated electric light bulb and could make in it a hole which would admit only a million molecules of air per second it would take 100 *million years to fill the bulb with air. A gold beater can beat gold so thin that it will cover a floor* 17 *ft. square—we can see light through it. If a better gold beater could beat it so thin that it would cover the surface of the earth, a square centimeter of it would still weigh one hundred fifty thousand times as much as a hydrogen atom, would weigh* 150,000 *protols. If a gram molecule of salt were added to the ocean, after the centuries of mixing a glass of sea water would contain* 50 *of these same molecules. If all the persons on earth should start counting molecules each at the rate of a hundred per second, it would take a million years to count those in a gram molecule. Inconceivable figures!*

And these molecules travel at fairly high speeds. Each perhaps has its own unalterable path to follow according to an inevitable law of nature—more of this later; of it we are not so sure. Colliding continually, going now fast, now slow, these molecules play their game of chance, always looking to an increase of entropy. The game goes on, fair weather and foul. A war may aid the dissipation now; again some invention of man's may reduce the waste. But the game of chance goes on, heedless of loves and hates anti of good and bad, this relentless mechanism of nature. Always this equipartition, this greater and greater equalization of energies. The game of blind chance goes on. Awful in its ruthlessness through all time.

Here is something of nature—seen through the eyes of the scientist. It lacks proper perspective—shall we call it a sense of relativity? In omitting the sunsets and the witchery of moonlight and human aspirations and good and evil, in omitting you and me, our picture has omitted the only things that count. A stupendous game of chance. This is one aspect of nature, a wonderful aspect BECAUSE A MAN HAS SEEN IT.

CHAPTER VII

WHAT THIS MATTER IS

Being a short résumé of the chemical nature of the 92 different elements.

In playing at riddles it is a good custom to announce the riddle before giving the answer. Our riddle is the nature of the atom. It will be well if we pause to give something of the properties of the elements, properties which we shall later hope to explain.

Alchemy.—Aristotle considered all things to be made of the four elements: earth, air, water, and fire. Possibly a case could be made for these categories as describing states of matter: solid, gaseous, and liquid states and radiant energy. Hardness and softness, cold and heat are certainly common qualities. The doctrine of four elements lasted down to the seventeenth century. The alchemists found in it the justification for their belief in transmutation of metals. The metals, noble and base, differed one from another in *quality* but were all made from the same elements, just as "a good man differs from a bad though both are made of the same stuff." By mystic incantations the alchemists attempted to exorcise the baseness from the other metals and refine them into the noblest of all—gold.

That fine old "Skeptical Chymist" Robert Boyle (1660) laughed these "vulgar Spagyrists" to scorn. We must distinguish, said Boyle, between qualities like hot, cold, wet, and dry, and the stuff of matter. But in Boyle's day it was not known that matter was indestructible, the nature of the air was not understood, nor were gases differentiated. Some of the commoner chemical affinities were known. The alchemists were acquainted with most of the common metals and their salts, a few acids and nonmetallic elements.

A new chemistry was born at just about the time that the new American nation was fighting its war for independence. Cavendish[1] recognized elementary hydrogen, Rutherford nitrogen

[1] Cavendish is noted for his electrical experiments; for him the Cavendish Physical Laboratory is named. Read his story in "Encyclopaedia Britannica."

("azote"), Priestley oxygen, and Scheele chlorine in the years between 1766 and 1774. Then came Lavoisier and in 1803 Dalton published his atomic theory.

Elements and Atoms.—Lavoisier was a great chemist. He developed the modern idea of elements, substances not to be further decomposed by known chemical process of analysis. As such he listed "light," "caloric," oxygen, azote (nitrogen), and hydrogen. He also recognized the elemental character of chlorine, sulphur, phosphorus, carbon, and many metals (platinum, nickel, cobalt, molybdenum, manganese, bismuth, arsenic, and antimony, as well as the common metals of the alchemists). As an aristocrat and as a farmer of taxes, Lavoisier was thoroughly disliked by the revolutionists; he died on the guillotine in 1794.

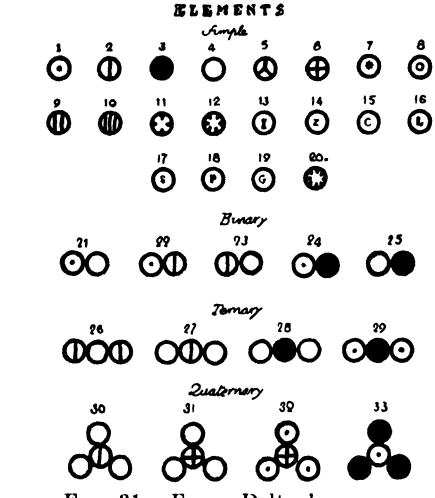


FIG. 31.—From Dalton's paper on Chemical Synthesis. "This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or untimate particles." The following table gives Dalton's "elements" and atomic weights.

1. Hydrogen....	1	11. Strontites...	46
2. Azote	5	12. Barytes.....	68
3. Carbone.....	5	13. Iron.....	38
4. Oxygen	7	14. Zinc	56
5. Phosphorus ..	9	15. Copper.....	56
6. Sulphur	13	16. Lead.....	95
7. Magnesia....	20	17. Silver	100
8. Lime.....	23	18. Platina.....	100
9. Soda.....	28	19. Gold.....	140
10. Potash	42	20. Mercury ..	167

In modern symbols the compounds shown are: H_2O, NH_3, N_2O, C_2H_4, CO; N_2O, N_2O_3, CO_2, CH_4; N_2O_5, SO_3, H_2S, C_2H_5OH.

This was a period of chemical discovery. Zirconium, titanium, tungsten, and the rare earth yttria were discovered before 1800. In the next decade the platinum-like metals iridium, osmium, palladium, and rhodium, as well as vanadium, neodymium, and tantalum and the rare earth cerium were discovered. Sir Humphrey Davy developed electrolysis as a chemical tool and sodium and potassium and boron and silicon were separated as elements.

Dalton founded the atomic theory; to each of Lavoisier's chemical elements he attributed an atomic weight. And during the nineteenth century while the physicist was developing his kinetic theory of heat in which the molecule was the chief actor, the chemist was acquainting himself with his atoms.

At first there was no conception of valence; Dalton's weights are really combining weights. But even as combining weights Dalton's values are none too good. (Notice the oxygen-hydrogen ratio.) Indeed Dalton was a better philosopher than experimental chemist. The Swede Berzelius was a chemist to the finger tips. He recognized the importance of accurate combining weights. In ten years he determined the combining weights in some two thousand compounds and gave the new chemistry its firm foundation.

Given the combining weight, what multiple should be taken for the atomic weight? The answer to this was furnished from the researches of Avogadro studying gas volumes (1811), Dulong and Petit studying specific heats of solids (1819), and Mitscherlich studying isotropism in crystals (1819). It is, however, a surprising fact that the implications of this work were not quickly accepted. The atomic weights did not receive their definitive values until well after the middle of the century.

Chemical Groups.—As the number of known elements increased and as their properties became more thoroughly known, it became ever clearer that certain of the elements should be grouped into families. There was the family of alkalis: lithium, sodium, potassium, rubidium, caesium—soft metals, monovalent, attacking water and forming hydroxides (lyes)—most positively active of elements, forming strong salts with chlorine, bromine, iodine, and other negative radicals. Although they differ very much in weight, in chemical properties these elements are so similar that they are often hardly distinguishable. Again there were the alkaline earths, lime formers: calcium and strontium and barium; in properties they lie midway between the alkalis and the earths (aluminum, etc., clay formers); they are bivalent. There were the halogens: fluorine, chlorine, bromine, iodine, gaseous or easily evaporated, combining with hydrogen to form acids—most negative of elements. Oxygen, sulphur, selenium, and tellurium formed another, and nitrogen, phosphorus, arsenic, antimony, and bismuth yet another group of elements with obviously similar properties. (The noble gases, which form a unique family with no chemical affinities, were not known in that day.)

The Periodic Law.—Now if all the elements are arranged in order of increasing atomic weights, it is found that these ele-

ments of similar properties occur at regular intervals in the arrangement. This fact forms the basis of the periodic classification of elements which was developed by Mendeleef and others about 1867. A nitrogen-like element is always followed by an oxygen-like one; then come a halogen, a noble gas, an alkali and an alkali earth, and so on; and then after a number of intervening elements another member of the nitrogen family occurs, another oxygen-like element, and the sequence repeats. The elements can be arranged in six periods containing 2, 8, 8, 18, 18, 32 elements, respectively. The first period begins with hydrogen and the others with an alkali; each period ends with a noble gas. Finally a seventh period is started but contains only six elements.

TABLE 13.—THE SEVEN PERIODS OF ELEMENTS

I.	Hydrogen and helium	2 elements
II.	Lithium to neon	8 elements
III.	Sodium to argon	8 elements
IV.	Potassium to krypton	18 elements
V.	Rubidium to xenon	18 elements
VI.	Caesium to radon	32 elements
VII.	Only six elements known	

Atomic Volume.—The periodic properties are most clearly shown if an appropriate physical property such as atomic volume is followed from element to element. In Fig. 32 (due to Lothar Meyer, 1869) are shown the volumes occupied by a gram atomic weight of each element in the solid or liquid state. The periods of 2, 8, 8, 18, 18, 32 stand out clearly. The lightest elements are the alkalis—lithium, sodium, potassium—lighter than water. They are metals but soft as putty. The elements heaviest in proportion to their atomic weights are those in the middle of the long periods: iron, nickel, cobalt; ruthenium, rhodium, palladium; and, heaviest of all, osmium, iridium, and platinum—heavy metals and hard.

Each period begins with an alkali at the peak of the volume curve. These are followed by other heavier metals. The last few elements of a period are always nonmetallic in character; in fact the last four elements are, respectively: nitrogen-like, oxygen-like, halogen, noble gas.

Tabular Arrangement.—The periodic table is usually arranged in eight columns. Into these the elements of the second and third periods (elements from Li 3 to A 19) fit naturally. Hydro-

gen, being at the same time the first and the next to last member of its period, may about equally well be placed in the halogen as in the alkali group. The long periods IV, V, and VI are each represented in two rows, 14 elements from period VI being omitted from the table proper.

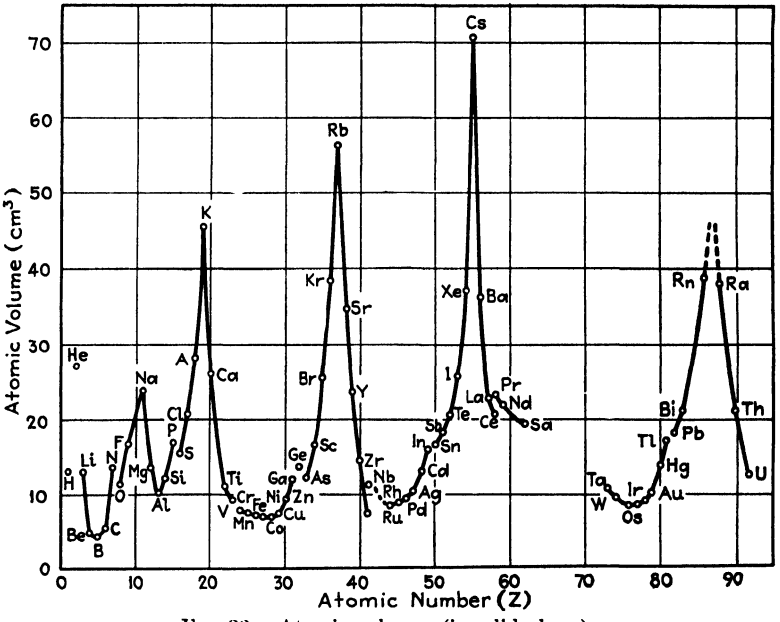


FIG. 32.—Atomic volumes (in solid phase).

Among the lighter elements there are eight groups; of the 18 elements in the longer periods, only 8 (the first 2 and last 6) have the fundamental characteristics of these groups. The others are called transition elements; these are shown boxed by the heavy line in the table.

There are in this periodic classification places for 92 elements. These 92 elements are the only raw materials which Mother Nature has in her pantry; out of these ingredients must come all the rocks and trees and smells and tastes and running, crawling, swimming, flying things that nature has produced. The chemists, who have appointed themselves as nature's chefs, must know all the shades of differences in the properties of these 92 elements. By and large, however, the properties of the elements are readily classified, well enough for our purposes, by the periodic table.

TABLE 14.—THE PERIODIC SYSTEM OF ELEMENTS

	I	II	III	IV	V	VI	VII	VIII	0
1	1 H 1.0078								2 He 4.002
2	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.00	9 F 19.00		10 Ne 20.183
3	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 31.02	16 S 32.06	17 Cl 35.457		18 A 39.944
4	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 27 Co 28 Ni 55.84 58.94 58.69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.93	34 Se 79.2	35 Br 79.916		36 Kr 83.7
5	37 Rb 85.44	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 93.3	42 Mo 96.0	43 Ma.	44 Ru 45 Rh 46 Pd 101.7 102.91 106.7	
	47 Ag 107.88	48 Cd 112.41	49 In 114.8	50 Sn 118.70	51 Sb 121.76	52 Te 127.5	53 I 126.92		54 Xe 131.3
6	55 Cs 132.81	56 Ba 137.36	RARE EARTHS	72 Hf 178.6	73 Ta 181.4	74 W 184.0	75 Re 186.31	76 Os 77 Ir 78 Pt 190.8 193.1 195.23	
	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.22	83 Bi 209.00	84 Po (210.0)	85*		86 Rn 222.0
7	87*	88 Ra 225.97	89	90 Th 232.12	91	92 U 238.14			

Rare Earths								
	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il	62 Sm 150.43	63 Eu 152.0	64 Gd 157.3
	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 16764	69 Tm 169.4	70 Yb 173.5	71 Lu 175.0	

The Abridged Table.—Let us disregard for the moment the transition elements; the others fall naturally into an abridged table of eight groups which we may call the sodium-like, calcium-like, aluminum-like, carbon-like, nitrogen-like, oxygen-like, chlorine-like, and argon-like groups.

The basic properties increase as we go from group to group toward the left of the table and within any group the basicity increases as we go toward the bottom of the table; the strongest of alkalis is caesium. The acidic properties increase to the right and up (omitting the inactive gases in the eighth group, of course). The halogens are most negative of elements and fluorine the most negative of halogens. A diagonal line across the table divides the metals from the nonmetals.

Valence.—Mendeleef in his classification emphasized valence. Chemical affinity is often an attraction of opposites.[1] Sodium unites with chlorine and with oxygen; it forms the compounds NaCl and Na_2O showing a positive valence of 1.

The calcium group shows a positive valence of 2; the aluminum group of 3, and so on up to 7 in the chlorine group. This ascending valence is evident in the oxygen compounds. We have Na_2O, CaO, Al_2O_3, CO_2, N_2O_5, SO_3, and Cl_2O_7.

The elements in groups IV to VII show also a negative valence. They unite with alkalis and hydrogen in such compounds as CH_4, NH_3, H_2O, HCl. The negative valence decreases from 4 for carbon to 1 for the halogens. So chlorine has valences $+7$ and -1; oxygen $+6$ and -2, etc.

Alkaline, Acidic, and Amphoteric Groups.—While the elements in each of the first seven groups form oxides, the earlier and later of these oxides show markedly different characteristics when combined with water. In the first two groups

$$Na_2O + H_2O = 2(Na^+ + OH^-)$$

and

$$CaO + H_2O = Ca^{++} + 2(OH^-).$$

These oxide molecules form hydroxides which break at the metal-oxygen bond, giving "basic" reactions. In groups V, VI, VII, on the other hand, the oxides when hydrated form compounds which are weakest at the hydrogen-oxygen bond

[1] By no means always. Nonpolar compounds such as H_2, Cl_2, etc., are equally important.

$$N_2O_5 + H_2O = 2(H^+ + NO_3^-)$$
$$SO_3 + H_2O = 2H^+ + SO_4^=$$

and

$$Cl_2O_7 + H_2O = 2(H^+ + ClO_4^-)$$

The hydrated oxides are acids. The elements in groups III and IV form oxides which may be either basic or acid. For instance, alumina, Al_2O_3, in nitric acid forms $Al(NO_3)_3$ and in NaOH forms $NaAlO_2$; either aluminum salts or the aluminates may be formed. Such elements are called amphoteric; groups III and IV are amphoteric groups.

Transition Groups and Rare Earths.—After the twentieth element calcium comes scandium, then titanium and vanadium, and the other elements of the first transition group. These 10 elements do not fit into the classification by octaves. The elements in this transition group are much alike. Titanium, vanadium, chromium, manganese, cobalt, and nickel are more or less iron-like and each alloys itself with iron to make special steels. Iron, cobalt, and nickel (and at low temperatures manganese) are the strongly magnetic elements. It is in these transition groups that the stronger, heavier metals occur, not soft metals like sodium but metals "strong as iron."

Each element in this group of elements may have a valence of two—they form FeO, MnO, CrO, CuO, etc. These elements also at times show a higher (or, for copper, lower) valence, and this valence is characteristic of the group in the abridged table under which they appear. Chromium has a maximum valence 6, manganese 7, iron, cobalt, and nickel 8, copper may have a valence 1, etc. To this extent there is a suggestion of the octave periodicity continuing into these longer periods.

After the next alkali-earth element strontium, another second transition group of 10 elements begins. These are heavy metals, much like those in the first group. The commoner elements in this group are molybdenum, palladium, silver, and cadmium. These elements resemble one another and resemble even more closely corresponding elements in the first transition group. In each transition group there is the fundamental resemblance of all the elements, yet a gradual transition of properties throughout the group.

After barium (56) comes another transition group, this time of 24 elements. This in reality is a transition group of 10 ele-

ments with another transition group of 14 elements within it. After lanthanum (57) come the elements 58 to 71, the rare-earth elements. These elements are so like unto one another that in many cases succeeding elements cannot be separated chemically. All of the rare earths form oxides with valence 3; they resemble lanthanum and yttrium and scandium and thorium, which in fact are also sometimes classed as rare earths.

The other 10 elements in this group form a third transition group quite similar in properties to the iron group and the palladium group. Here are found tungsten, closely resembling molybdenum and chromium, the very heavy precious metals osmium, iridium, platinum (resembling iron, cobalt, and nickel); gold, related to silver and copper; mercury, related to cadmium and zinc.

After radium a fourth transition group is started—barely started with thorium—and the periodic table ends with uranium.

Prediction of Elements.—When Mendeleef fashioned his periodic table, a number of places were vacant. Mendeleef predicted the existence and the properties of what he called ekaboron (scandium, 21), ekaaluminum (gallium, 31), ekasilicon (germanium, 32), ekamanganese (masurium, 43), divimanganese (rhenium, 75), all of which have since been discovered.

Of the noble gases he could have had no suspicion; yet when found[1] they fitted well into his table, these elements of zero valence forming a new group which fitted naturally between the halogens with unit-negative and the alkalis with unit-positive valence. Since Mendeleef's day a number of elements have likewise been added to the rare earths. Radioactive elements (84, 88, 89, 91) have been discovered.

Here are nature's elements—92 of them. One of the most remarkable things about these elements is the vast differences in their frequency of occurrence. Every other atom we meet is oxygen. In the earth's crust out of six atoms there are three oxygen, one hydrogen, and one silicon atom. The 89 other types of atom compose only one-sixth part of the earth's crust. Now

[1] Helium was first identified by its prominent yellow absorption line on the sun. It was later separated by Sir William Ramsey. Ramsey also discovered argon in the atmosphere.

divide this remaining sixth into 10 parts: there are 3 parts aluminum and 1 part each of iron, calcium, sodium, potassium, and magnesium—and the remaining 83 atoms, the carbon and nitrogen and chlorine and the rest, make up together the remaining 2 parts, make up less than 3 per cent of the earth's crust. In making this earth of ours, Mother Nature has used but a very few of the elements, the lighter elements, as a foundation; she has added here a spoonful of chlorine, there a pinch of gold or silver, or perhaps here and there about 1 part in a million million of rhenium or masurium or radium for seasoning.

Here are the 92 elements from Nature's pantry. We may imagine them before us as bottled samples arranged in order of weight—hydrogen, helium, lithium, and so on. As we go along the line, we see remarkable disparities in properties. Here No. 6 is carbon, a solid, boiling at some 3700°C. and next to it is nitrogen No. 7, which is already boiled away at room temperature; its boiling point is −190°C. But, as we proceed, we find the same properties recurring at regular intervals. Here No. 2 and Nos. 10 and 18 and 36 and 54 and 86 are those prime individualists, the noble gases; next to them 3, 11, 19, 37, 55 are the lye-producing metals, the alkalis; next to them the lime producers, the alkali earths. The same property repeating in intervals of 2, 8, 8, 18, 18, 32 elements, an arrangement by octaves together with transition groups—this is the sense of the periodic system.

This is nature. And this is part of our riddle. Why this periodicity of atomic property?

About You, Me, and Aristotle.—We should not, you and I, look down too much on Aristotle. That earth, air, fire, and water cosmology of his rates as fairly childish when weighed in the agate balances of the modern chemist. But will not our theories sound equally naive in A.D. 3930 when viewed without sympathy? Aristotle was a much better biologist than physicist, yet even his physics must have had some ring of truth to have stood through two millenniums. Perhaps he meant just a little something different by his element than what we mean by chemical element today; he seems to have been more interested in the qualities of things than in the stuff of them. Dryness and wetness, weight and lightness, heat and cold, these are indeed fundamental qualities and may perhaps be symbolized by earth and air and fire and water. Underlying all bodies

(in his philosophy) was a matter stuff; the earth, air, fire, and water impressed upon this gave the body its particular form.

But the implications of Aristotle's cosmology are more important than its form; underlying it was the broad principle of transmutation of matter from one form into another. In this age when we can obtain temperatures at which even tungsten melts and evaporates, at which even helium liquefies and freezes, when we make artificial rubber, make from aluminum a substitute for steel and from lead glass a sparkling diamond for a cheap ring, surely we must be sympathetic with this early prophet. In a certain limited sense Aristotle was entirely right. Unfortunately his disciples of a later day persisted in attempting to transform mercury into gold. After centuries of this the idea of an immutable element finally arose. But the significant fact is that Aristotle had the kind of brain which would ask such questions. This was the genius of the Greek philosophers: it was not what they believed but that they could look to the stars and ask, "What?" and "Why?"

Of course, from our own points of view we are right; of course, there are some 92 chemically different elements—possibly in the interior of stars more—and, of course, these elements have periodic properties and, of course, the other elements are made of the same stuff as is hydrogen. We owe this penetration of ours into nature not to any greater intellect, any greater canniness, but mostly to machinery—telephones and chemical balances and fountain pens and reference books. Nevertheless, these things are true—they will not change. But they are only true for us. They may be scientifically true but perhaps some future thinker as unsympathetic to us as we are to Aristotle will ask whether they were ethically, esthetically, humanly, personally, importantly true. Is the fact that element 43 is masurium and that there is one such atom for every 10 million million oxygen atoms on this earth and that it melts at 2300°C. and that we know little more about it—is this kind of truth to be compared with the truth that bread is good and that the widow has lost her mite in the business depression and that you possess the cleverness to win a golf game or to paint a picture or to solve a scientific riddle?

Aristotle looked closely at the world, probed into it with what tools he had, asked questions, and dreamed dreams. He spoke the truth as he saw it.

CHAPTER VIII

RAYS

A new world is discovered. Rays to explore the atom. Charged particles and electromagnetic waves.

Now back from these adventures of the chemist. The kinetic theory of gases was developed during the latter part of the nineteenth century. Physics of that period was devoted to describing the behavior of matter in bulk. It established the general laws of heat and sound and light and electricity. Only here in the kinetic theory were the problems of the atomic world seen, dimly and afar off. That atomic world appeared to be a thing apart; scientists of that day lacked the tools to explore it.

The nineteenth century physicists did a good job in laying the foundation of this bulk physics, so good indeed that there seemed little more to do. The French savant Renan, viewing the field in 1890, was of the opinion that the golden age of physics had passed—little was left for discovery. And then, almost immediately, began for physics a period so fertile in discovery as to be without parallel in scientific history. This period has continued down to the present. It is the period in which the story of the atom began to be written.

The immediate occasion for the new era was the discovery of several unsuspected types of rays of energy—x-rays, alpha, beta, gamma rays, cathode rays, canal rays, positive rays, all discovered in the eighteen-nineties. Most of our knowledge of nature, after all, comes to us in the form of rays—especially light rays—carrying energy through space from the outer world into ourselves. These newly discovered rays came to serve as most sensitive probes for the analysis of the atom. The last five years of the last century was a period hot with discovery.

Birth of Radio.—Perhaps we should first mention the discovery of radio waves. Such radiation had been predicted by Maxwell in 1868. Maxwell followed in the steps of Faraday; he gave mathematical expression to the fundamental laws of electricity.

Particularly was he interested in the electric field about the charge at rest and in the magnetic field existing when the charge was in motion. The Maxwell equations of the electromagnetic field remain today the fundamental law of electricity; even the theory of relativity produced no modification in them.

Maxwell realized that whenever a charge was put into motion or retarded, in brief whenever it was accelerated so that the magnetic field was altered, it would send out an "electromagnetic wave." He shrewdly deduced that light was such a wave produced by a rapidly vibrating charge in the atom. He predicted that such waves of much longer wave length than light would be produced when the pulsating electric charge was due to a current oscillating to and fro in a wire.

In 1888 Hertz succeeded in producing such oscillations and detecting the electromagnetic waves. These waves were of short wave length; longer ones were produced ten years later by Marconi and transmitted for great distances. Wireless telegraphy, the parent of our modern radio, was born.

So, even as Renan's words were being uttered, one new form of radiation destined to revolutionize electrical communication was being discovered.

X-rays.—These radio waves are usually millions or billions of times longer (and even the very shortest ones are some thousands of times longer) in wave length than visible light. A few years after Hertz's discovery another German physicist, Roentgen, discovered a ray whose wave length is usually thousands of times shorter than that of light. Crookes had observed such rays earlier but knew not what he saw. Crookes was investigating electric discharges in gases and was troubled by his photographic plates becoming fogged when kept within the laboratory. So he moved the plates to another room; here they were unharmed—and Crookes missed discovering x-rays. (At least such is the story that is told.)

Roentgen, on the contrary, investigated the effect; he found that a mysterious kind of ray was emitted from the discharge tube, which not only affected the photographic plate but caused certain substances to fluoresce. The rays were very penetrating; they went through wood or rubber as well as through glass; they even passed through metals. What the rays were, whether particles or waves, was unknown. This was a totally new form of energy; because of their unknown nature Roentgen called

them x-rays. Their true nature was only established some seventeen years later.

Radioactivity.—This was in 1895. In 1896 radioactivity was discovered. Three generations of Becquerels had made names for themselves in French physics and now Henri was investigating the nature of fluorescence. He found coming from compounds of uranium a radiation resembling the newly found x-ray. Like x-rays these spontaneously generated rays were capable of producing fluorescence and affecting the photographic plate and ionizing the atmosphere.

Pierre and Marie Curie immediately undertook the investigation of such substances and two years later, in 1898, succeeded in separating a substance some millions of times more active than uranium. They called it radium. Polonium was also isolated; it was named for Poland, the native land of Madame Curie. And in 1899 a young New Zealander, Ernest Rutherford, analyzed the nature of the Becquerel rays. He found a less penetrating, positively charged ray which he named alpha (α) and a more penetrating, negative, beta (β) ray. Gamma (γ) rays were discovered shortly after.

With all this, a strange world was coming to light. Becquerel rays were emitted spontaneously; nothing that man could do would increase the emission or decrease it. The rays were very penetrating, very energetic. The emission apparently continued forever, in undiminished intensity, producing no apparent change in the material. It was all just a little bit confusing; it sounded like getting something for nothing. Did the conservation of energy still hold?

This was a question which the old century gave to the new—this and a new tool of marvelous efficiency for probing the depths of the atom.

Cathode Rays and Positive Rays.—Now, although their nature was not definitely known until later, the x-rays and gamma rays are in fact electromagnetic waves like light and radio waves. They are not deflected by a magnetic or by an electric field. Alpha and beta rays are charged particles. Somewhat earlier an elementary charge of electricity, the "electron," had been hypothesized; it was not until this closing decade of the century that such a charge was separated and identified.

In the evacuated discharge tube of Crookes a ray was found which was projected from the cathode. Normally it traveled in

a straight line but it was deflected by a magnetic field. The elements of this ray are electrons. In 1898 J. J. Thomson in the Cavendish Laboratory (Cambridge) succeeded in separating the individual electron and measuring its charge. Then, by comparing the deviation of the cathode ray in magnetic and electric fields, he determined the mass of the electron.

Other rays were observed to be going in the opposite direction in the discharge tube (toward the cathode). These were called positive rays; they consist of atoms or molecules positively charged. So the same years that saw the discovery of the radio waves and x-rays and gamma rays saw the discovery of these more material cathode rays, positive rays, alpha and beta rays and saw the isolation of the electron.

These were great discoveries opening a new era. The pioneers Roentgen, Becquerel, the Curies, Thomson and Rutherford each in his turn received the Nobel prize; in England Crookes and Thomson and Rutherford were knighted. Madame Curie took her place as the greatest of woman scientists.

In very recent years three other types of ray have been discovered. It is hard to say just when the existence of a cosmic ray was first suspected. It was long known that some few ions were produced in ordinary air but the cause was not suspected. The work of Kohlhörster and of Millikan has shown that these rays come from space and are extremely penetrating; they are still rather mysterious. They are possibly electromagnetic waves of far shorter wave length than the shortest ray; possibly charged particles hundreds of times more penetrating than any hitherto known. Another ray, material but without charge, has recently been found by Chadwick (working with Rutherford in the Cavendish Laboratory). He calls it the neutron. Very recently a positively charged electron, the positron, has been discovered.

Electromagnetic Radiation.—Let us leave these rays of charged particles to another chapter and consider here some of the properties of electromagnetic waves.

We know that light is a wave motion because of the diffraction and interference phenomena which can be observed when it passes by a small obstacle or through a small orifice or a slit or a diffraction grating (see frontispiece). Similar interference can be observed with radio waves and, if we use the atoms of a crystal for our diffraction grating, with x-rays and gamma rays. The wave lengths of the spectrum are represented in Fig. 33. The

lengths extend from about a ten-thousandth part of an angstrom for the cosmic rays up to some 20 miles if we limit ourselves at the longest wave lengths which can be used in wireless communication—60 octaves! (But actually there is no upper limit to possible wave lengths.)

Of this (with some overlapping) there are 8 octaves of gamma rays, 14 octaves of x-rays, 5 octaves of ultra-violet, and 9 of infra-red rays with 1 octave of visible light between them, and then 28 octaves of Hertzian waves! Sixty octaves, of which our eye is attuned to one!

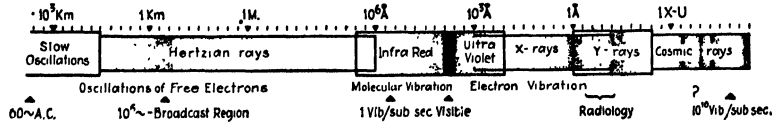


FIG. 33.—The electromagnetic spectrum. Scale divisions are "octaves," *i.e.*, 1, 2, 4, 8, etc., angstroms. (It is questionable whether the *primary* cosmic rays are electromagnetic waves.)

Frequencies.—The frequency (ν) is obtained by dividing the velocity of light (c) by the wave length (λ). $\nu = c/\lambda$. The frequencies are usually very high, of the order of a million per second even for the long wave lengths of several hundred meters used in radio broadcasting. Yellow light has a wave length of about 6000 angstroms and its frequency is 500,000,000,000,000 vibrations per second or 50 vibrations per subsecond.

In terms of daily experience such frequencies are not comprehensible. Suppose you close your eye and then open it for but a second. During that time an electron in your retina has vibrated somewhere between 4 and 7 hundred million million times (depending upon the color). This is a greater number of vibrations than the number of waves which have beat upon the shores of the ocean in 10 million years—and yet it is over and counted and registered in the brain in a second! And this is by no means the greatest electromagnetic frequency. During each of these vibrations of visible light, x-rays would be making several thousand oscillations.

Production.—Radio waves are produced by rapidly oscillating electric currents in wires (antennae). Other forms of radiation are similarly due to oscillations of charges, usually within the atom. Light, infra-red, visible, and ultra-violet, is produced by heating of a solid or liquid, and in gases usually by electron bombardment of the molecules. High-speed electrons produce

x-rays when they are stopped. Gamma rays come spontaneously from the radioactive elements and cosmic rays from free space. Recently voltages of several million volts have been used to produce x-rays with wave lengths as short as gamma rays.

Penetrating Power.—Our radio set picks up energy from the "ether" when its frequency is tuned to that of the radio wave. A light wave is absorbed when its frequency is in resonance with the atoms or electrons of the material through which it passes. When the atoms in a solid or liquid vibrate, the frequencies are usually 30 per subsecond or less. This corresponds to a wave length of 10,000 angstroms, or more, in the infra-red. The complex structure of the solid or liquid results in many such natural modes of vibration and hence any infra-red radiation is generally absorbed.

The electrons within the atoms have much higher frequencies and are attuned to radiation in the ultra-violet. Starting in the near ultra-violet and extending down to wave lengths of a few angstroms is a region of the spectrum which is absorbed by practically all material bodies.

The result is that radio waves pass through substances (other than metals) fairly well; their wave length is too long for absorption. Then in the visible spectrum and the nearest infra-red and nearest ultra-violet, many substances such as glass, quartz, salt, fluorite, water, alcohol are transparent. This region lies between the atomic (infra-red) and the electronic (ultra-violet) absorption regions. And finally in the region of short x-rays and gamma rays, where the rays have a higher frequency than the electrons in the atoms, the medium again becomes transparent.

Glasses are transparent in the ultra-violet down to 3500 or 3000 angstroms; to transmit the ultra-violet quartz lenses and prisms are usually used; quartz is transparent to about 2000 angstroms and fluorite even farther. Lenses for use in the infra-red are usually made of rock salt. Metals are always opaque for light and radio waves—indeed for any wave of longer length than x-rays. This is because a metal has free electrons present which are capable of vibrating readily with any except the very highest frequencies.

Fluorescence and Phosphorescence.—Usually a substance absorbs or transmits or reflects light without altering the frequency. In other cases, however, a type of reflection occurs in which the frequency is changed. It is not true reflection but

rather an absorption followed by reemission of the new color. When the reemission takes place at once, we have fluorescence; when it is delayed for an appreciable time, phosphorescence. With very few exceptions the fluorescent or phosphorescent light is of longer wave length than the exciting light (Stokes' rule). Fluorescent screens of uranium glass or zinc sulphide or barium platinocyanide are of much service in rendering visible ultra-violet light or x-rays.

Chemical Activity.—Sometimes a special band of frequencies is effective in producing chemical changes. Some such reason may account for the sensitivity of the eye in the region between 4000 and 7500 angstroms. Usually, however, the rule is that a long wave-length limit of sensitivity exists and activity takes place for all shorter waves. For instance, the ordinary photographic plate is slightly sensitive to the green and blue and more so to the violet and continues sensitive through the ultra-violet and down through the x-ray and gamma-ray regions. One does not get sunburned behind glass; it takes ultra-violet light to sunburn the skin and x-rays and gamma rays produce very painful (and deep) burns. Many chemical compounds are decomposed by violet or ultra-violet light but not by the longer wave lengths.

Photoelectric Effect.—When light of sufficiently short wave length falls on a metal, electrons are ejected. Light energy is converted to electrical energy. This process is the reverse of that in which electrical energy from a moving electron is converted into light or x-rays (page 106). For the alkali metals (sodium, potassium, etc.) this photoelectric effect is produced by visible light, and the phenomenon is used in the photoelectric cells of television; for most metals, in which the electrons are more strongly bound to the atom, ultra-violet light is required to produce electron emission. The photoelectric effect usually becomes of increasing importance as the wave length is shortened.

To set electrons free photoelectrically from gas molecules requires a shorter wave length than does the ordinary photoelectric effect from surfaces. This gas ionization becomes very important in the x-ray region; in some cases it has been observed to set in in the ultra-violet.

Detection of Rays.—Any ray, wavelike or particle-like, if of sufficient energy can, of course, be measured by the heat generated when it is absorbed. This is a very insensitive method of detection and is seldom used except in the infra-red where, unfortu-

nately, it is often the only method available. The bolometer (in which the heat changes the resistance of a wire) and the thermocouple are two types of thermometers used to measure radiation in this way.

The methods of detecting Hertzian waves by tuned radio circuits are familiar. Visible light can be seen or photographed. The simple photographic plate is not sensitive to red and orange but plates may be sensitized to respond throughout the visible and even for a short way into the infra-red.[1] Ultra-violet radiation and x-rays and gamma rays may be observed on the fluorescent screen or, better, can be photographed. Ionization of gases also plays its important role in the measurement of x-rays and gamma rays.

Spectroscopic Resolution.—For analysis of the visible and near-visible spectrum, prisms or diffraction gratings or interferometers are used. The prism spectrometer has a great advantage in intensity, since with a prism all of the light is dispersed into a single spectrum. But the resolving power of a prism is not large.

Resolution means sharpness of discrimination between neighboring frequencies. The resolution constant (or *resolving power*) is the ratio $(\lambda/\Delta\lambda)$ between the wave length (λ) and the least measurable wave interval $(\Delta\lambda)$. A resolving power of 1000 is necessary to separate the yellow lines of sodium 5890 and 5896. Resolving power ultimately depends upon *a counting of waves.* In the interferometer or diffraction grating—and indeed in the prism as well—it depends on the number of waves in the interfering wave train.

This means that resolution depends on the physical dimensions of the apparatus.[2] In the case of a prism, the resolving power is proportional to the base thickness, usually about a thousand per centimeter of base. A diffraction grating of similar size has a resolution about ten times as large. The largest Rowland gratings were 6 in. long and had 15,000 lines to the inch. This gave a theoretical resolving power of 90,000 in the first order spectrum (see Fig. 78 which was taken in the third order of such a grating).

[1] Such plates are being used for photography at extreme ranges of several hundred miles. Objects are photographed which to the eye are quite invisible in the blue haze.

[2] Similarly the resolving power of a lens—the ability to produce sharp images—depends on its aperture.

There are several types of interferometers: the Michelson (which has been described), the Fabry and Perot, the Lummer-Gerhke plate, and the echelon grating. When Michelson determined the wave length of his red line of cadmium in terms of the standard meter, there was a difference of 22 cm. between his two mirror distances—a retardation of 44 cm., 700,000 waves, and a corresponding resolving power.

Closing the Spectrum.—The spectrum in the far ultra-violet and far infra-red is comparatively little explored. In the short-wave ultra-violet (or long-wave x-ray) region all substances, even gases, become opaque; vacuum spectrometers of the reflection type without lenses must be used. In the far infra-red (or short-radio) region the difficulty is one of detection. However, it is of importance to "close the spectrum." If all these radiations are indeed essentially one in nature, we should be able to make radio waves so short and infra-red waves so long that the two would be identical; similarly there should be an overlap between the ultra-violet and x-ray regions.

Hertz used the discharge between small balls as a source for his first radio waves. The size of these electrodes has been reduced more and more until Nichols and Tear succeeded in producing the oscillating discharge between small cylinders 0.1 mm. long and 0.1 mm. in radius with a spark gap of 0.01 mm. between them![1] The fundamental wave length of this radio system was 1.9 mm. but a prominent overtone at about 0.2 mm. was observed. Glagolewa-Arkodiewa has since measured Hertzian waves down to 0.1 mm.

The name of Rubens is associated with much of the work in the far infra-red. In 1921 Rubens constructed a diffraction grating of wires 1 mm. thick and 1 mm. apart and measured the spectrum of the mercury-vapor lamp in the far infra-red. The longest wave lengths measured were 4,000,000 angstroms, or 0.4 mm. Hence the Hertzian and infra-red regions have been made to overlap.

The longest x-rays which have been measured by crystal diffraction have a wave length of 14 angstroms; the shortest ultra-violet ray has a wave length of 137 angstroms. The intervening interval presents great difficulties to the spectrom-

[1] *Bell Tech. Jour.*, Vol. 3, No. 3, 1928. See also "Encyclopaedia Britannica," Radiation, pp. 876–879.

etrist. However, by using other methods (critical potentials, page 216) this hidden region has been roughly explored.

Continuous and Discontinuous Spectra.—In radio practice very constant frequencies of oscillation can be obtained with radio tubes.[1] Each station operates on a single well-defined frequency. On the other hand, when the discharge across a spark gap is used (as in the older wireless telegraph installations), a single undamped frequency is not obtained; the result in this case is a *band* of frequencies and the bands between two neighboring radio stations may well overlap. This illustrates, for this part of the spectrum, the difference between discontinuous (line) and continuous spectra.

Similar differences are found in the other parts of the electromagnetic spectrum. We have referred to the molecules of a gas as being in the "wide-open spaces." Here each one can express its own individuality, and each gives a spectrum consisting of definite frequencies peculiar to this molecule. In the solid or liquid this individuality is suppressed. Any natural frequency of vibration is interrupted by continuous bombardment of neighboring molecules. A continuous spectrum is omitted. The predominant frequency of this continuous spectrum depends primarily upon the temperature and very little upon the substance. The colors from all heated solids are at first dull red. Then, changing to yellow, the emitted light becomes whiter and whiter as the temperature is raised.[2]

The distinction between line spectra and continuous spectra is also important in x-rays and gamma rays.

Birth of the Quantum Theory.—We have considered the vast range in this electromagnetic spectrum. Gamma rays, perhaps a hundredth angstrom long, are followed by x-rays whose wave lengths are of the order of 1 angstrom. Then light, several thousand angstroms long and then, in the millions, billions, and trillions of angstroms, come the Hertzian waves. The shortest of these radio waves of any technical importance are measured in centimeters or meters and commercially used waves extend to several miles in length. But beyond these are other waves of as

[1] Recently the vibrations in quartz crystals have been used to control the frequency or (in terms of spectroscopy) to "make the line finer."

[2] Exceptions are found in certain rare earths where the emitting electrons are protected from outer influence and a line spectrum is emitted. Witness the Welsbach mantle.

long wave length as one chooses; the wave length depends only upon how slowly one chooses to oscillate an electric charge. Except for the cosmic rays all these types of radiation had been detected (although the wave lengths were not all measured) by the beginning of this century.

As contrasted with particle-like rays which could have any speed (up to the speed of light), these wavelike rays all had the same speed, differing among themselves only in frequency. Now, each particle has a definite amount of kinetic energy associated with it, depending only on its velocity. No such elemental quantum of energy existed in the waves, although it was apparent that high-frequency radiation could do many things which the lower frequencies could not. And then, at the very end of the century, all this was changed. On Dec. 19. 1900, Max Planck proposed the quantum theory.

CHAPTER IX

CONDUCTION THROUGH GASES

In which are listed a few of the habits of electrons and ions; how they move through a gas, at times disappearing by recombination, at times producing new ions by impacts. The discharge at low pressure. Electric force and magnetic force.

The phenomena of discharge through gases have been long known. Faraday observed the discharge at low pressures, Sir Oliver Lodge and Sir William Crookes investigated the phenomena in the discharge tube (which is often known as a Crookes tube). Of course, the electric spark and the aurora and lightning are examples of gas discharges. No real understanding of the phenomena was attained, however, until the nineties. At moderately low gas pressures an electric discharge through gases is readily obtained. The phenomena are very complicated. They involve ionization of gases by collision of rapidly moving ions and the mobility of the ions in an electric field and their recombination and the emission of light and the photoelectric properties of this radiated energy and the effect of ionic bombardment on the electrodes—a whole science full of phenomena enter into the process. And perhaps it were as well to look to some of the simpler elements of this process first.

Ions in the Atmosphere.—When precautions are taken such that no leak can occur across the insulator, an electroscope will still slowly lose its charge. This is due to the ions always present in the atmosphere. There are usually about a thousand of these per cubic centimeter, half of them negative and half positive.[1] These ions attract each other and are continually recombining. About ten of them disappear and ten new ones appear each second.

[1] These are the small ions. The dust particles in the air are also charged. The number of positive ions always is slightly greater than the number of negative. This is due to the earth's electric field's driving negative charges upward. The earth is negatively charged and has a field about it of about 150 volts per meter. Hence the positive ions are pulled downward and how this negative charge of the earth can be maintained is something of mystery.

Whence comes this ionization in the atmosphere? It might be supposed that such ionization might occur as the result of the collision of two air molecules moving with extraordinary velocities. Actually, at ordinary temperatures, gas velocities even of the exceptional molecules are far too small to produce ionization. The ionization in normal air is due in part to radioactivity (from the almost negligible amount of radioactive material in the soil or in the atmosphere) and in part to cosmic rays (page 342).

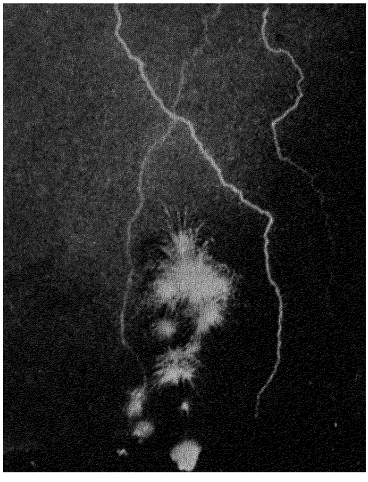


FIG. 34.—Ball lightning. (*Jensen.*)

Ten ions per second out of the 2.7×10^{19} molecules per cubic centimeter are not many. A charged electroscope usually holds something like 10 e.s.u. If the volume of air in the electroscope chamber were 100 cc., a thousand ions would be formed per second and before they could recombine these would all be drawn to the charged leaves. Each charge is 4.8×10^{-10} c.g.s. units (page 126). Thus there is a leak of 4.8×10^{-7} unit per second. How long would it take such an electroscope to lose 1 per cent of its charge? Such experiments require much patience and good insulation.

Sensitive Measuring Instruments.—For measuring such minute charges the instruments commonly used are either the electroscope (with microscope and scale) or the even more sensitive quartz-fiber electrometer. With the simple gold-leaf electroscope the student is familiar.

In the electrometer a light vane is suspended by a very fine fiber between four "quadrants." This vane is charged to 50 or 100 volts. Two of the oppositely placed quadrants are grounded, the other two are connected together and insulated. Any slight charge changes the potential of the insulated quadrants and attracts or repels the vane. This is a very sensitive device.

Any such instrument must be calibrated. Either the electroscope or the electrometer is in the first instance a voltmeter. The number of divisions of deflection per applied volt must be determined. For the electrometer this "sensitivity" may be several thousand millimeter divisions per volt.

In order to deduce the charge from the observed voltage, the capacity ($C = Q/V$) of the instrument (together with any auxiliary apparatus

connected to the insulated plate) must be known. For the electrometer the capacity may be 10 or 20 e.s.u.[1] Finally, the rate of leakage must always be determined.

Mobility of Ions.—Intense ionization in gases is readily produced by using x-rays or rays from radioactive materials. For measurement the ionization is usually produced between two parallel plates, one connected to the electroscope or electrometer and the other to the ground—an "ionization chamber."

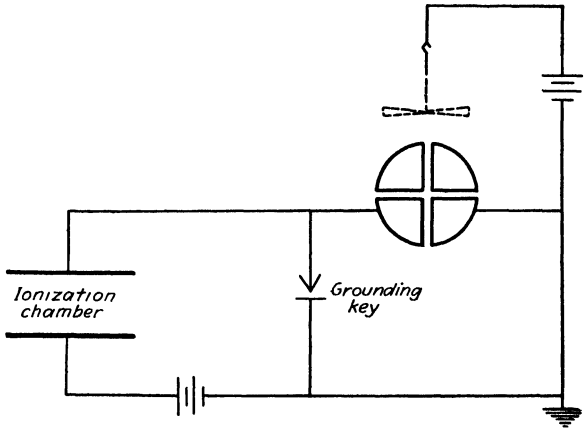


FIG. 35.—Electrometer and ionization chamber (quadrants and needle shown schematically).

By suitably charging the plates of the ionization chamber, the charge of either sign can be collected on the ungrounded plate and measured.

The time required for ions to travel between such plates can be observed and hence the mobilities of ions determined. The ions, of course, are rushing about hither and thither with the usual gas velocities and are continually colliding with other molecules; superimposed on this random motion is a comparatively slow drift produced by the field. The rate of drift in a given field depends on the size of the ions. At ordinary pressures most of the ions produced are molecules which have gained or lost an electron. The mobility of such molecular ions produced in air is about 1.3 cm. per second for a field of 1 volt per centimeter. Free electrons also occur and their mobilities are several hundred times greater. However, in most gases at atmospheric pressure any free electrons are quickly captured by the molecules. Not

[1] An electrostatic capacity unit is almost a micromicrofarad.

so in nitrogen and the noble gases. Negative ions in these gases are usually electrons.

The mobilities which have been given are for atmospheric pressure. The values will, of course, for both the electron and the heavier ions, be much greater at reduced pressure. The mobility is proportional to the mean free path of the ion.

Recombination.—The simplest method of measuring the rate of recombination of ions in a gas is to form them (by x-rays or Becquerel rays) in a stream of gas flowing through a long tube and to determine the number of ions remaining still dissociated at successive distances along the tube.

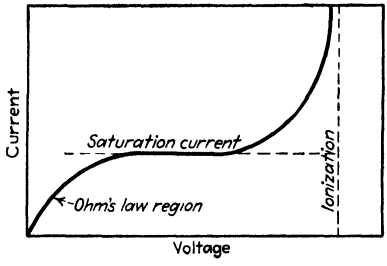


FIG. 36.—Characteristic curve for gas conduction.

It takes two ions, a positive and a negative, to effect a recombination and, of course, the number combining per second in a cubic centimeter (n') will be proportional to the number of positives (N^+) and the number of negatives (N^-) per cubic centimeter. That is

$$n' = \alpha N^+ N^- \qquad (10)$$

or, if the numbers of positive and negative ions are equal, $n' = \alpha N^2$. α is called the coefficient of recombination. For air its value is 1.6×10^{-6}.

Saturation Current.—Let us suppose that ions are being produced at a constant rate (by x-rays for instance) between the two plates of an ionization chamber. We can apply a difference of potential to the two plates and measure the number of ions attracted to the top plate. As we vary the strength of the field, the current at first increases in proportion to the field, then reaches a steady value, and finally, when the difference in potential becomes very great, begins to increase again and rises to large values. All this we can observe by measuring the rate of charging or discharging of the electroscope connected to the plate of the ionization chamber.

The explanation is not far to seek. At first, when the field is weak, the ions are dragged only slowly out of the gas toward the plates. Most of them recombine. When the field is increased, a larger and larger proportion of the ions are pulled to the plate

leaving fewer to recombine. Or the field may be made so great that practically every ion formed is captured by the plate; a moderate increase in field can do no more and this gives the flat portion of the current curve. The current is said to be "saturated." The value of the saturation current is just equal to the number of ions produced per second.

Ultimately the electric field may become so great that the rapidly moving ions ionize other molecules when they collide with them. This increases the current. In fact when one ion can produce two and two produce four and the four eight, and so on, the current, even from a very small saturation value, may mount to unlimited values. When this takes place, a spark or arc occurs.[1]

Sparking Potentials.—The voltages required to produce a spark in air are shown in the following table. The measurements are usually made with small spheres for electrodes. A field of about 30,000 volts per centimeter is required for the smaller spark gaps. This may be taken as the normal breakdown field; for the greater gaps the field is far from uniform.

TABLE 15.—SPARKING POTENTIALS

Spark gap, centimeters	Sparking potentials	
	2-cm. spheres, volts	Points, volts
0.1	4,700	3,720
0.2	8,100	4,600
0.5	17,500	6,300
1.0	30,800	8,670
2.0	47,000	10,140
4.0	64,000	12,210

Arc Discharge.—The foregoing are the values required to start the spark. When once the discharge is started, the electrodes may become vaporized, the potential difference falls to a low value, and we have the arc discharge.

Discharge at Low Pressures.—A field of about 30,000 volts per centimeter is required to start the discharge in air. It

[1] It is always essential to use a resistance in series with an arc lamp on account of this tendency of the current to mount without limit, to follow the compound-interest law.

requires an energy of only a few electron-volts to ionize most gas molecules; this field of 30,000 volts per centimeter seems rather large. But as the ion moves through the field, colliding with molecules perhaps a hundred thousand times per centimeter, it usually loses energy by collisions just as fast as it gains energy from the field. It may never have a chance to acquire the ionizing speed. If the gas pressure is reduced, the field required for the discharge can be reduced in proportion. At half an atmosphere the mean free path of the ion is doubled and the discharge is obtained with a field of 15,000 volts per centimeter. The sparking potential attains a minimum value at a pressure of about a millimeter of mercury; clearly the reduction in pressure must not be carried so far as to remove too many of the molecules which by their ionization must support the discharge.

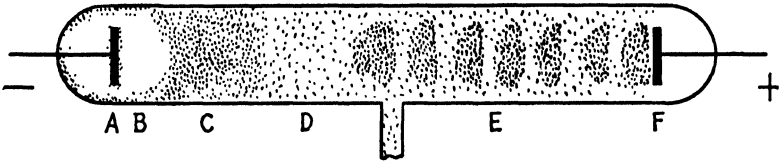


FIG. 37.—The Geissler discharge.

The Discharge Tube.—The discharge in gases at low pressure presents phenomena of fascinating interest. The appearance of this discharge is well-known. The cathode itself is covered with a velvety luminous glow, *the cathode glow* (*A*). This is followed by a comparatively dark space (*Crookes dark space B*) and then a region of luminosity (*C*) called the *negative glow*. Beyond the negative glow comes the *Faraday dark space* (*D*) and beyond that, filling the remainder of the tube, *the positive column* (*E*).

Throughout the tube, electrons and negative ions are moving toward the anode and positive ions are moving backward toward the cathode. Electrons are swept to the anode away from the cathode region; this makes this a poorly conducting region (at *B*) and hence the high voltage drop here. There are many ions, positive and negative, in the Faraday dark space and positive column and this region acts as a rather good conductor. The greatest part of the total drop in potential occurs between the cathode and the negative glow. At the most favorable pressure, the drop here is usually about 200 volts; in the positive column the field is only a few volts per centimeter.

The size of the Crookes dark space in which this large voltage drop occurs depends on the pressure. The discharge tube is often used as a qualitative pressure gage. For air the dark space extends 3 mm. at 1 mm. pressure; the dark space grows in inverse proportion as the pressure is reduced.

The general features of the discharge can now be explained. Given a few electrons near the cathode, these will be speeded up in the electric field as they go toward the anode; they will ionize molecules by collision and double their number, ionize again and quadruple it, and so on. The positive ions created by these ionizing impacts move toward the cathode. Hence a few electrons near the cathode can multiply their number greatly. The problem before the gas is how to get this supply of cathodic electrons which will act as a trigger to set off the whole action. A few electrons—not many—must be liberated from the cathode and this can be accomplished by bombarding the cathode with high-speed positive ions. When charged molecules bombard a surface with a speed given by several hundred volts, electrons are set free. The function of the high voltage drop in the Crookes dark space is to furnish the requisite speed to these bombarding positive rays. These positive rays set free electrons which are pulled rapidly away, bombarding molecules as they go.

Cathode Rays.—The electrons leaving the cathode are accelerated by the large local field and are propelled in straight lines through the tube. They produce fluorescence when they strike the glass walls; an object placed in their path will cast a sharp shadow in the fluorescence of the tube. These rays are electrons and are easily deflected by a magnetic field.

Lenard Rays.—These high-speed electrons in the cathode ray will penetrate small distances into solids. Lenard closed one end of a tube with aluminum foil and made this the anode of his tube; the cathode rays passed through this thin foil and produced a glow extending several centimeters into the atmospheric air.

Positive Rays.—If a small hole is made in the cathode, the positive ions will pass through and ionize the gas in the region beyond. The ions are in this case atomic or molecular in size and are deflected with some difficulty by a magnetic field. Stark showed that these charged molecules in the positive ray have speeds of some hundreds of miles per second and their spectrum shows a Doppler shift toward the violet.

Cathode Sputtering.—When positive rays strike a metal surface, molecules of the metal are splashed off and a metallic film is deposited on neighboring surfaces. The cathode surface is disintegrated by such ionic bombardment. The effect is called cathode sputtering. It is rather useful for depositing silver, platinum, or gold mirror surfaces. Quartz fibers in electrometers are rendered conducting in this way. The amount of the sputtering depends on the metal and on the gas in the tube. Aluminum shows comparatively little of it and for this reason aluminum electrodes are commonly used in discharge tubes.

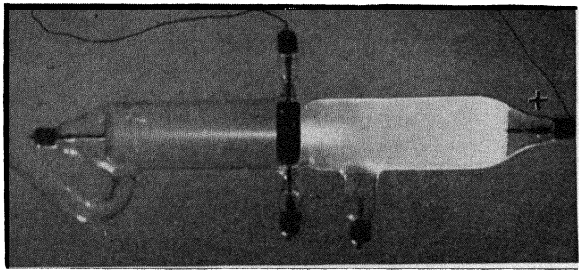


FIG. 38.—Discharge tube showing positive rays. Right half of tube shows fluorescence due to cathode rays.

Rectification by Discharge Tube.—The size of the discharge tube has little effect on the current, provided only that the space about the cathode is sufficient for the formation of the Crookes dark space and the negative glow. If the space about the cathode is so restricted that the negative glow cannot form, the discharge is very difficult to obtain.

This gives an opportunity for rectifying currents by a properly designed tube. One electrode is placed in a small side tube; this effectively prevents this electrode from serving as cathode and rectification of the current is effected.

Luminosity.—The remarkable character of the glow from a discharge tube requires rather close analysis for its explanation. This radiation is in part the energy released when ions recombine; in part it is due to simple excitation of molecules without ionization. The heavy positive ions which are moving toward the cathode and the lighter, faster electrons which are moving toward the anode excite the molecules which they strike in different ways and produce somewhat different spectra. There is also a difference in the spectrum produced by the high-speed electrons in the negative glow and that produced by the more slowly

moving charges in the positive column. The striations often observed in the positive column correspond to variations in the voltage along the tube.

Cathode-ray Oscillograph.—A narrowly defined beam of cathode rays which can be deflected by a variable transverse field is used to indicate the shape of the wave form of an alternating current. The beam acts as an almost weightless pointer which will follow very accurately high-frequency fluctuations. Such tubes are provided with deflecting plates for electrostatic deflection or the magnetic deflection can be used. The cathode-ray oscillograph was first devised by the German radio pioneer Braun and is often called a Braun tube.

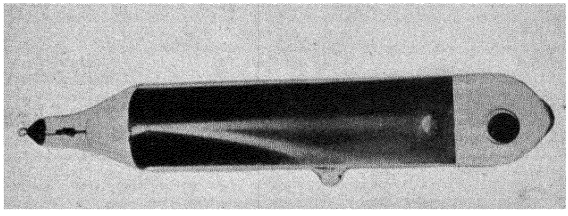


FIG. 39.—Cathode ray, with and without magnetic field.

Lightning and Northern Lights.—In lightning we observe the gigantic sparks of nature. Imagine the tremendous potentials required to create such sparks. Nature also furnishes in the Aurora Polaris a splendid display of electric discharge at lower pressure. The Aurora is produced by electrons from the sun. Near the Equator these electrons are turned back in their paths by the magnetic field of the earth. They reach the upper atmosphere near the poles and there (at a height of almost 200 miles) produce the luminescent streamers.

The Electron in a Force Field.—The phenomena of the discharge tube were but poorly understood in the nineties. But in certain respects the behavior of the cathode ray itself is very simple. In Fig. 39 the electrons, after being accelerated from the cathode (on the extreme left) to the anode, pass through a slit in the latter and the ray makes its trace on a fluorescent screen. The electrons in this cathode ray can illustrate for us several of the simplest types of motion.

1. *A body not acted on by a force moves in a straight line,* with constant velocity. When no field is applied, the electrons after passing through the anode leave the straight trace shown in the figure.

2. *Acceleration from rest.* Just as the speed of a falling stone is proportional to the square root of the potential (*i.e.*, the height) through which it falls, so as the electrons leave the cathode and are accelerated to the anode the speed of these electrons depends on the root of the cathode-anode potential difference (V). If e is the charge, m the mass, and v the velocity of the electron, then its potential energy at the cathode is eV; it obtains kinetic energy $\frac{1}{2}mv^2$, and we have

$$\frac{1}{2}mv^2 = eV \text{ or } v = \sqrt{2\frac{e}{m}V} \tag{11}$$

3. *A body thrown into a parallel force field moves in a parabolic orbit.* Such is the orbit of a ball thrown from the surface of the earth. Such a field can be applied to the electrons in the cathode ray if the ray passes between two oppositely charged plates as in Fig. 40. The electrons pursue a parabolic path. If the strength of the electric field here is represented by E, the force on the electron is eE and the acceleration (which corresponds to g for the gravity case) is given by

$$F = eE = ma \text{ or } a = \frac{e}{m}E \tag{12}$$

4. *A force transverse to the motion, constant in magnitude, causes a body to move in a circle* with unchanging velocity. An electron moving across a magnetic field experiences such a force. Figure 39 shows the discharge in a magnetic field. (See also Fig. 124.)

The radius of curvature (r) of the path is (by elementary mechanics) given by

$$F = \frac{mv^2}{r}$$

where F is the centripetal force. The value of the transverse (centripetal) force on an electron in a magnetic field is

$$F = evH \text{ (in e.m.u.) or } F = \frac{evH}{c} \text{ (in e.s.u.)}^1 \tag{13}$$

[1] In case the reader is unfamiliar with this relation, it may be easily derived from the equation given in elementary physics for the force on a wire carrying a current. If the current (I) is expressed in electromagnetic units, the force

Asked our fathers: What is this mysterious influence, electricity? Here the discharge tube seemed to give the answer. Electricity apparently is composed of small material particles which move according to the ordinary laws of mechanics. Here again, as in the kinetic theory of gases, the ordinary laws of bulk physics seemed to be applicable to the smallest physical entities. Does this not seem almost unbelievable? Does it not seem *a priori* improbable that just the same laws which apply to an aggregate should apply to the individual in the aggregate?

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on unit length of the wire is: $F = IH$. If the number of free electrons per unit length of wire is n and if these are drifting along with velocity v, then the number passing a given point in the wire per second is nv and the current is: $I = env$. Substituting this value, we have for the total force: $F = envH$; or for the force on a single electron: $F = evH$.

Note concerning Electrical Units.—We shall always use electrostatic units (e.s.u.). The simplification introduced into magnetic formulas by the electromagnetic system (which consists only in the elimination of the constant c from magnetic formulas) is more than balanced by the confusion introduced by having two systems. The magnetic force on an electrical charge always depends upon the ratio of the charge velocity v and the limit velocity c (compare p. 20). The fundamental difference in the two systems is occasioned by the fact that the e.m. system uses for its unit of charge a charge $3 \cdot 10^{10}$ times greater than the electrostatic unit.

The most important units are charge (and current) and potential (and field). One coulomb of charge (or ampere of current) equals $3 \cdot 10^9$ e.s.u. Three hundred volts equal 1 e.s.u. of potential. The reader should consult the general table for corresponding atomic units.

CHAPTER X

CHARGE AND MASS OF THE ELECTRON

How Millikan hunted for the charge of the electron and found the mass of an atom—but Faraday had to help. Weighing the electron and measuring its speed. And what Aston found when he measured the mass of an atom.

J. J. Thomson first measured the charge of the electron and C. T. R. Wilson after him. Millikan refined the experiment. The measurement of the charge on the individual electron opens the way to determining the mass of the individual atom and hence to finding Avogadro's number. When the charge of the electron was measured the atomic theory was no longer merely the hypothesis of Dalton but a demonstrated fact. Before 1898, when Thomson measured the electron, there were good reasons for skepticism; almost from that time the atomic theory has been universally accepted.

The Oil Drop Experiment.—Wilson found an approximate value for the charge on the electron by measuring the rate at which a cloud of charged water particles moved in an electric field. Millikan used oil droplets (which would not evaporate) and observed the motion of the individual droplet. Two horizontal plates are placed one above the other about a centimeter apart. Through a hole in the upper plate some droplets of oil, produced by an ordinary atomizer, can fall. The oil droplets are very small, so small that they show Brownian movement, but they can be seen as points of light in a microscope. As they are torn apart in the atomizer, these droplets usually become charged with one or two or three electrons; or if they are uncharged, the air around them can be ionized by x-rays and the droplets will pick up a positive or negative ion.

The droplets of this oil mist slowly drift down in the air between the plates; or they may be attracted up or down by applying a proper electric field. In this way a single drop, now falling, now pulled upward, may be kept in view for long periods of time.

In the experiment the *weight* of the oil drop must first be measured. This is done by observing its rate of fall. The

charge on the drop is then measured. This is done by noting the strength of the electric field necessary to support it and keep it from falling. Finally, the *number* of electrons on it must be determined.

Stokes' Law of Fall—Weight of the Drop.—Small particles fall through the air without acceleration; this is due to the viscosity of the air; the larger the particle, the faster it falls. Stokes[1] gave the law of fall. The exact derivation is not simple but except for the proportionality constant the general form of the relation can be easily deduced. Evidently the velocity of fall should be proportional to the gravitational field (g) and the density (ρ)—since this latter affects the weight—and it will depend on the radius of the drop (r), being actually proportional to r^2.[2] It should be inversely proportional to the viscosity (η); a body falls more slowly in molasses than in air. The actual law of Stokes is

$$v = \frac{2}{9}\frac{g\rho r^2}{\eta}$$

Millikan, observing the oil drop in his microscope, measured its velocity of fall and hence (knowing ρ, η, and g) was able to determine its radius and its mass. So the drop was weighed.

Measuring the Charge.—The two plates were then charged and, by choosing the proper potential difference (several thousand volts), the droplet could be held suspended in mid air. Here the electric field just compensates for gravity. The electric force equals qE, where q is the charge on the drop [see Eq. (12)] and this force now equals the weight (mg) of the drop. Hence comes the equation $mg = qE$ which gives the value of q, the charge on the drop. (E is found by dividing the potential difference in e.s.u. by the distance between plates. Three hundred volts equal 1 e.s.u.)

In the actual experiment it was not convenient to adjust the potential difference between the plates. Rather the potential was kept unchanged at a value greater than that required for

[1] We have heard of Sir George Stokes in connection with fluorescence (p. 108). Stokes and Maxwell and Kelvin and Rayleigh were preeminent in the remarkable development of mathematical physics in Great Britain during the last half of the nineteenth century;

[2] The weight is proportional to the volume: $wt = \frac{4}{3}\pi\rho r^3$. However, the larger drops also meet with more air resistance. The result is as stated: that the velocity is proportional to the square of the radius.

equilibrium, the droplet was attracted upward, and its upward velocity observed. The force could be obtained by proportion. Evidently if the droplet ascended upward with a speed just equal to its earlier velocity of fall, the electric force was twice its weight; if the upward velocity was twice the velocity of fall, the force was three times its weight, and so on.

Atomicity of Electricity.—The charge on the droplet under observation could be changed by ionizing the air in the chamber and the value of q again determined. And now, after several such observations, the counting of the electrons on the drop was the simplest task of all. For when the data were inspected it was found that the charge q as determined was invariably a small multiple of a certain value. This highest common divisor was taken as the elemental quantum of electricity: the electron. Sometimes the charge found on a drop was one or two or three times this elemental value, sometimes more; but, except for small experimental errors, never was a droplet found with a fractional charge. Thus was established the fact that electricity was essentially atomic in character. And out of this followed the atomic nature of matter.

Experimental Data.—In a typical experiment, 5051 volts was the difference between the plates. A certain droplet was observed as it passed through a distance of 0.5222 cm. The observed time of fall and rise and the corresponding velocities are given in Table 16.

It is seen that the times of rise in several instances agree closely, indicating an unchanged charge. The average of these is given in the third column. Now from the average time of fall (13.595 sec.) through the observation interval (0.5222 cm.) the velocity of fall (v_f) is computed (nearly $\frac{4}{10}$ mm. per second). Similarly the velocities of rise (v_r) are computed. In the fifth column the two velocities (v_f and v_r) are added to give the effective velocity contributed by the electric force. And when this is done the numbers obtained are almost exact multiples of a common velocity value 0.00891. Evidently the droplets carried respectively 5, 6, . . . 9 elemental charges.

The Charge on the Electron.—The value of the charge on the electron as found by Millikan is 4.770×10^{-10} e.s.u. (The value in our atomic units is 37.1).

The charge on the electron is nearly 5×10^{-10} e.s.u.; there are about 2 billion electrons in a unit charge. Suppose by rubbing on wool or silk we charge a small marble with 1 e.s.u. of charge. (Assuming a half-inch marble, this would raise the

potential about 500 volts.) This charge is 2 billion electrons. We add 2 billion extra electrons if the charge is negative; we steal as many away if it is positive. These are goodly numbers but the *relative* number of electrons added or lost in a charged body is always rather small. If our marble were metallic, there would be in it some 10^{23} free electrons altogether. Charging a body

TABLE 16

Fall, seconds	Rise, seconds	Average time of rise	v_r, centimeters per second	v_{r+f}, centimeters per second
13.6				
13.8				
13.4				
13.4	12.5	12.45	0.041960	0.08038
13.6	12.4			
13.6	21.8	21.85	0.023900	0.06232
13.7	34.8	34.70	0.015050	0.05347
13.5	84.5	85.00	0.006144	0.04456
13.5	85.5			
13.8	34.6			
13.7	34.8			
13.8	16.0	16.00	0.032640	0.07105
13.6	34.8			
13.5	34.6		Average velocity of fall $v_f = 0.03845$	
13.4	21.9			
13.8				
13.4				
Mean 13.595				
5)0.04456	6)0.05347	7)0.06232	8)0.07106	9)0.08038
0.008912	0.008911	0.008903	0.08883	0.008931

effects the inner electrons not at all and even on the surface usually only one electron out of a million or a billion is affected.

In "practical units" the value of the electronic charge is 3×10^9 times smaller than this. The electronic charge is about 1.6×10^{-19} coulomb—about one-sixth of a sextillionth of a coulomb. My lamp takes about an ampere of current: 6 sextillion electrons course through its filament every second. This is about the number of free electrons in a centimeter length of a small copper wire. The free electrons in each centimeter of my lamp cord must be displaced by others every second. The rate

of drift of these electrons, the diffusion of this "electron gas" through the copper ions in this wire, must be about a centimeter per second.

The Mass of the Atom.—Michael Faraday it was who, years before this (1830), discovered the fundamental law of electrolysis. He found that the mass of any substance deposited was proportional to the charge. It takes 96,500 coulombs to deposit 1 gram atom of any monovalent element such as hydrogen or silver. This is 2.895×10^{14} e.s.u.[1] Since the charge carried by each such atom is the elemental electronic charge, it is but a matter of division, after finding the charge on the electron, to find the number of atoms in a gram atomic weight.

$$\frac{2.895 \times 10^{14}}{4.774 \times 10^{-10}} = 6.062 \times 10^{23}$$

the accepted value of Avogadro's number.

When Avogadro's number is known, all the absolute atomic weights follow from the relative weights of the atomic table. The weight of the hydrogen atom is

$$\frac{1.0078}{6.062 \times 10^{-23}} = 1.662 \times 10^{-24} \text{ gm.}$$

The other atoms can be found from this by proportion. The weight of an atom whose relative atomic weight was unity would be 1.6494×10^{-24} or, within the probable error of the experiments, 1.650×10^{-24} and this we have taken as a "protol."

Millikan measured the charge on the electron in 1909. The experiment is famous as a beautiful piece of precision; it was the monumental culmination of a series of correlated experiments on viscosity of air, motion of charged particles, validity of Stokes's law, etc. His result stands today as classic; it gives the surest approach to the magnitudes of the atomic world.

At some time we must all have wondered how a physicist with such clumsy tools as electroscopes and balances can measure an atom. The atoms are so small that, if a large marble were magnified up to the size of the earth, the atoms within it would themselves appear about the size of marbles. The atoms are a hundred million million million times too small to be weighed

[1] There are 3×10^9 e.s.u. of charge in a coulomb.

on a chemical balance, some billions of times smaller than the smallest particle visible in an ultramicroscope.

Here in Millikan's experiment we have one answer to this question. Measuring such quantities probably still seems like doing the impossible; yet we have the method explained and we do it ourselves and we watch the individual oil droplet as it rides now up, now down, following our reversals of the electric field; and then everything seems very simple—like getting the explanation of a magician's trick. As we watch these droplets, shining points before the microscope like a constellation of stars, falling under gravity, rising in the field, and then when we actually compute for ourselves the charge and then the mass of the atom, this world of the atom becomes real to us—no longer a world of fancy. This experiment of Millikan's makes real to us the size of this atomic world just as Brownian movement impresses us with the reality of the ceaseless molecular motion.

There are other methods of weighing the atom and determining Avogadro's number. We can do it by observing Brownian movement (Chap. IV) or by counting the alpha particles which are hurled out by the occasional explosion of a heavy atom (Chap. XXV) or by listening to the growl of a radio tube (Chap. XI) or by measuring the minute diffraction of x-rays from gratings (Chap. XXVI) or by considering the blue of the sky. But this method of Millikan's allows much the greatest precision.

TABLE 17.—ELECTRONIC CHARGE (IN ELECTROSTATIC UNITS)

Observer	Method	$e \times 10^{10}$
Wilson (1897)	Water cloud	3
Millikan	Oil drop	4.770
Perrin	Brownian movement (p. 67)	4.2
Regener	Charge on α particles (p. 302)	4.79
Planck	Theory of radiation (p. 155)	4.69
Hull and Williams	Thermionic emission (p. 144)	4.76
Compton	X-ray diffraction (p. 339)	4.804

A Convenient Energy Unit.—The work which the charge can do is as important as the charge itself—electric power companies do not charge us for amperes but for ergs or joules or kilowatt-hours. An electron at 1 volt potential can do 1.6×10^{-19} joule of work; this is 1.6×10^{-12} erg or a little less than 100 atomic ergs. This work per electron per volt is a very useful unit of

energy. We shall call it an *electron-volt* (*e*-volt). One *e*-volt equals 96.5 atomic ergs.

The Mass of the Electron.—The ratio of electron charge to electron mass (e/m) was found by Thomson in 1897 before the value of e was known; from this ratio m itself was determined when, in the following year, he obtained a preliminary value for the electronic charge. The electron is about 1840 times lighter than the hydrogen atom.

If a rapidly moving electron in a cathode ray is deflected by either a magnetic or electric field, the deviation will evidently depend on the charge (which results in the deflecting force), on the mass (for inertia is the tendency to travel in a straight line), and on the velocity. Now this velocity affects the magnetic and the electric deflections differently as was seen in the last chapter [compare Eqs. (12) and (13)] and hence by a comparison of the separate effects of these two fields the velocity can be determined; then can be found the ratio e/m.

In Thomson's experiment the cathode rays proceed as a narrow beam down a long discharge tube between two long parallel plates; these plates can be oppositely charged to produce a uniform field and give the electric deflection.[1] A coil about the tube produces a magnetic field. The direction of this field is such that the magnetic deflection of the cathode ray will be just opposite to the electric deflection.

Balancing Fields and Measuring v.—The force produced by an electric field of strength E on a charge e is Ee [Eq. (12)]. When at rest, a charge is not affected by a magnetic field. When the charge is in motion directly across the lines of force, the force produced by a magnetic field of strength H is Hev/c [Eq. (13)].

The two fields, electric and magnetic, may be applied simultaneously and adjusted so as to give two opposite equal forces and the cathode ray is undeflected. Then

$$Ee = \frac{Hev}{c} \text{ or } \frac{v}{c} = \frac{E}{H}$$

Hence the velocity of the electrons in the cathode ray is obtained. It has the same ratio to the velocity of light c that the electric field has to the compensating magnetic field.

[1] Actually the deflecting plates in Thomson's experiment did not extend the whole length of the tube but it makes the description slightly easier to assume this.

Finding the Ratio of e/m.—If the magnetic field is applied alone, a deflection (s) will be obtained. What will be its value?

1. The time of travel (t) of the electron along the tube is equal to L/v where L is the length of the tube.

2. In constantly accelerated motion the displacement (s) is equal to $\frac{1}{2}at^2$.

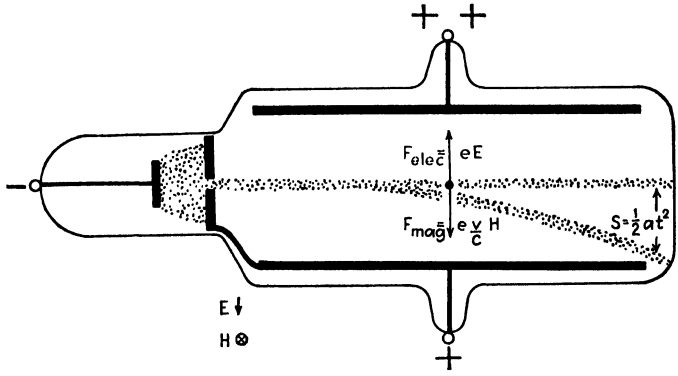


FIG. 40.

3. Combining 1 and 2 gives

$$s = \frac{1}{2}a\frac{L^2}{v^2}$$

4. The acceleration is always obtained by dividing the force (Hev/c) by the mass. Hence $a = Hev/mc$.

5. Now substituting this value in 3, we have

$$s = \frac{1}{2}\frac{HeL^2}{mcv} \text{ or } \frac{e}{m} = \frac{2scv}{HL^2}$$

This result allows the ratio of e/m to be computed from the deflection s, since the velocity v of the ray has already been found and the magnetic field and the length of the tube is, of course, found directly. J. J. Thomson's value of e/m was about 10^{-7}. Many later determinations have been made; the story of these successive experiments is summarized in Fig. 41. The accepted value[1] is 1.76×10^{-7}. By using Millikan's value of e, this gives for the mass of the electron about 9×10^{-28} gm. or $\frac{1}{1830}$ in atomic units.

[1] Values of equal precision have been obtained by spectroscopic methods (pp. 191 and 223).

Kaufmann and later Bucherer, using very refined methods, measured the masses at high speeds; they observed the relativity increase in mass which has been described in Table 1.

Positive Rays.—Electrons leave the cathode and form the cathode ray. Positive ions move through the discharge tube in the opposite direction and strike the cathode. They are the atoms of the gas, ionized. If the cathode be perforated, these

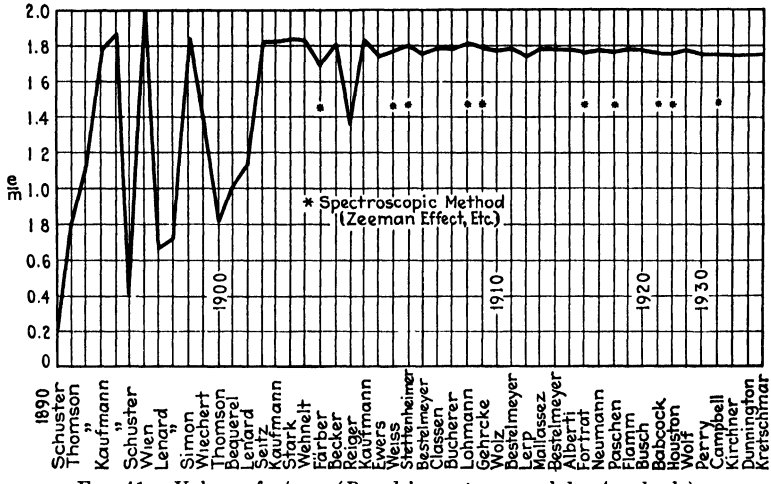


FIG. 41.—Values of e/m. (*Based in part on graph by Auerbach.*)

positive rays pass through the perforations and can be obtained by themselves as a beam. These rays consist of charged atoms, many times more massive than the electron. They are therefore much less readily deflected by a magnetic field than are the cathode rays. They can be deflected by strong fields and their e/m ratios obtained.

Prout's Hypothesis.—Prout had suggested (1830) that all atoms were built up from hydrogen and he concluded that the atomic weights in all cases should be integral multiples of the hydrogen weight. When the atomic weights were accurately measured by the chemist and it was found that they were certainly *not* integral numbers, then this hypothesis was given up. But nothing more than average atomic weights had ever been measured. Even Millikan's determination of the weight of the "individual atom" was only an average value. Was it not possible that chemical elements were actually mixtures of two kinds of atoms which were chemically inseparable? As a

matter of fact, as the phenomena of radioactivity were unfolded, it became clear that for these heavy radioactive elements just such atoms identical in chemical properties but with different masses did exist. These chemically identical but physically different atoms were called *isotopes* (from the Greek *same place;* the isotopes occupy the same place in the periodic table).

Were most chemical elements really mixtures of isotopes? After a desuetude of a century was Prout's hypothesis to be

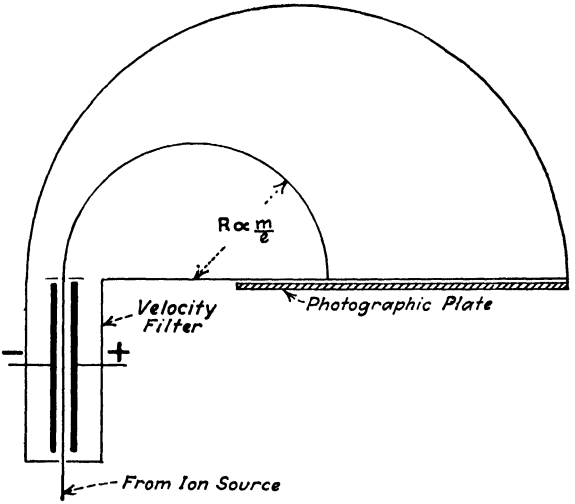


FIG. 42.—Mass spectrograph of Bainbridge. Ions pass first through the "velocity filter" where an electric field compensates the magnetic field for ions of a certain velocity [$E/H = v/c$ (page 130)]. In the main chamber the ions are bent in a circle of radius $R = cv/H \cdot m/e$ [from Eq. (13)]. The relative atomic masses are determined with a probable error of less than 1 part in 10,000.

resurrected? The measurement of the e/m ratio and hence the mass of the individual positive ion offered the opportunity to test the validity of Prout's hypothesis once for all.

Discovery of Isotopes.—Again it was J. J. Thomson who first "weighed" positive rays in the Cavendish Laboratory. His results were surprising enough. They indicated the presence of an H_3 molecule (!) and also the presence of isotopes in neon. But it was Aston (also at the Cavendish Laboratory) who perfected the method and developed the "mass spectrograph." Aston was not content with merely deflecting a narrow beam of positive rays; by an ingenious combination of electric and magnetic fields he succeeded in focusing at a single spot on his plate all rays with a common e/m whatever their velocity. In

his latest mass spectrograph the accuracy obtained is extraordinary. Relative atomic weights can be determined to 1 part in 10,000; this gives weights for *individual* atoms of greater accuracy than is usually possible for the *average* weights by the most refined chemical means!

The result of such measurements showed definitely that many of the chemical elements were composed of two or more isotopes. His results for a few of the lighter elements are given in Table 18. (We shall in a later chapter add to this list other elements in which the isotopes, present in very small quantity, were detected by other means.)

TABLE 18.—ISOTOPES AMONG THE LIGHTER ATOMS

	Atomic weight	Isotopic weights
3. Lithium	6.94	7, 6
5. Boron	10.82	11, 10
10. Neon	20.2	20, 22
12. Magnesium	24.32	24, 25, 26
14. Silicon	28.06	28, 29, 30
17. Chlorine	35.46	35, 37
18. Argon	39.91	40, 36
19. Potassium	39.10	39, 41
20. Calcium	40.07	40, 44

Packing Effect.—It can be said in general that atomic weights markedly different from whole numbers are due to isotopes. Hence Prout's hypothesis is justified and it is unquestioned today that the other elements are all formed from the simplest—hydrogen. It is not true, however, that the atomic weights of the isotopes are exactly integral. Indeed the very simplest atom—hydrogen—has a weight 1.0078 and this fractional value is not due to the presence of isotopes.[1] The fact is that, when 16 hydrogen atoms are combined as in the oxygen atom, some mass is lost. It has been remarked (page 18) that mass is a form of energy. When four hydrogen atoms (weight 1.00778) unite to form a helium atom (weight 4.00216) 0.02846 gm. or 2.5×10^{19} ergs of chemical energy are lost from the system.[2] When four

[1] The basis of the atomic table, of course, is oxygen, to which is attributed a weight 16.00. Recently spectroscopic evidence has shown that both oxygen and hydrogen have isotopes, but their amounts are very small and do not greatly alter the average atomic weight.

[2] We are using Aston's values.

helium atoms combine into oxygen 0.00864 gm. (4×0.00216) of energy disappears. This loss of mass is sometimes called the packing effect.

Bulk Separation of Isotopes.—Positive-ray analysis while separating the isotopes completely deals with but a relatively small number of atoms and usually does not separate enough of any isotope to be chemically perceptible. Other methods have been devised which separate isotopes in bulk but the separation has usually been very tedious and very imperfect. Such methods always employ the fact that a lighter molecule will have a larger mean velocity. Hence it will diffuse more rapidly or evaporate more rapidly. The diffusion through pipe clay has been used. After many repetitions two samples of neon were obtained differing by 0.1 unit in atomic weight. When 19,000 liters of hydrochloric acid were used, small residual samples showed a difference of atomic weight of 0.055. By repeated evaporation lasting hundreds of hours, two samples of mercury 0.2 cc. in volume were obtained differing by 0.1 in atomic weight. The bulk separation of isotopes is no easy task. Quite recently Hertz has set up a battery of diffusing elements in conjunction with mercury-vapor pumps and has succeeded in attaining a remarkable degree of separation in the case of the neon isotopes.

Recently a mass spectrometer of remarkable intensity has been developed (by Smythe and his coworkers) which effects isotopic separation of micrograms, and in favorable cases even of milligrams, of material in a few hours. It will play an important part in future investigations of the elements.

"Balances."—With a very good chemical balance we can weigh a hundredth of a milligram; we can weigh a piece of paper, then write our name on it, and find the weight of the writing!

A delicate microbalance has been developed. It uses a quartz fiber for suspension instead of a knife edge; it is operated in a vacuum. This balance will weigh a millionth part of a milligram; it could measure light pressure; it pushes the limit of the weighable down ten thousand times.

Millikan, observing his oil drops, measuring their rate of fall, and using Stokes's law, has a balance of ten thousand times greater sensibility than the microbalance. These droplets may each weigh as little as a ten-billionth part of a milligram. Such a droplet, the smallest of visible things, forms a "micromicro"

self-weighing balance. On the drop we can put several electrons as "weights" and balance the drop in an electric field.

But Aston weighs the charged atom instead of the charged droplet. The hydrogen ion traveling in a magnetic field is a "micromicromicro" balance, weighing a particle about ten billion times smaller than the smallest oil drop.

We weaken the field in Aston's "balance" a thousand times and we measure the mass of the electrons—nearly two thousand times lighter than the lightest atom—except for the photons of electromagnetic radiation, the lightest of particles.

The Electron as a Sphere.—The charge and mass of the electron we have found. How large is this electron, is it spherical and, if so, what is its diameter? A natural question, but one, I am afraid, with only a moderate amount of meaning. An electron acts at a distance, repels other electrons quite strongly while their centers are yet several angstroms apart. In a certain sense each electron is everywhere. Yet there is a certain limited sense in which a definite radius may be ascribed to an electron. The reasoning is as follows:

A charge on the surface of a sphere raises the sphere to a certain potential. The charge has a definite potential energy. If, while the charge is kept the same, the sphere is made smaller, the charges on its surface pushed closer and closer together, the electrical potential energy is increased. The energy of a charged sphere is $q^2/2r$.

Now the mass of an electron is $\frac{1}{1830}$th protol or (multiplying by c^2) represents about 5×10^7 atomic ergs of energy. This mass of the electron would be completely accounted for by its ordinary electrical energy if the electron sphere were taken of appropriate size. When atomic units are used for e,[1]

$$\frac{1400}{2r} = 5 \times 10^7 \text{ or } r = 1.4 \times 10^{-5} \text{ angstrom}$$

This theory is attractive in so far as it explains away mass as being only the self-induction of a charged sphere.

This effective radius of the electron is a little more than a hundred-thousandth angstrom, a little more than 10^{-13} cm. The electron is small compared with the atom (the radius of which is usually about 1 angstrom). The radius which would account

[1] It will be convenient to remember the e^2 (or 38.1^2) is approximately 1400.

for the mass of a proton is 1840 times less. But it hardly seems possible today to consider electrons and protons as having objective existence as small charged balls.

Summary.—Faraday found the value of e/m for the ions of electrolysis in 1830, Thomson for the electron in 1897, and Aston for positive rays in 1919. The charge on the electron was measured by Millikan in 1909. The fundamental formulas used in Millikan's experiment are the Stokes law of fall and the expression for the force on a charge (qE). In deflecting either ions or electrons in a magnetic field, the relation is

$$He\frac{v}{c} = ma$$



MILLIKAN

R. A. MILLIKAN *is the dean of American scientists. He graduated from Oberlin. In college he taught physical education, studied the classics and then felt the call to physics. He got his Ph.D. degree from Columbia and in* 1896 *he was appointed assistant at Chicago. He remained there* 25 *years, being appointed professor in* 1910. *Since* 1921 *he has headed the California Institute of Technology. He received the Nobel prize in* 1923.

Millikan is hardworking, forceful, sure; looks like the efficient, enthusiastic man of business. He was nearly forty years of age when he first achieved fame by the elegant precision of his oil drop experiment. Five years later he devised his "machine shop in a vacuum" and did his definitive experiment on the photoelectric effect. By this time he was preeminent in America.

In California Millikan has been an extraordinary type of university executive. His scientific interests have never flagged. His recent studies in the far ultra-violet spectrum and his studies of cosmic rays are well known.

CHAPTER XI

RADIO TUBES

How electrons are distilled from wires; Maxwell's distribution law. Speed and voltage. How the growl of a radio tube betrayed the charge in the electron. Controlling the tube current. Other methods of extracting electrons from metals.

Edison (1883) was first to discover that electrons are evaporated from the surface of hot metals. He was experimenting with one of his early incandescent filament lamps. Because of a manufacturing technicality, these early lamps had a third wire sealed into the bulb. Edison noticed that this wire would receive a negative charge when the filament was heated; current would flow across the tube if this wire was made the anode and the filament the cathode but would not flow in the reverse direction.

Nothing was done with this Edison effect for nearly twenty years. Then Fleming in England conceived the idea of using a thermionic tube as a rectifier in wireless telegraphy; about the same time DeForest in the United States invented the three-element tube which could be used as an amplifier. Since then, the thermionic tube has been extensively developed. In addition to the simple rectifying diode and the amplifying triode, there are tubes with four elements (filament, two grids, and a plate) and even the five-element pentode. There are high-amplification tubes, low-resistance tubes, screen-grid low-capacity tubes. Tubes are used in radio sending, in radio receiving, in rectifying currents and amplifying currents, and producing high-frequency alternating currents. They are used in telegraphy and long-distance telephony, in transmitting pictures—these things play a deep role in our civilization—and this little thermionic tube is at the heart of each. Whenever a sensitive regulator of electricity of almost instant response is wanted, then the thermionic tube is used.

Thermionic Emission and Temperature.—In the two-element tube we have a filament to emit electrons, a plate to receive them. Electrons can go to the plate only when it is positive. If the

positive voltage on the plate is kept sufficiently high so that all electrons which leave the filament are pulled into the plate, none returning to the filament, we can measure the total electron emission from the metal as a function of the temperature. It is then found that the electron current increases according to nearly the same law that was found to hold for evaporation of molecules (page 81). Indeed electrons are evaporated from a filament with exactly the same speeds and in exactly the same numbers as predicted by the M-B law.

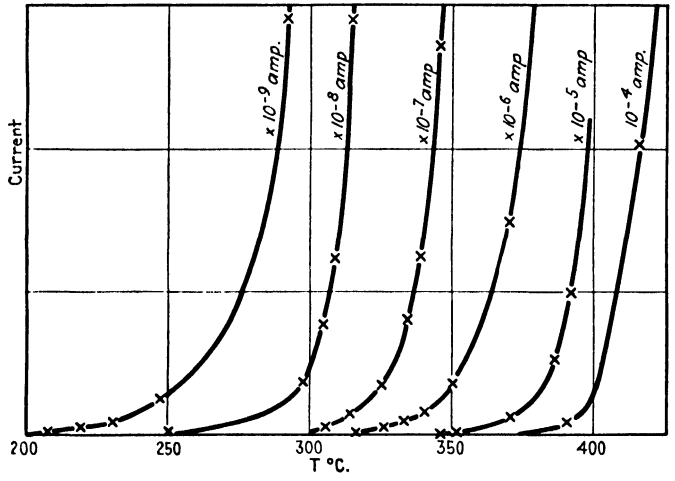


FIG. 43.—Thermionic emission from sodium. (*Richardson.*)

Of all metals it is the alkalis which most readily lose their electrons. Figure 43 shows the current from sodium. The current shown on successively different scales increases from about a millionth of a milliampere to over a hundred milliamperes, while the temperature rises hardly more than 200°C. This current seems to have very nearly the proportional increase which is characteristic of the compound-interest law—the current increases about ten fold for every 25° temperature rise.

The most commonly used filament is tungsten. At 1700°C. its saturation current is 1 milliamp. per square centimeter of surface. This emission rate is approximately doubled for every 50° rise in temperature.

A trace of thorium is often placed in the tungsten wire. Some of this diffuses to the surface and there forms a monomolecular layer which releases electrons very readily. Such a filament

emits a current equivalent to that from pure tungsten at a temperature nearly 600° lower.

Heats of Vaporization of Electrons.—By the M-B law the electron emission is closely related to the heat of vaporization. Table 19 gives this work required to remove an electron from a metal, both in atomic ergs and in *e*-volts. This heat of vaporization of electrons is often called the *work function.*

TABLE 19.—HEATS OF VAPORIZATION (W_0) OF ELECTRONS

Metal	Atomic ergs	*e*-volts
Caesium	170	1.8
Nickel	270	2.8
Tungsten	430	4.5
Platinum	490	5.1
Thorium on tungsten	250	2.6
Barium oxide on tungsten	160	1.7

These values have here been determined indirectly from the shape of the current-temperature curves. The heat of vaporization may be determined directly. When electrons are allowed to evaporate, the filament is cooled slightly; the heat of vaporization determined in this manner agrees closely with the values given above. A third method of determining the energy of vaporization is described in Chap. XII.

Thermionic Current and Tube Voltage.—So much for the relation between current and temperature. It has been assumed here that the voltage on the plate was sufficient to attract all emitted electrons. Let us now reverse our viewpoint. We now suppose the temperature to be very high so that the electron flow is limited by the voltage (V), not by the temperature; the current is then found to be proportional to $V^{3/2}$ (Langmuir-Childs law). This is shown by the ascending line in Fig. 44.

This increase of current with voltage may be surprising. It might be supposed that every electron leaving the filament would reach the plate as long as the latter was not lower in voltage than the former. Actually this is not the case. Evaporated electrons, while traveling toward the plate, give to the space a negative charge and tend to repel other electrons back to the filament. The slower of the evaporated electrons will be turned back. It is the function of the plate potential to neutralize this backward force of this "*space charge.*"

Characteristic Curve.—In practice the current is usually limited by the voltage as long as the voltage is small. After the voltage is raised to 10 or 20 volts (depending, of course, upon the temperature) it is the temperature which usually sets a limit to the current. We then have "saturation"—a greater voltage does not produce an increased current.

The curves in Fig. 44 represent the relation between current and voltage in such a case. The current at first increases accord-

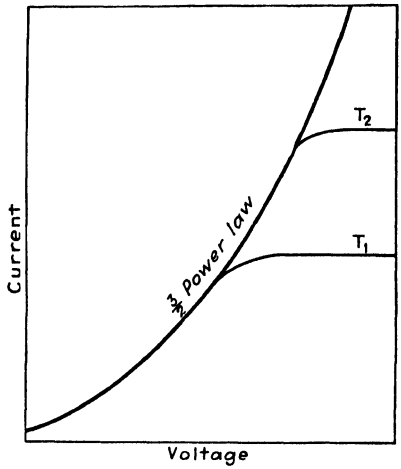


FIG. 44.—Characteristic curve of diode. Showing saturation currents at two different temperatures.

ing to the three-half power law; the increasing voltage pulls a greater and greater proportion of the evaporated electrons across to the plate. Then comes the time when practically all the electrons reach the plate. The curve bends away and becomes horizontal—the current is saturated. This is the *characteristic curve* for a two-element tube. As the temperature of the filament increases, the saturation current of this curve mounts to higher and higher values by the first law of thermionics.

Speed of Evaporated Electrons.—When electrons are evaporated from a glowing wire, the average kinetic energy of the electron in the "electron gas" is (by the usual kinetic theory) the same as its speed in the metal and the same as the energy of any other monatomic gas molecule; it equals $\frac{3}{2}\kappa T$. The electron is about 3600 times lighter than hydrogen and hence travels about sixty times faster—its mean speed is about 60 miles a second or about 100 km. per second at room temperature; its

speed is about three times as great at incandescent temperatures. The kinetic energy at 2100°C. is $\frac{1}{3}$ *e*-volt.[1] This is an average value. Of course, the newly emitted electrons have a variety of speeds, some higher, some lower; Richardson has shown that the numbers with each different speed follow the Maxwell distribution law (page 71).

This initial velocity of thermal agitation of the evaporated electrons is usually negligible in comparison with the applied voltage. As the electron travels from place to place, with the decrease in potential, of course, comes an increase in kinetic energy. The energy equation is

$$eV = \tfrac{1}{2}mv^2 \qquad (11)$$

For 1 volt, this gives $\frac{1}{2}mv^2 = 96$; putting $m = \frac{1}{1830}$ protol we have $v = 600$ km per second. This is the speed with which an electron strikes the plate when the latter is 1 volt above the filament.

Equation (11) shows that there is a quadratic proportion between electron speed and voltage. When the plate potential is 100 volts (a usual value in the radio tube), the electron velocity is 6000 km. per second (9600 atomic ergs of energy). When the voltage is 10,000 volts (as it may be in the tube of some high-powered radio transmitting station), the electron speed is 60,000 km. per second. At this voltage the plate is apt to be heated red hot by the impacts of the impinging electrons.

We do not dare carry our formula to higher speeds. The mass of the electron is now beginning to increase appreciably and a relativistic equation must be substituted for Eq. (11). The continuance of the simple quadratic proportion would lead at a million volts (the voltage of recent high-power x-ray tubes) to a velocity of 600,000 km. per second or twice the velocity of light—which, of course, is impossible.

Fluctuations in Thermionic Emission.—Just as the pressure on a small particle varies in Brownian movement and as the number of molecules evaporating from a surface must show minute irregularities from moment to moment, so the number of electrons evaporated from a filament is subject to chance fluctuations. These fluctuations result in a background of noise which must always persist in a radio tube after all sources of outside

[1] $W = \frac{3}{2}\kappa T = \frac{3}{2} \times \frac{1}{120} \times 2400 = 30$ atomic ergs or about $\frac{1}{3}$ *e*-volt. This is the temperature of a tungsten lamp.

static have been removed. It is like the noise from a rain of shot; it is often called the "shot effect." This is an independent proof of the atomic nature of electricity. The magnitude of these fluctuations has been carefully studied and has given an evaluation of the electronic change. The experiment is the electrical analogue of Perrin's experiment determining the mass of the molecule (see page 65).

Characteristic for the Triode.—In the three-element tube a grid is placed midway between plate and filament. Here it presides over the ebb and flow of electrons from filament to plate. The plate potential is usually quite high (say 100 volts), the grid potential low (say 2 or 3 volts above or below the filament). Few, or perhaps none, of the electrons are caught by the grid. It consumes little energy, but by slight changes, plus or minus, in potential it produces great fluctuations in plate current. It is like the trigger of a gun, where a very slight effort releases a great source of energy.

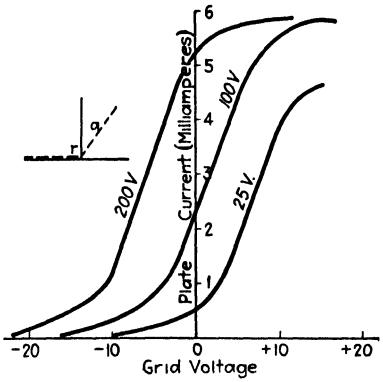


FIG. 45.—Characteristic curve for three-element curve.

The characteristic curve for this three-element tube depicts the current to the plate as it is related to the potential on the grid. The exact setting of the characteristic curve (Fig. 45) depends upon the voltage of the plate. If the plate is 200 volts above the filament in potential (and the filament not too hot), enough of this field will reach through the interstices in the grid perhaps to saturate the current when the grid is zero or even slightly negative. If the plate is comparatively low in potential, the same kind of characteristic curve is obtained but for higher corresponding grid voltages.

Use of Thermionic Tube as Rectifier and as Amplifier.—The ideal rectifying tube, changing alternating current into pulsating direct current would be one in which no current could flow for negative potentials. Such an ideal curve is indicated by the dotted line in Fig. 45. Such a characteristic curve is not attainable but it is quite as satisfactory to work at the inflection point of a characteristic curve; at the knee in the curve an increase

of grid voltage increases the current by a much larger amount than a decreased voltage diminishes it. The resultant distortion produced in alternating current is shown in Fig. 46. The current is almost completely rectified.

For amplification without distortion, just the opposite conditions are desired. Now an increase in voltage must increase the current, a decreased voltage decrease it, each in the same proportion. We wish a straight-line characteristic. The ideal curve would now be the dotted curve at point *a*. Over a considerable region the characteristic curve of a standard thermionic tube is practically straight, giving faithful amplification; in another region it has a strong curvature, giving here efficient rectification.



FIG. 46.

In the radio receiving set, the incoming signal usually comes first to one or more amplifying tubes. These will have perhaps 100 or 150 volts on the plate, giving the straight part of the curve for zero grid voltage. Then follows the rectifying tube; perhaps 25 volts is on the plate, which brings us to the knee of the characteristic curve. Usually the signals, after rectification, are now further amplified—again the high plate voltage.

All are familiar with the nomenclature which the radio engineer has adopted for his various electromotive forces: the A battery which lights the filament, the B battery to furnish the plate voltage. The C battery is used to apply a proper "bias" to the grid, so that (with higher plate voltage) the tube will still be operating in the region of the bend in the characteristic curve for rectification, or for amplification or oscillation in the straight part of the curve.

Photoelectric Effect.—In these radio tubes the electrons are obtained by evaporation from the heated filament. There are three other ways of persuading an electron to leave the metal: (1) it can be thrown outward by light falling on the surface and (2) an electron may be ejected when another electron or a fast-moving ion strikes the metal and (3) electrons can be pulled out of the metal by the application of very intense fields.

When ultra-violet light falls on a metal, electrons are thrown from the surface. This is called the photoelectric effect. Photoelectrons can be precipitated from alkalis even by visible light. But the effect usually becomes more prominent for light of shorter wave length. X-rays produce a very strong photoelectric effect.

Perhaps the strangest thing about this effect is that the speed of the ejected electrons does not depend in the slightest upon the intensity of the light. More light, more electrons; but the speed of these ejected electrons is just as great when they are expelled

by the gentle vibrations reaching a photoelectric cell from some twinkling star as when expelled by the violent waves of the noonday sun.

The photoelectric effect seldom yields a current as large as those obtainable in thermionic tubes. Yet the effect, changing as it does light energy directly into electrical energy, is the key to television.

Secondary Emission.—When an electron strikes a metal, it is sometimes reflected; or it may on entering the metal create such a disturbance that one or possibly several electrons in the neighborhood are ejected. Radio tubes have been developed which employ this effect: every electron which strikes the plate causes several electrons to leave it and hence each electron gives to the plate a *positive* charge.

Extraction in Strong Fields.—Electrons must rush about in a metal in very much the same way that the molecules of a gas do when absorbed in a piece of charcoal. The electrons must repeatedly attempt to break through the surface but they are as often pulled back by the near-by positive ions. We have just seen that at higher temperatures an electron with extraordinary speed does occasionally break free. Some 2, 3, 4, or 5 *e*-volts of energy are needed to free an electron; such energy is not apt to be available in a cold metal. If a strong outer field is applied, however, it should be possible to help these electrons free themselves.

The field of force which an electron meets as it attempts to leave the surface of a metal is surely very strong. All of this attraction between electron and metal must take place within a few angstroms from the surface. If we suppose, for example, that the 5-volt barrier which an electron meets in attempting to leave platinum is confined to a distance of 10 angstroms from the surface—beyond that the electron is free—then we have a field of 0.5 volt per angstrom or 50 million volts per centimeter! It will require very great fields indeed to appreciably counterbalance this strong surface field.

Actually the problem of helping electrons from the surface of metals has proved easier than was expected. Large fields are most readily obtained from points or, almost as strong, from very fine wires. Millikan used very fine tungsten wires in the highest obtainable vacuum. A current, increasing rapidly with voltage, occurred when the applied field was in the neighborhood of a

million volts per centimeter. There can be no question that some of the faster of the electrons in the metal, as they thrust their way out from the surface, were enabled by this added field to escape. But the field which was used seems surprisingly low. Possibly the wire had on its surface minute points where the actual field was much above the average value and the electrons found in these points an easy spring board for their flight into space. However that may be, it appears that electrons may be pulled from metals by the application of sufficiently high fields. The complete description of the phenomena demands the new quantum mechanics (Chap. XXVII).

CHAPTER XII

RECENT HISTORY

Three acts and a prologue.

However you look at it, this has been a great century—so far. And, as I write, the prospects are that there will be plenty of adventure in the future. Only a third of a century! What changes these years have seen in social customs, in industrial methods and in education! So rapid has been the progress that we, more accustomed to the slower evolutionary changes, scarcely know how to live in this new world. In science, and particularly in physical science, the greatest part of what we know has been written since 1900. We have a completely new physical horizon. In these years man has become acquainted with the atom.

The unfolding of the atom before our eyes appears like a great drama of science. Out of many tangled threads, we can find in the development of *quantum theory* the underlying motif of the piece.

It is a drama in three acts—with a prologue. We have been sketching the prologue. Here in the prologue most of the *dramatis personae*—electrons, protons, electromagnetic waves—have been introduced. We have seen how the atomic theory was introduced into chemistry about 1800 and the atom discovered a century later; and how the physicists developed a kinetic theory of molecular motion; and how electrons and atoms and rays of one sort or another were discovered just before the close of the century.

The Birth of the Quantum Theory.—Act I begins in 1900 when Planck announced to the German Physical Society his new quantum theory of energy. The action of the act lasts for some twelve years. The new theory was not high in the regard of physicists but in this period it had two notable successes: Einstein used it to explain the photoelectric effect and Debye used it to explain specific heats of solids.

In this period Lenard and Thomson and Wilson and Townsend studied the behavior of electrons in gases, Richardson studied

the evaporation of electrons from surfaces, Millikan measured the charge, and Bucherer measured the mass, of the electron with great precision. Of this we have seen a little in the last chapters. Lorentz worked out the electron theory of conduction. These are great names and the experimental studies in electronics of this period have had the greatest consequences. But the theories of that decade were rather futile; they lacked one thing to make them "click" with truth and this was the quantum of action. If we would read the story of the period as it was told by contemporaries, we may look to Lorentz's "The Theory of Electrons," or to Richardson's "The Electron Theory of Matter." Thomson's "Conduction through Gases" (1910 edition) covered much of the experimental work of the period. Very influential books these, but the quantum theory is hardly mentioned.

This was the period of infancy of the new theory, when it was perhaps seen but certainly not heard from to any extent. The significance of the theory was then recognized only by a few mathematical physicists. Einstein recognized it and Debye recognized it.

The Discovery of the Atom.—Act II starts in 1912–1913. In 1912 Laue and Friedrich and Knipping measured the wave lengths of x-rays. In 1913 Bohr proposed his atomic theory. This is a brilliant period of discovery despite a world war. The quantum theory now comes into its own. This is the golden age of spectroscopy. In 1912 no spectrum had a meaning; in 1925 no spectrum was so complicated that the physicist did not venture to analyze it. The nature of the atom, the meaning of the periodic arrangement of elements, the building up of the inner atom, the x-ray levels, all this became clear in these dozen years. It was the quantum theory which had given meaning to it all. The physics of this period is summarized in earlier editions of Sommerfeld's "Atomic Structure and Spectrum Lines." This book was regarded at the time as the "physicist's Bible." In it we read of success after success—it is a book of scientific triumphs.

Quantum Mechanics.—Act III begins in 1925 when DeBroglie and Heisenberg and, shortly after, Schroedinger and Dirac interpreted the meaning of quantum theory. So successful had Bohr's theory been, so rapid the progress, that there had been little chance for contemplation. The quantum theory of Planck and of Bohr was simple, direct, but not consistent. Now in Act III the theory is interpreted, restated, a few blemishes

removed from the picture of the atom, and the softer tones filled in. The result has been a new quantum mechanics which, in rather strange language, describes the law of the atomic world. We are in this third act now; its story is being written from week to week in the scientific magazines.

The three acts deal with preparation, conquest, and fruition; we may call them the periods of Planck and of Bohr and of the younger physicists. These names typify the major motifs of these periods. But other motifs are there. There is the Einstein motif. In the middle of the first act of our drama the special theory of relativity entered the stage, and the general theory entered in the second act, and now in our third act the far harder task of complete generalization of the theory to embrace all physics and the problems of cosmology face us—with what result only the future can say.

And then there is the steady development of radioactivity. During all these years the investigation of the heart of the atom has been carried on. With all of this nuclear investigation the name of Rutherford has been associated. In 1899 just after the discovery of radium, Rutherford discovered the alpha and beta rays, then Rutherford and his coworkers discovered the transmutation of the heavier elements and discovered isotopes and (preparing the way for Bohr) discovered the nucleus and then artificial nuclear disintegration and now, even as this is being written, comes word of artificial synthesis of nuclei and of the discovery of neutrons!

Nuclear dimensions are to atomic dimensions much as atomic dimensions are to those of our touch-see-hear world. And in this nuclear world a unique kind of physical law must rule. Rather removed from the thoughts of most physicists was this physics of the nucleus. The nucleus is to furnish the riddle of tomorrow.

CHAPTER XIII

THE QUANTUM OF ACTION

Equipartition among ether waves; but the short waves do not get their share of energy—they are too greedy. "Chunks" of energy. The photoelectric effect and specific heat attest the new theory.

The quantum theory is a child of the twentieth century. Max Planck published his first formulation of the theory in December, 1900. A daring, revolutionary concept was this which he gave to the scientists of the new century.

The Quantum of Action.—By *action* is meant the product of momentum by distance. If a 2-gm. ball moves 3 cm. per second, its momentum is 6 units; after it has traversed (in the first second) 3 cm., its action is 18, after 6 cm. 36 c.g.s. units, etc. If a hydrogen atom in a molecule oscillates with an average speed of 2 km. per second, it has (as a mean) 2 atomic units of momentum. If the range of the oscillation is 1 angstrom, the vibrator has for each complete (to and fro) vibration an action of 4 atomic units. Action is momentum times distance.

Now if an atom is free to vibrate or if a pendulum is free to swing or if I choose to pace back and forth, there was according to the old physics no restriction upon the speed or upon the amplitude of this periodic motion. For me it seems obviously a matter of my choosing; for the atom the vibration would presumably depend upon the chance blow from another atom which set it in motion. But all this is not entirely so. It would appear that all amplitudes of periodic motion are in fact not permissible in nature. Indeed for any such repetitive motion as these the motion must be such that the action in one oscillation is just 4 atomic units or a multiple thereof. The atom can vibrate with 4 or 8 or 12 or 16 units of action, etc., and in no other ways. Similarly for a large pendulum, the action must be a whole number (billions of billions of billions in this case) of times this fundamental element of action; in this case this quantic restriction to a whole number is no real restriction.

This 4 atomic units[1] (or 6.55×10^{-27} c.g.s. units) is called Planck's quantum of action and is represented by the letter h.

$$\text{Action} = nh \tag{14}$$

Chunks of Energy.—In the special case of simple oscillatory motion (and only in this case) we may equivalently define the action as the energy times the time—the energy (W) times the period (T)—for the action of a single cycle. The quantum restriction which we have just stated is

$$WT = nh$$

where n represents an integer; or in terms of the frequency (which equals $1/T$)

$$W = nh\nu$$

This means that the atom must vibrate with an energy just equal to $h\nu$, or $2h\nu$, or $3h\nu$, or that the pendulum must swing with an energy of some uncountable number of billions of $h\nu$; the energy of any oscillator must occur as exact multiple of the fundamental energy quantum $h\nu$. $h\nu$ appears to be the "atom" of energy, the unsplittable ultimate. An "atom of energy," surely a strange-sounding theory this!

Today this quantization of energy seems to be forced upon us by experiment in every field of physics. In many cases the implications of the experiment are so direct that we can hardly overlook them. It is remarkable that Planck should have first discovered the law in some rather involved applications of the laws of chance to radiation from heated bodies.

Black-body Radiation—Total Emission.—A good absorber of light is a good radiator; the perfect absorber and the best radiator is a black body. Regardless of material the perfect black body absorbs all the radiant energy falling on it; regardless of material, every perfect black body emits at the same temperature exactly the same energy, both in quality (color) and in amount. Because of these facts the radiation from black bodies has been extensively studied both by the experimental and by the mathematical physicist. But, as it happened, for a while the experimenter and theorist could not agree.

In the first place Stefan (1869) showed how the emission (the total of all colors) from a heated black body depended on

[1] More exactly 3.97 atomic units.

the temperature. We are all familiar with the rapid increase of radiation with rising temperature; as the stove approaches red heat, its emission increases greatly. A white-hot tungsten filament, small as it is, emits many watts of energy. Stefan found that the emission was proportional to the fourth power of the temperature. In this instance the theorist (Boltzmann) was able to predict this same result. The law is known as the Stefan-Boltzmann law.

$$E = W/t = \sigma T^4 \qquad (15)$$

where $\sigma = 5.7 \times 10^{-5}$ c.g.s. units and is called Stefan's constant. (This is for unit area of surface.) The sun is about 6000° abs., a tungsten lamp about 2000°; hence per equal area the sun emits 3^4 (or eighty-one) times as much as the lamp. (These are not black bodies but the law applies approximately.)

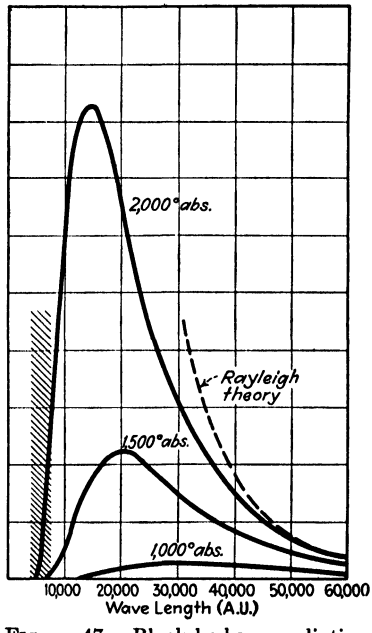


FIG. 47.—Black-body radiation. (Visible region hatched.)

"Red Hot and White Hot."—The quality of the emission as well as its quantity varies; at low temperatures the emission can be felt but is invisible (infra-red); when the temperature is raised, the body becomes first red hot, then red-yellow hot, and finally (when it emits all colors) we call it white hot.

The distribution of the emission among the different parts of the spectrum is shown in Fig. 47 for several different temperatures. The wave lengths are given in angstroms. The visible region lies between 4000 and 7500 angstroms. The greater part of the emission is for any available temperature in the infra-red. As the temperature rises, the curve as a whole rises rapidly, since the total emission (its area) is proportional to the fourth power of the temperature; but at the same time the curve shifts toward the visible. At 1000° abs. (727°C.) the visible red is just beginning to show and the maximum is at a wave length of 30,000 angstroms; at 2000° abs. (incandescent-lamp temperature)

the maximum is at 15,000 angstoms and at 6000° abs. (solar temperature) at 5000 angstroms.

The same thing can be stated in terms of frequency. At 1000° abs. the ether waves are vibrating in many modes, faster and slower, but the most intense vibration has a frequency of 300,000/30,000 or 10 vibrations per subsecond. Double the temperature and the maximum has shifted to 20 vibrations per subsecond. Raise it sixfold to the temperature of the sun and the maximum falls in the visible (green) at 60 vibrations per subsecond. This is the substance of *Wien's displacement law:* with rising temperature the emission curve shifts over to higher frequencies; corresponding frequencies are proportional to the temperature.

The first careful emissivity measurements were made by Lummer and Pringsheim in 1899.

Energy Partition in the Ether.—Now all of this perhaps seems commonplace enough to you and me, but to the mathematical physicist it seemed very amazing. Thinking in terms of the laws of chance, of equipartition of energy, of increase in entropy, he felt that most of this radiant energy should appear not here in the infra-red but in shortest conceivable wave lengths. His reasoning was interesting. The type of black body which is always used in these radiation measurements is a hollow box with a hole in it. This hole is, of course, the perfect absorber. This box serves as a quiet pool of ether in which the electromagnetic waves, moving back and forth from the heated walls, should soon establish equilibrium conditions. We may liken it to a pool of water. If we throw a rock into the water pool, large waves are sent out; these large waves are reflected, break up into smaller waves, the smaller waves into ripples, and the ripples become smaller and smaller and smaller until finally the energy is localized in that undirected molecular motion which we call heat. The law of equipartition of energy can be applied to waves. It states that, in the ultimate equilibrium, the energy to be found in waves of each different possible wave length must be equal. Each different wave acts as a degree of freedom. This pool of water (or of ether) can vibrate as one "loop" or can have a node in the middle, or two or three; it may have a countless variety of small waves, only a few large ones. The vibrations resemble the standing waves in a string. A string a meter long has about a hundred different modes of vibration longer

than 1 cm.—how infinitely many modes of shorter wave length! The energy for each mode of vibration is to be the same, no more in the single longest wave than in any single one of the countless short ones. Therefore practically all of the energy must appear in the infinite numbers of infinitesimal ripples.

In water or in any other material body this process of breaking up into smaller and smaller waves must stop when we reach atomic dimensions. Surely a wave of atoms shorter than the distances between atoms cannot be; there is nothing there to wave. In the ether there is no such limitation. Wien and Lord Rayleigh and Planck and the others expected from their analysis of black-body radiation that, if long red rays were present, these would break up into violet rays, twice as many types of violet waves, twice as much energy. And then into still more kinds of ultra-violet waves, still more energy. And thousands of more modes of vibrations in the x-rays, and still more gamma rays, and then shorter unknown rays. Indeed this reasoning led to an infinite number of waves shorter than the shortest observable wave and all the radiant energy in that region. Actually in this range there is no energy; except at the highest temperature the energy maximum is in the infra-red.

Now a mathematical physicist does not like to admit that he does not know what he is talking about. He starts with some facts, pins these facts down with numbers, and then follows where those numbers lead him—such is the logic of mathematics. And if the result is in error, it must be that his assumed facts were not facts. Now the chief "fact" that Rayleigh put into his reasoning machine was this: Any kind of ether wave is possible, of any wave length, of any intensity. Could this be wrong? Could it be that the ether, like matter, is granular, atomic in structure, giving a lower limit to waves? Could there be here, as in material waves, some constraint upon the possible lengths of waves?

Planck's Distribution Law.—I suppose that Planck, in looking over this work, did as any of us would do when we have made a mistake and have failed to get what we know to be the right answer; I suppose that he worked from both ends of the problem. These observed curves for distribution of energy in different wave lengths look something like Maxwell's distribution curves for molecules and the equation may be expressed in about the same form. Actually the function

$$\frac{1}{e^{h\nu/\kappa T} - 1} \tag{16}$$

which is similar (except for the -1) to M-B distribution function, fitted the experimental results very well. Then Planck tried his laws of chance again. This time he worked as follows: Suppose that the radiant energy in the black-body box is divided into small elements each of size ϵ. We can let this energy element be as small as we please; it may approach zero in size, to agree with the usual idea that energy is continuous, infinitely fine grained. We can see in how many ways these energy elements can be shared among the different wave lengths. This is all quite straightforward—only turning the crank of the statistical machine—and it led Planck to the conclusion that the energy should be distributed as

$$\frac{1}{e^{\epsilon/\kappa T} - 1}$$

And then, just as he was about to do the sensible thing and let ϵ approach zero, which would have led to the old wrong result, he stopped. If this ϵ, the smallest element of radiant energy, is proportional to the frequency ν, then the statistician's result will agree perfectly with nature. And Planck made this assumption—not a very "sensible" assumption I am afraid but it happened to be right. Energy is radiated in chunks—quanta.

$$\epsilon = h\nu \tag{17}$$

where h is 6.55×10^{-27} erg-sec. In atomic units h is 3.97. We shall usually use the approximate value 4.

Planck's formula for black-body radiation agrees with the observation perfectly, *i.e.*, within the error of the experiment.

Quanta.—This was revolutionary. Of course, it was not generally accepted for a number of years. The idea is that there is a minimum quantity of energy just as there is a minimum quantity of matter—quanta and atoms. There are 92 species of atoms, each with its atomic weight; there are an indefinite number of sizes of energy quanta, one for every different frequency, the "quantum weight" (so to speak) being proportional to the frequency.

There is an atomicity in electricity. Your electric-power company can furnish you practically any amount of electricity; it cannot split a charge of 1.6×10^{-19} coulomb. A radio station

can send out practically any quantity of radiant energy but, supposing that it is operating at a million cycles per second (10^{-7} cycles per subsecond), it cannot radiate less than 4×10^{-7} atomic erg of energy. This is the sense of the new theory.

Of course, for such low frequencies as those used in radio the quanta are too small to be significant. The energy for radio waves is very finely pulverized indeed; for visible light the granular structure of energy becomes significant, perhaps we may compare it with grains of sand; in the ultra-violet the energy is as small pebbles and in x-rays is as great rocks whose quantum nature cannot possibly be overlooked.

In atomic units Planck's constant is approximately 4. Yellow light (6000 angstroms) has a frequency of 50 vibrations per subsecond. Its quanta are 200 atomic ergs, about 2 *e*-volts in size. For red light the quanta are in the neighborhood of 170 atomic ergs, for green 220 atomic ergs, blue 240, violet up to 300; for x-rays of 1 angstrom length ν is 300,000 and the quantum is 1,200,000; for short gamma rays the quantum of energy is over 100 million units (over a million *e*-volts).

We may compare these large quanta with the energy of the average monatomic molecule at ordinary temperature. At 300°abs. $\frac{3}{2}\kappa T$ is about 4 atomic ergs—no wonder visible radiation is not emitted from a solid at this temperature, no wonder the emission of radiant energy is in the infra-red. Even at 1200°abs. when red light is being emitted the mean energy, potential and kinetic, of the atoms in the solid is only 16 atomic ergs, about one-tenth of that making up the quantum of red light.

Where Degrees of Freedom Cease to Function.—The black-body radiation curve drops off at high frequencies because at these frequencies the energy quanta are individually so great that there is very little probability of such amounts of energy being available for a single degree of freedom. This is especially true at lower temperatures. The mean energy-wealth of the community is too small. (The 10-ct. store does more business than the store with exclusive prices in a nonexclusive neighborhood.)

X-rays do not come in for their share in the equipartition of radiant energy because they are too greedy—asking for too large quanta, they get none. Here is a limitation to the equipartition of energy. Many other similar instances will appear. Vibrating atoms in the molecule or in a solid, or revolving electrons in the

atom, whatever the mechanism whenever the frequency is too high the degree of freedom, demanding its extravagantly large quanta, usually fails to come in on the partition, except in very "wealthy communities" (*i.e.*, at high temperatures).

Photons.—This theory of Planck's was not received exactly with open arms. Most physicists felt it were better to leave black-body radiation unexplained than to pull down the whole wave theory of light. Planck tried to soothe these fears of the conservatives. He insisted that radiant energy was emitted as quanta but (said he) this does not necessarily mean that light consists of particles. It means only that a certain number of the light waves, or, more exactly, waves totaling a certain definite energy, must be emitted as a unit. The wave theory was preserved but there was a certain restriction placed on the amount of vibrating energy. Einstein accepted Planck's theory and indeed went a step further: he supposed light to consist of particles, *photons* as they came to be called.

So after two hundred years the old theory of Newton came back on the stage. Strange that Newton's optics was called back by the same man who after two hundred years challenged the Newtonian mechanics—and in the same year 1905. Einstein applied the theory to the photoelectric effect.

Theory of Photoelectric Effect.—Einstein's theory of the photoelectric effect was as simple and direct as Planck's theory of radiation was complicated. Said Einstein: when light falls, photon by photon, on a piece of metal, these photons will, if their energy ($h\nu$) is sufficient, cause electrons to be emitted. For an electron to leave a surface in this fashion requires a certain amount of work; this is indeed the latent heat of evaporation of an electron (W_0); any further energy will appear after evaporation as kinetic energy ($\frac{1}{2}mv^2$). Hence when the quantum of energy is delivered to an electron, we have

$$\frac{1}{2}mv^2 = h\nu - W_0 \tag{18}$$

This is Einstein's photoelectric equation. It might seem reasonable that more intense light would produce electrons with greater velocity. Einstein said no, velocity depends on the color of the absorbed light. After allowing for the energy of vaporization (W_0), the square of the electron velocity increases proportionally with the frequency of the exciting light.

Nine years later this equation was strikingly verified by Millikan. The greatest care was necessary to have absolutely clean surfaces; others had distilled metals in a vacuum and tested the photoelectric effect of surfaces which have never been in contact with the air; Millikan devised a machine which would cut fresh surfaces of sodium, potassium, etc., inside the vacuum chamber—"the machine shop in a vacuum" it came to be called. As a result of these experiments Millikan showed that the energy ($\frac{1}{2}mv^2$) did indeed (except for the constant W_0) vary directly as the frequency. *And the constant of proportionality was Planck's constant, h!*

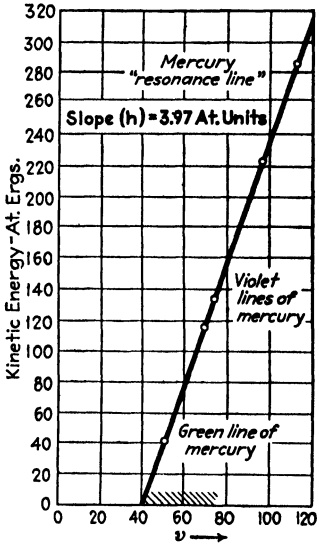


FIG. 48.—Energy of photoelectrons as function of exciting frequency.

Heat of Vaporization of Electrons.—Each metal has its own characteristic heat of vaporization (work function) of electrons W_0 and hence each has a critical frequency limit below which electron emission cannot occur. Electrons are most readily removed from the alkalis. For caesium the value of W_0 is about 180 atomic ergs[1] and hence the threshold frequency is 45 vibrations per second or the threshold wave length is 6500 angstroms (red). When such light falls on the metal, the electron barely escapes with zero speed. If green light or violet light or ultra-violet or x-rays fall upon the metal, the ejected electron has velocity proportional to the square root of the excess of the frequency over the threshold value.

Consider again the remarkable way in which this photoelectric effect acts. If into a pool of water a plank is dropped, a wave goes outward, extending and growing less and less intense as it goes. Surely we should not expect all the energy of this wave to act upon some other distant plank floating on the water and throw it upward to a height equal to that from which the first plank fell. Rather we should expect dissipation of energy. But when an electron is suddenly stopped and hence emits

[1] Compare with 40 atomic ergs, the heat of vaporization of water.

radiation, it sends out into the pool of "ether" a wave which acts in its entirety upon some single other electron, possibly 90 million miles away, giving to this latter a speed equal to that which the first originally had. No wonder that Einstein felt doubtful about this wave picture, felt the need of a "photon."

Rubidium finds its threshold for the photoelectric effect in the yellow, potassium in the green, and sodium in the blue. The nonalkalis require ultra-violet light for photoelectric emission. For platinum W_0 is 500 atomic ergs (see Table 19) and the threshold frequency is 125 vibrations per subsecond. Alkalis are the prime electron losers of all the elements; they are the formers of positive ions *par excellence*. The photoelectric effect gives an independent method of measuring the heat of vaporization of the electron. The agreement between these values of the work function W_0 and the values obtained from thermionics is conclusive evidence of the soundness of the theory.

Now this theory of Einstein's was predicated on the assumption that light is absorbed in quanta, of value $h\nu$. (Planck had required only *emission* by quanta.) If a single quantum of light as emitted spreads out in all directions as an expanding wave, how can that energy be reconcentrated into some single photoelectron? This was a quandary for Einstein and he advocated the corpuscular theory of light. At the time few followed him to this conclusion. The photoelectric effect at all events certainly confirmed conclusively the fundamental quantum hypothesis. But by 1914, when the conclusive experiment of Millikan was performed, the quantum theory was already generally accepted.

TABLE 20.—VALUES OF h AS DETERMINED BY DIFFERENT METHODS[1]

Total radiation (Stefan's constant, p. 153)	6.539
Spectral distribution of radiation (p. 156)	6.548
Rydberg constant (p. 192)	6 547
Photoelectric effect (p. 159)	6.543
Continuous emission of x-rays (p. 260)	6 550
Ionization potential (p. 215)	6.560

[1] Compiled by R. T. Birge, *Rev. Mod. Phys.*, Vol. 1, 1929.

Specific Heats at Low Temperature.—In the decade after its pronouncement the new theory of Planck received two confirmations. One has just been mentioned; the other also originated with Einstein and the theory was developed in improved form

by Debye. We have seen (page 63) that in most cases the atomic heats of solid elements are approximately 6. Several light elements have anomalous values. For example, the atomic heat of carbon as diamond is 1.5 and as graphite is 2.0. But these unduly low atomic heats increase as the temperature is raised; the atomic heat of diamond is 5.3 at 600°C. And, on the other hand, every substance becomes "anomalous" at sufficiently low temperature. The atomic heat even of lead (one of the heaviest elements) is 2.5 at the temperature of liquid hydrogen (−253°C.).

TABLE 21.—ATOMIC HEATS OF LIGHTER ELEMENTS AT 20°C.

Lithium	5.5
Beryllium	3.8
Boron	3.3
Carbon:	
Diamond	1.5
Graphite	2.0
Sodium	6.8
Silicon	5.0

Such anomalies were quite inexplicable on the basis of simple equipartition of energy. The quantum theory suggested a solution. Einstein and Debye remarked that light atoms would have high natural frequencies of vibration in the crystal; hence the quantum of vibrational energy would be large and hence, as they demonstrated, this mode of vibration would be largely unexcited at low temperature. For instance, in diamond the highest natural vibration frequency is 4 vibrations per second with a corresponding element of energy ($h\nu$) of 16 atomic ergs; on the other hand, the heavy lead atom vibrates only once in 5 subsec. ($\nu = 0.2$) and the energy quantum is 0.8 atomic erg. Evidently at ordinary temperature where the mean energy per oscillator is 7½ atomic ergs,[1] the average lead atom will have nearly 10 quanta of energy, some more, some less. The diamond

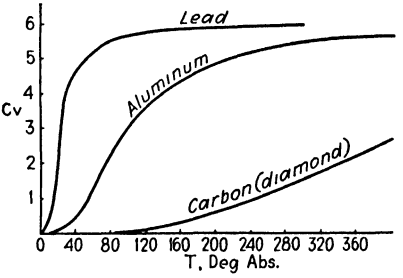


FIG. 49.—Atomic heats of lead, aluminum, and diamond.

[1] $3\kappa T$ for an oscillator with three degrees of freedom. But this average value is somewhat modified here in the quantum theory.

atoms, demanding 16 atomic ergs, are apt in most cases to get none.

Einstein assumed that each crystal had but a single frequency, that of the individual atom vibrating under the influence of its binding forces; Debye recognized that groups of atoms could also vibrate as a unit giving many lower frequencies. Einstein's original theory was quite successful; Debye's theory agreed almost exactly with the experimental values. The theory ties together with great exactness the specific heats, the hardness, the melting points. (For the effect of hardness compare diamond and graphite or silicon and sodium.) The natural vibrational frequencies, of course, depend upon the lightness of the atom and the stiffness of the binding forces.

The Limitation of Equipartition.—At low temperatures certain degrees of freedom of highest frequency are lost to the statistical equilibrium of the solid. This is a most consequential idea. In the old kinetic theory each atom was thought of as a rigid ball. Although from its spectrum its interior structure seemed to be "more complicated than a grand piano," as it played its role in the gas equilibrium an atom acted as a single rigid particle. Why did not the electrons and protons in the interior, each key and string of the "grand piano," come in for its share of energy? When two hydrogen atoms are united as a molecule, the molecule can rotate; why not vibrate? Why this rigid protection of the interior of atoms and molecules from the vicissitudes of collisions? The answer we find in the quantum theory. The frequencies of electron rotation in the atom, of atomic vibrations in the molecule, are too high; the energy quantum is too great; these degrees of freedom are not excited at ordinary temperatures.

In the molecular world there is the law of equipartition of energy. But this partitioning does not go so far that each atom within the molecule, each electron or proton within the atom, can claim its share of the energy. It is the quantum theory which puts a limit to this dividing and subdividing of energy. It is the quantum theory which makes the molecule the natural unit in the gas community.

Before its tenth birthday the quantum theory was applied to these three fundamental problems—problems in three divergent fields, one in radiation, one in photoelectricity, one in specific heats. In each case it led to an exact solution of the problem.

Such problems did not occupy the center of the stage, however, and the young theory was generally ignored. But when, two years later, Bohr used the theory to elucidate the nature of the atom and the significance of spectra, the case was different. Then the quantum theory achieved its true position as one of the most fundamental of physical laws.

CHAPTER XIV

SPECTRUM SERIES

We meet spectra: absorption and emission, line and band, principal and sharp, singlet and triplet; the Balmer series, red, blue, violet, and on into the ultra-violet—and other hydrogen spectra—and spectra from other elements all cut to the same pattern. Facts and relations in this chapter but none of the "reasons why."

The spectrum is the language of the atom. Newton broke white light into its components; Fraunhofer observed the absorption lines of the solar spectrum. In 1859 Kirchhoff and Bunsen laid the foundations of spectrometric chemical analysis.[1] A few years later Balmer discovered the series which is associated with his name. By the close of the century a great collection of spectroscopic data was available. This is summarized in 5000 pages in Kayser's "Handbook of Spectroscopy."

These accumulated data were the words of the atom but until Bohr's time they lacked an interpreter. Bohr's theory was the Rosetta stone for the atomic world. With that theory a new period, the golden age of spectroscopy, began. Vast accretion of fundamental spectroscopic lore went hand in hand with interpretation. Within ten years even the more complicated spectra of iron and of manganese, etc., were being successfully analyzed.

Spectrum Types.—The reader should have some familiarity with spectra. It is to be hoped that he has had the opportunity to see for himself several types of visible spectra—absorption, emission, line, band, continuous, etc. He should become acquainted with several characteristic line spectrograms. As an introduction let us look at a few types of spectra as illustrated in the "Encyclopaedia Britannica." (This reference will certainly be accessible to all.)

Plate 1 ("Encyclopaedia Britannica," Vol. 21, p. 182) shows spectrograms, natural size, as taken with a large quartz spectro-

[1] It is possible to detect spectroscopically a billionth of a gram of sodium. Most of the newer elements have been discovered spectroscopically.

graph. Panchromatic films were used. These films are evidently sensitive well up into red at 6800 angstroms—rather less sensitive in the green in the neighborhood of 5000 angstroms.[1] The visible portion of the spectrum extends down to 4000 angstroms. The thousands of lines in the iron arc are shown in the lower spectrograms. They extend down to about 2250 angstroms. The quartz prism and lenses of the spectrograph begin to absorb the light in this region; quartz becomes quite opaque for wave lengths below 1800 angstroms.

The upper set of spectrograms shows the absorption characteristics of several kinds of glasses. Vita glass transmits very well down to 2700 angstroms. Crown and flint glass show marked differences. Wood's remarkable glass (often used in ultra-violet demonstrations) is nearly opaque throughout the visible but transparent to the near ultra-violet.

The second series of spectrograms shows the solar spectrum, extending down to about 3100 angstroms; some absorption lines are seen, not very clearly in the visible.

Plate II shows characteristic types of spectra. Figures 2 and 4 are absorption spectra; others are emission spectra.

Of all spectra the simplest is that of the hydrogen atom. Figure 6 shows the first six lines of this spectrum: H_α in the red, H_β in the blue, H_γ and H_δ in the violet. Beyond the last line shown here others can be found, coming closer and closer together in regular progression, giving the "Balmer series."

A beautiful example of another similar series extending to over 20 lines is found in the "principal series" of potassium (*2b*). Only the first line of this series is in the visible part of the spectrum. The plate represents an absorption spectrum. (In *2a* is shown a rather unusual phenomenon—line absorption in a solid; see the note on page 111.)

Gaseous spectra are either of the line or of the band type. The spectrograms *1a* and *1b* show the line spectrum and the band spectrum of nitrogen. Line spectra are characteristic of monatomic molecules; here it is obtained from dissociated nitrogen molecules. The bands are in reality composed of many close lines, and such spectra are obtained from diatomic or polyatomic molecules. The discussion of band spectra will be postponed to Chap. XXIII.

[1] Dim green light is sometimes used in the developing room when handling panchromatic films.

The spectra obtained at low voltage and high voltage (as in the metal arc and in the spark, respectively) are rather different. Figure 3 illustrates this. Spectrogram 3*b* is due to the excitation of a single electron in the atom. The additional lines appearing in 3*a* ("spark lines") are due to the excitation of two or more electrons in the atom, which can take place only at higher voltage.

Very simple series were shown in 2*b* and 6. Usually the series are more complicated than these. In the first place, several different types of series may exist and the lines of these different series may overlap. In 2*b* was shown the principal series (absorption) of potassium. Spectrograms 8 and 9 show similar series (but in this case for emission lines) for other alkalis. The red color of the lithium flame and the yellow color of sodium flame are due to the first lines of the principal series. (These were not panchromatic plates and the first lines of the principal series do not appear on the spectrograms shown in Plate II.) For sodium the wave length of the first line is 5890 (5896) angstroms followed by 3302, 2852, 2680, etc., the series approaching a limit at 2513 angstroms. But there is also a "sharp series" (5152, 4752, 4546 angstroms, etc.) and a "diffuse series" (4983, 4669, 4500 angstroms, etc.). (The other lines shown in these spectrograms are due to impurities, chiefly air.)

Not only do we find in every substance[1] several series; principal, sharp, diffuse, etc., instead of one, but also each individual line of the series usually is broken up into a *multiplet*. Although it cannot be seen on these spectrograms, each of these lines in the lithium and sodium and potassium spectra is in reality a *doublet*. The first member of the principal series of sodium is not one line but two, differing 0.1 per cent in wave length (5890 and 5896 angstroms).

The separation in multiplet components is much greater in zinc (Fig. 10), and it is even greater in cadmium (which is present in Fig. 10 as impurity). Here the lines are triplets rather than doublets. The sharp (*S*) and diffuse (*D*) series of triplets are shown running from the visible far down into the ultra-violet, five members of each series.

These are samples of the very simplest spectra. Multiplets of much greater complexity sometimes occur. Such a multiplet

[1] For even in hydrogen very high resolution shows that the lines of the Balmer series are complex (p. 189).

of iron with 15 components is shown in 7. This high multiplicity accounts for the complexity of the iron spectrum; notice in Fig. 4 the great number of lines in a very small part of the iron spectrum. Notice that Figs. 4 and 7 are on much larger scales than the other spectrograms (compare with Plate I, where the region 4400 to 4500 angstroms extends but an eighth of an inch). The iron spectrum, so rich in lines, is often used for comparison, as a secondary standard, to compare other wave lengths (Fig. 5).

This has been a hurried survey over the field. These spectra must be directly perceived in all their prismatic beauty; there is something satisfying to the eye in seeing these purest of colors. And as we contemplate the meaning of all of these radio messages from the atomic world, our imagination and curiosity are piqued. There must be a great story behind all of this.

Wave Length and Frequency.—The wave length (λ) is usually expressed in angstroms. The frequency (ν) is given by $\nu = c/\lambda$. In using normal units c is 3×10^{10} cm. per second and the wave length must be reduced to centimeters. The frequency of yellow light ($\lambda = 6000$ angstroms) is

$$\frac{3 \times 10^{10}}{6000 \times 10^{-8}} = 5 \times 10^{14} \text{ per second}$$

In atomic units the frequency is a conveniently small number—the velocity of light in these units is 300,000. This divided by the wave length in angstroms gives the vibrations per subsecond. Red light has a frequency of approximately 40 (*i.e.*, 300,000 ÷ 7500); yellow light, 50; the shortest visible violet light, 75 vibrations per subsecond.

In the succeeding chapters, as we try to unravel the meaning of the atom, we must be continually discussing frequencies—the number of revolutions of an electron or vibration of a molecule or alternations of a light wave in a subsecond. We have noted how comparatively infrequently come the collisions between gas molecules (about one in a thousand subseconds under S.C.); we have seen how the diatomic molecules (Table 6) usually take some 5 or 10 subsec. for a rotation. Now we deal with faster alternations—from 40 to 75 cycles per subsecond for the visible. And ultra-violet and x-rays still higher, into the thousands and millions.

A very little has been selected for illustration from the vast body of spectroscopic data; even this little can be confusing at a first reading. Out of it must come a realization of relative frequencies and the laws governing frequencies. And for any frequency of radiation, the quantum of energy is (approximately) 4ν.

The Best Known Hydrogen Series.—Figure 50 shows the Balmer lines of hydrogen as observed in the spectrum of a star.

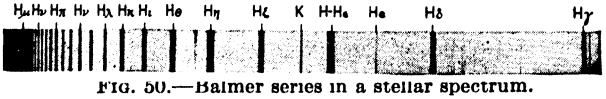


FIG. 50.—Balmer series in a stellar spectrum.

In Table 22 are given the wave lengths and frequencies of the spectrum of hydrogen which is found in the visible and near visible. The lowest frequency is 45.7 vibrations per subsecond (the red line). This, with the three following lines, constitute the visible spectrum. More than 20 additional lines have been observed, coming nearer and nearer together and approaching a limit of 82.2 vibrations per subsecond.

TABLE 22.—BALMER SERIES

	Wave length, angstroms	Color	Frequency per subsecond	Limit ×
H_α	6563	Red	45 7	$\frac{5}{9}$
H_β	4861	Blue	61 7	$1\frac{2}{16}$
H_γ	4340	Violet	69 1	$2\frac{1}{25}$
H_δ	4102	Violet	73 1	$3\frac{2}{36}$
H_ϵ	3970	.....	75 6	$4\frac{5}{49}$
H_ζ	3889	.....	77 2	$6\frac{9}{64}$
H_η	3825	.....	78 2	$7\frac{7}{81}$
	....	30 lines observed		
Limit	3647	.....	82.2	

Now, it will be noticed that the frequency of the first line is exactly five-ninths of the limiting frequency, the next line is twelve-sixteenths (or three-fourths), the next twenty-one twenty-fifths of the limit, and so on. The denominators of these fractions are the natural squares (9, 16, etc.) and the numerators four less. Balmer (1885) observed this simple relation and gave the true series relationship; the series has been given his name.

The simplest way of expressing the frequencies of this Balmer series is

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

where the value of R is 329 and n is any integer larger than 2. This is the Balmer formula; the constant R is called the *Rydberg constant.* Taking $n = 3$, we get $\nu = 329(\frac{1}{4} - \frac{1}{9}) = 45.7$, the frequency of the first line of the series; the next has a frequency of 329 $(\frac{1}{4} - \frac{1}{16})$, etc. As n is made larger and larger, the second fraction becomes smaller and smaller and the frequency approaches as a limit $329 \times \frac{1}{4} = 82.2$ vibrations per second.

A Far Ultra-violet Spectrum.—It was many years after Balmer's day before the technique was developed so as to take spectrograms for wave lengths as short as a thousand angstroms. The name of Lyman (of Harvard University) is associated with this work in the far ultra-violet. He discovered in this region a new spectrum of hydrogen with a limiting frequency exactly four

TABLE 23.

FAR ULTRA-VIOLET SERIES

Wave Length		Frequency
Lyman Series		
1,216		246.8
1,026		292.5
973		308.5
.....		.....
912	Limit	329.0
INFRA-RED SERIES		
Paschen Series		
18,751		16.0
12,817		23.4
10,938		27.4
.....		....
8,206	Limit	36.6
Brackett Series		
40,500		7.4
26,300		11.4
.....		....
14,600	Limit	20.6

times that of the Balmer series. The frequencies of the new series are given by an extension of the Balmer formula:

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

where n is any number larger than 1. (This Lyman series was discovered in 1915.) The limiting frequency ($n = \infty$) is, of course, here equal to R (*i.e.*, 329 vibrations per subsecond).

Infra-red Spectra.—Analogous to these spectra with limits R and $\frac{1}{4}R$ should we not expect other series in the infra-red with

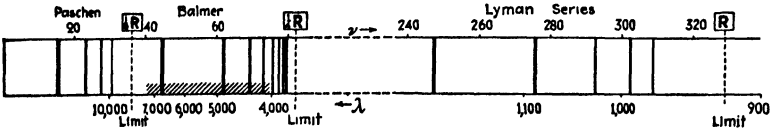


FIG. 51.—Complete spectrum of hydrogen.

limits at $\frac{1}{9}R$, $\frac{1}{16}R$, etc.? Actually such have been found by Paschen and by Brackett. These series have the formulas

$$\nu = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \text{ Paschen series (discovered 1896)}$$

$$\nu = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \text{ Brackett series (discovered 1922)}$$

One line of a series with limit at $\frac{1}{25}R$ has also been observed in the very far infra-red and doubtless it is only the experimental difficulty which prevents finding more of the lines and still other series. In general the frequencies of hydrogen are given by

$$\nu = R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{19}$$

where n_1 and n_2 are integers, n_2 being the larger. Placing n_1 equal to 1, 2, 3, 4 gives, respectively, the Lyman, Balmer, Paschen, and Brackett series.

Relations between Series—Ritz Combination Principle.—The limiting frequency of the Balmer series (82.2 vibrations per subsecond) is equal to the difference between the first line and the limit of the Lyman series; the limit of the Paschen series equals the difference between the first line and the limit of the Balmer series. This can be seen from the table; the relation can be seen to follow directly from the series formula. We can thus easily compute the limits of series which have never been observed.

Ritz observed (1908) that the sum or difference of two frequencies often gives the frequency of another line of the spectrum. This is illustrated here in the spectrum of hydrogen. If the frequency of H_α is added to that of the first line of the Lyman series, it gives that of the second line. H_β or H_γ similarly

combined gives the third or fourth line. The difference between H_α and H_β gives the first line of the Paschen series; $H_\gamma - H_\beta$ gives the first line of the Brackett series. So the whole spectrum can be worked out from the Balmer lines with the aid of the combination principle. The difference in frequencies between any two lines of this series always gives a line of another series.

Spectroscopic Terms.—The frequency of each line is seen to be given as a difference between two terms. In the Balmer series the first term is 82.2 (*i.e.*, $\frac{1}{4}R$); the second term takes the values $\frac{1}{9}R$, $\frac{1}{16}R$, etc.; the whole story of the hydrogen spectrum is summarized by the values of these *spectroscopic terms.* With somewhat greater precision than we have previously used, these values are tabulated in Table 24.

TABLE 24.—SPECTROSCOPIC TERMS R/n^2 FOR HYDROGEN
(Vibration numbers)

n	1	2	3	4
Term[1]	329.033	82.258	32.559	20.564
Wave number	109,678	27,419	12,186	6,855

[1] Computed using $c = 3 \times 10^{10}$ cm. per second. The most precise value is $c = 2.99796 \times 10^{10}$ cm. per second but it will be simpler to consistently use the round number 3×10^{10}.

Exactness of the Series Formula.—The spectrometer yields some of the most accurate results obtainable by measurement. The probable error for exactly measured wave lengths is usually of the order of 1 part in 10 million. And yet the Balmer formula agrees with results within the probable error of the experiment. Below we compare the observed values and those computed from the foregoing terms which are based upon a value of Rydberg's constant of 329.033073.

TABLE 25

	Red	Blue	Violet	Violet
Frequency (theoretical)	45.6990	61.6937	69.0969	73.1184
Wave length (theoretical)	6563.04	4861.49	4340.66	4101.90
Wave length (observed)	6563.07	4861.52	4340.52	4101.90

The Wave Number.—Wave numbers rather than frequencies are usually computed in the literature. In ordinary units the frequency of light (waves per second) is always an inconveniently large number (10^{13} times greater than in our system). By the wave number ($\bar{\nu}$) is meant the number of *waves*

per centimeter. It is found by taking the reciprocal of the wave length (in centimeters). $\tilde{\nu}$ is 3×10^{10} times smaller than ν(c.g.s.). We obtain these wave numbers of conventional use from our ν(atomic units) by dividing the latter by 3 and multiplying by a thousand. The visible spectrum extends from $\tilde{\nu} = 14{,}000$ to $\tilde{\nu} = 25{,}000$. The limit of the Lyman series is $\tilde{\nu} = 109{,}677.7$ waves per centimeter.

When we use wave numbers rather than frequencies in the hydrogen formula $\tilde{\nu} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$, the Rydberg constant equals 109,677.7. This is the value found in the literature. Since with the atomic-unit system the frequencies are small numbers, we shall in general use the frequency ν rather than the wave number $\tilde{\nu}$ and take $R = 329$ (approximately).

Correspondence Principle.—This series relation as found by Balmer was quite inexplicable to the physicists of his day. With the atom thought of as an electric vibrator, series would indeed be expected but these series should consist of a fundamental and overtones of twice, three times, four times, etc., the fundamental frequency. Now as a matter of fact if we could go to spectra extravagantly far in the infra-red, we should find there approximately this relation holding. Consider a series far beyond the Brackett series, as

$$\nu = 329\left(\frac{1}{20^2} - \frac{1}{n^2}\right)$$

The first lines of this series have frequencies 0.075, 0.145, 0.200, 0.250, etc., approaching the limit 0.82 vibrations per subsecond. Here the frequencies roughly appear as fundamental and first, second, third, etc., harmonics. This is another instance of phenomena agreeing with classical theory at low frequencies and diverging more and more from it as the frequency is increased.

When we shake an egg or rotate it back and forth not too rapidly, the egg acts as a rigid body, much as an oval stone. At higher frequencies its nature betrays itself; you cannot spin an uncooked egg. I wonder if we may not find in this an analogy. At higher frequencies the inner nature of electrons and protons, their hardness, softness, rigidity, fluidity—whatever term one uses for electron and proton properties—begins to play a role and the ordinary mechanics which treats them as particles breaks down.

However this may be, certainly the correspondence with classical theory invariably occurs at low frequencies and invariably breaks down at higher frequencies. Bohr recognized this and

made it his "correspondence principle." It was the guiding principle in the upbuilding of his system of atomic theory.

More Complicated Series Formulas—the Defect.—The hydrogen series which have been considered are the prototypes of the series found with other elements. With these other elements, however, the series become more complicated and the series relations found are only approximate. The essential difference is that the terms now become $R/(n+\epsilon)^2$ where ϵ is a fraction to be added to the whole number n. ϵ will be called the "defect."

The general form of the series is as in hydrogen. This fact was discovered by Rydberg (1910). The same Rydberg constant[1] is used and the frequencies of the lines are given by a difference of two terms. Very significant these common properties of all spectra!

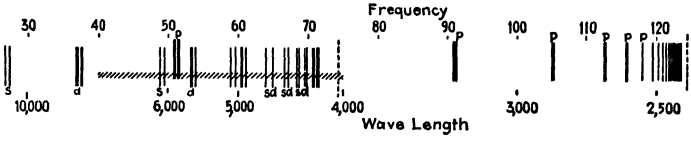


FIG. 52.—Spectrum of sodium vapor (with exaggerated doublet intervals).

So the frequency of the yellow line of sodium is given by $\nu = 329\left(\frac{1}{1.626^2} - \frac{1}{2.116^2}\right) = 50.8$ vibrations per subsecond, the defects of the two terms being 0.626 and 0.116, respectively. The defect can assume several different values; the result is that, corresponding to a single series of terms of hydrogen, there will be several series each characterized by its own defect in the case of heavier elements.

Alkali Series.—The Rydberg constant R (329 vibrations per subsecond) or (for spark spectra) a multiple thereof is the basic frequency number in all spectra.

The spectrum of sodium is quite typical of the alkalis. In the most important lines four different shielding defects are found. In the S terms the value of the defect is between 0.6 and 0.7; in the P terms it is about 0.1; in the D terms it is about -0.01 and in the F terms -0.001. More exact values are given in Table 26.

Principal Series.—The "principal series" of sodium consists of the lines

[1] Except for a correction of about 0.05 per cent (p. 191).

λ	5890	3302	2852	2680	2414
ν	50.8	90.7	105.1	111.9	124.3 etc.

The series formula is

$$\nu = 329\left(\frac{1}{(1+S)^2} - \frac{1}{(n+P)^2}\right)$$

where S equals 0.626 and the first term equals 124.3; the second (variable) term is given by

$n+P$	2 116	3.133	4.138	5.140
Term	73.5	33.8	19.2	12.4

This series expression can naturally be made as accurate as we please by choosing the proper values of the defects P; when we speak of an exact series relationship, however, it is implied that P should be constant. To what extent this is true is evident in the foregoing figures—ϵ (in this case P) is constant as to order of magnitude, but, especially between the first two terms, it is by no means exactly constant. The series relationship here is only suggestive rather than exactly valid. It is not, as in the case of hydrogen, an exact law.

Other Alkali Series.—The more important series found in the alkali metals are:

$$\begin{aligned}
&1.\ \text{Principal:}\quad R\left(\frac{1}{(1+S)^2} - \frac{1}{(n+P)^2}\right) \text{ written } 1S - nP\\
&2.\ \text{Sharp:}\quad\ R\left(\frac{1}{(2+P)^2} - \frac{1}{(n+S)^2}\right) \text{ written } 2P - nS\\
&3.\ \text{Diffuse:}\quad R\left(\frac{1}{(2+P)^2} - \frac{1}{(n+D)^2}\right) \text{ written } 2P - nD\\
&4.\ \text{Bergmann:}\ R\left(\frac{1}{(3+D)^2} - \frac{1}{(n+F)^2}\right) \text{ written } 3D - nF
\end{aligned} \qquad (20)$$

Of these four series one has the limit $1S\left(\text{symbolic for } \frac{R}{(1+S)^2}\right)$, two have the limit $2P$, and one the limit $3D$. For sodium these limits are, respectively, at 2414 angstroms in the ultra-violet, at 4080 angstroms in the violet, and at 8150 angstroms in the infra-red.

While these are the more important series, others can be found such as those of the principal series type $2S - nP$ or

$3S - nP$. Such series in each case will be in the infra-red, more or less inaccessible. The ones listed above are the strongest and most important.

Comparison with Hydrogen.—The values of the S, P, D, F terms for sodium are given in Table 26.[1]

TABLE 26

Hydrogen	n	1	2	3	4
	Term	329	82.3	36.5	20.6
S	$n + S$	1.626	2.643	3.647	4.649
	Term	124.3	47 1	24.8	15.2
P	$n + P$	.....	2.116	3.133	4.138
	Term	.....	73.5	33.6	19.2
D	$n + D$	.....	.....	2.990	3.988
	Term	.....	.....	36.8	20.7
F	$n + F$	.....	.....	.....	3.999
	Term	.....	.....	.....	20.6

Effective Term Number and Terms for Sodium.—The values of the S, P, D, and F defects can be read from the table. The defect is -0.010 for the $3D$ term, -0.001 for the $4F$ term. The D and more especially the F defects are seen to be very small. The corresponding terms differ little from those of hydrogen.

The frequency of any line is given as the difference of two terms; *e.g.*, for the principal series

$$\nu = \frac{329}{(n + S)^2} - \frac{329}{(n + P)^2}$$

From the values of these separate terms the frequencies of each spectrum line can be obtained by subtraction. The yellow line of sodium is $(1S) - (2P) = 50.8$.

Let us compare these sodium terms with those of hydrogen. Corresponding to $n = 1$, sodium has its "effective quantum number" $n = 1.626$; and the term is reduced from 329 to 124. The fraction 0.626 is the defect. Corresponding to $n = 2$ are two terms, the first of the P and the second of the S type. The simple term $n = 3$ for hydrogen here breaks up into S, P, D terms; $n = 4$ breaks up into four terms. The defects of the S and P terms are large; for the D and F terms the constants are

[1] Those values (in terms of wave numbers) are given to many more terms in the "International Critical Tables," Vol. 5, p. 401. In some 15 pages here all of the spectral data of the various elements are condensed.

small and negative. The D and F terms are very much "hydrogen-like." The difference indeed between these hydrogen-like terms and the S and P terms with larger shielding defects is very fundamental (page 197).

Multiplets.—This breaking up of a single term in the hydrogen spectrum into several terms with different defects is the first of the complexities introduced when we consider the spectra of other elements. A second complexity is introduced in the finer multiplicity of the term (or line). This we have so far ignored. Actually the "yellow line" of sodium consists not of one but of two lines with wave lengths 5890 and 5896 angstroms. The P, D, and F (but not the S) shielding defects have each two values instead of one. The first of the P defects has values 0.116 and 0.117 and the term has values 73.48 and 73.43. This difference, 0.05 vibration per subsecond, is too small to show a separation on the spectrogram in Fig. 52, were this drawn exactly to scale. The doublet interval is greater for potassium, rubidium, and caesium; in caesium the components in $1S - 2P$ are several hundred angstroms apart.

The alkalis are characterized by this doublet character of the spectrum. In the alkali earths (second periodic group) triplets and singlets are found instead of doublets; in the third group (the earths) quartets and doublets; in the next group quintets, triplets, and singlets, and so on in increasing complexity.

This is the background of spectroscopy which is necessary for our study of the atom; here we have summarized the accumulation of spectroscopic lore which Bohr found awaiting an explanation. Why the simple relations in the hydrogen spectrum: Why the defect? And why the breaking up into multiplets and why the close correspondence between multiplets and chemical properties? And why the Rydberg constant running through all spectroscopy? In brief, what after all is an atom and how does it radiate?

NEWTON
DISCOVERS THE SPECTRUM

Could Rembrandt but have painted him, in those hours
Making his first analysis of light
Alone, there, in his darkened Cambridge room
At Trinity! . . .
. . . He stood there,
Obscure, unknown, the shadow of a man
In darkness, like a grey dishevelled ghost—
Bare-throated, down at heel, his last night's supper
Littering his desk, untouched; his glimmering face,
Under his tangled hair, intent and still—
Preparing our new universe.
He caught
The sunbeam striking through that bullet-hole
In his closed shutter—a round white spot of light
Upon a small dark screen.
He interposed
A prism of glass. He saw the sunbeam break
And spread upon the screen its rainbow band
Of disentangled colours, all in scale
Like notes in music; first, the violet ray,
Then indigo, trembling softly into blue;
Then green and yellow, quivering side by side;
Then orange, mellowing richly into red.

Then, in the screen, he made a small round hole
Like to the first; and through it passed once more
Each separate coloured ray. He let it strike
Another prism of glass, and saw each hue
Bent at a different angle from its path,
The red the least, the violet ray the most;
But all in scale and order, all precise
As notes in music. Last, he took a lens,
And, passing through it all those coloured rays,
Drew them together again, remerging all
On that dark screen, in one white spot of light.

So, watching, testing, proving, he resolved
The seeming random glories of our day
Into a constant harmony. . . . He beheld
Gleams of the great new order and recalled
—Fraught with new meaning and a deeper hope—
That covenant which God made with all mankind
Throughout all generations: I WILL SET
MY BOW IN THE CLOUD, THAT HENCEFORTH YE MAY KNOW
HOW DEEPER THAN THE WRECKAGE OF YOUR DREAMS
ABIDES MY LAW, IN BEAUTY AND IN POWER.

ALFRED NOYES: "*Watchers of the Sky.*"

CHAPTER XV

ATOMS À LA BOHR

The atom is a solar system. But its action is limited to discrete values. Energy and the quantum number. Changing orbits and radiating energy; a remarkable derivation of the Rydberg constant. Energy levels. Ellipses and circles and what of it? Stronger and heavier nuclei—but always with a lone electron. S stands for slim and P stands for phatter. Relativity scores again.

The Bohr theory is based upon an idea of Rutherford's. Rutherford considered the atom to consist of a small positive charge (the nucleus) surrounded by a number of electrons. This differed from the theory of J. J. Thomson who had supposed that the positive charge extended throughout the whole volume of the atom proper and that the electrons were distributed through it—like the plums in a plum pudding. The suggestion of Thomson's had been very fertile; he had suggested

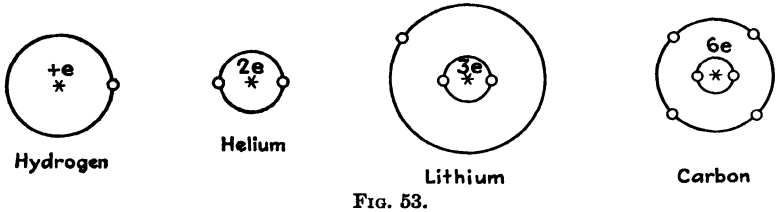


FIG. 53.

the building up of atoms by successive shells of electrons. But Rutherford's newer conception of the nucleus was by no means a gratuitous idea; the scattering of alpha rays had given unmistakable evidence of a small hard nuclear kernel.

A Planetary Theory.—The positive charge (e^*) on this nucleus of the atom is proportional to the atomic number of the element. For hydrogen the charge on the nucleus is equal (except for sign) to the electronic charge, 37.1 atomic units. This smallest of positive charges is called the proton. Outside this, attracted to it, is one electron. The helium nucleus has a charge of 2 protons; 2 electrons revolve about it. In lithium there is a nuclear charge of 3, attracting 3 electrons—and so on through all the elements

up to uranium. The nucleus of uranium has a charge of 92 protons and is surrounded by a cloud of 92 electrons.

The Law of Force.—Why should such atoms not collapse? Why in the case of hydrogen should the electron not fall into the nucleus? Bohr supposed that the electron rotated about the proton just as the earth goes about the sun. In his earliest development he supposed that the electronic orbit was circular. The force of attraction to the proton furnished the centripetal force (mv^2/r) holding the electron in its orbit.

There is then a definite relation between the velocity of the electron and the radius of the orbit. Since the force between two charges (nucleus e^* and electron e) is e^*e/r^2, we have

$$\frac{e^*e}{r^2} = \frac{mv^2}{r}$$

or

$$\frac{e^*e}{r} = mv^2 \tag{21}$$

Here the speed of the electrons is inversely proportional to the square root of the radius. This is the same law that governs the speed of the planets, Mercury, Venus, Earth, Mars, etc., at their different distances from the sun. In fact the theory of Bohr is a planetary theory of the atom. All three of Kepler's laws for planets hold for the motions of the electron around the nucleus in hydrogen.

Rotational Action Quantized.—But this theory meets with one difficulty at the very start. An accelerated charge must, by classical electrodynamics, radiate (page 103). The electron in the hydrogen atom, always with central acceleration, should always radiate energy, tend to slow down, and in consequence it should assume an orbit of ever-decreasing radius; the electron should spiral into the nucleus with ever-increasing frequency of rotation and ever-increasing frequency of the emitted light. The atom should always radiate and shrink to nothing; the atom should radiate but not with a definite set of frequencies as in the observed line spectrum, rather with ever-differing frequencies giving a continuous spectrum.

This was a most fundamental difficulty. Bohr did not compromise with it; he assumed that the classical electrodynamics was wrong and that certain orbits could exist so attuned that in them radiation did not occur. *These unique orbits were those in*

which the action was equal to h or a multiple of h. Only such orbits were possible for the electron. Since action equals momentum (mv) times distance ($2\pi r$) we have the condition

$$2\pi mvr = nh \tag{22}$$

where n is an integer. This is Bohr's quantum condition. It gives a *quantum relation* to be satisfied between v and r as well as the *mechanical relation* of Eq. (21). n is called the quantum number. The smallest possible orbit will have the quantum number 1; *i.e.*, its action equals h. Other possible orbits will have quantum numbers equal to 2, 3, 4, etc., with corresponding multiple values of action.

We may again compare the atom with the solar system. In the actual solar system the earth could, given a slightly different speed, occupy a slightly different orbit; there are no favored orbits.[1] The atom on the other hand is a solar system in which only certain orbits are possible.

From Eqs. (21) and (22) it is now possible to solve for the values of the velocity and the radius, since the other quantities, e, $e,^*$ and m, are known and n is an integer. We can eliminate v, getting

$$r = \frac{n^2h^2}{4\pi^2me^*e} \tag{23}$$

or can eliminate r, getting

$$v = \frac{2\pi e^*e}{nh} \tag{24}$$

Circular Orbits of Hydrogen.—From Eq. (23), it is clear that, since all other quantities are definite constants, the radius must depend upon n, *i.e.*, upon which multiple of the fundamental element of action (h) the orbit in question has. The radii of the different orbits will vary as n^2. (n is called the principal quantum number.) The radius of the fundamental orbit can easily be obtained by the reader. For hydrogen e^* is equal to e, the charge on the electron. The smallest orbit with $n = 1$ has a radius of ½ angstrom.[2]

[1] In the final analysis the restriction to quantized orbits must hold for any motion but this plays no practical role in this astronomical case.

[2] More exactly 0.53 angstrom.

Similarly the velocities are derivable. For example, for the first orbit $v = \frac{2 \times 3\frac{1}{7} \times 37.1^2}{1 \times 4} = 2160$ km. per second.

TABLE 27.—ELECTRON ORBITS IN THE HYDROGEN ATOM

n	1	2	3	4	
r	0.5	2.0	4.5	8	Angstroms
v	2160	1080	720	540	Kilometers per second
Action	4	8	12	16	Atomic units
Energy	−1305	−327	−145	−82	Atomic ergs

Here we see the orbital radii increasing as 1, 4, 9, 16, etc., and the velocities as the inverse roots of these radii: 1, ½, ⅓, ¼, etc. But perhaps the most fundamental property of each of these orbits is their action. The action in successive orbits increases as h, $2h$, $3h$, etc. The angular momentum (mvr) is equal to this action divided by 2π, $h/2\pi$ in the first state, $2h/2\pi$ in the second, etc. (We shall represent $h/2\pi$ by $\hbar$.)

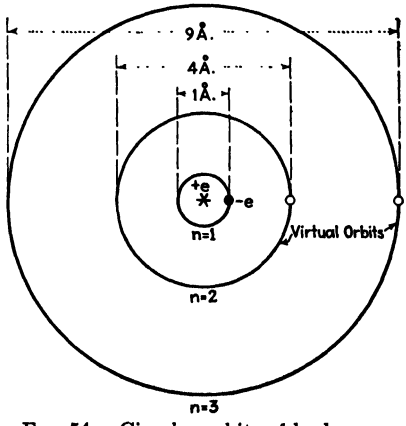


FIG. 54.—Circular orbits of hydrogen.

The electron is normally in the lowest orbit with quantum number 1. The other orbits are not usually occupied. They are "virtual orbits," orbits to which the electron can be displaced.

Energies of the Orbits.—All are familiar with the positive and negative potentials of electricity. It is conventional to speak of the potential energy of two charges placed infinitely far apart as zero. When like charges are brought close together, they have a positive potential energy, an increased ability to do work; when unlike charges are close together, their potential energy is negative. The unlike charges of the hydrogen atom have negative potential energy. The expression for potential energy is e^*e/r and for kinetic energy is $\frac{1}{2}mv^2$. The kinetic energy is positive and by Eq. (21) is (disregarding the sign) half as great as the (always negative) potential energy. The two are added

together to give the resulting total energy. *The total energy will be always negative and equal (except for the opposite sign) to the kinetic energy.*

To illustrate:

1. The electron and proton, about half an angstrom apart in the first orbit of hydrogen, have potential energy equal to

$$-\frac{e^*e}{r} = -\frac{37^2}{0.53} = -2600 \text{ atomic ergs}$$

2. The kinetic energy of the electron, with mass $\frac{1}{1830}$ and with velocity 2160 meters per second, is

$$\frac{1}{2}mv^2 = \frac{2160^2}{3660} = 1300 \text{ atomic ergs}$$

3. Net energy of the electron is -1300 atomic ergs.

The expression for the total energy (W) in the *nth* orbit is

$$W = -\frac{1}{2}mv^2 = -\frac{2\pi^2 me^{*2}e^2}{n^2h^2} \tag{25}$$

This negative energy is inversely as the square of the quantum number. In the first orbit

$$W_1 = -\frac{2\pi^2 me^4}{h^2} = -1300 \text{ atomic ergs;}$$

in the nth orbit

$$W_n = \frac{W_1}{n^2}$$

All values are negative; as n increases, the energy rises nearer and nearer to the zero limit.

In Fig. 61 are represented the energies of the different orbits of the hydrogen atom. The highest level represents the zero energy corresponding to the completely removed electron (ionization). The other levels represent the energies of other possible electron orbits. The depths of the different levels are in the ratios $1:\frac{1}{4}:\frac{1}{9}$, etc. Such energy-level diagrams are very useful.

Hydrogen Spectra.—Bohr now assumes that it is while jumping from one orbit to another that the electron radiates energy; by the quantum theory the frequency of the radiation is proportional to the energy.

$$\text{Radiated energy} = h\nu \tag{17}$$

Thus after an atom has been excited so that the electron is in (say) the third orbit (energy -145 atomic ergs, see Figs. 55 and

61), it may jump back to the second orbit (energy −327) or to the first (energy −1305). Each such energy difference (182 and 1178 atomic ergs, respectively) gives the energy of a radiated energy quantum. Dividing by h gives the frequencies 45.7 and 292, respectively (see Tables 22 and 23). By this transition from the third level to the second or to the first we get a line of the Balmer or of the Lyman series.

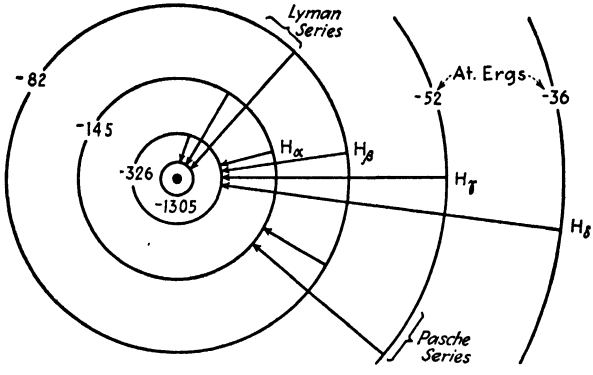


FIG. 55.—Electron transitions and spectrum lines in hydrogen.

The Series Formula.—Let us represent the constant $2\pi^2me^4/h^3$ by R. Then the energy of the nth orbit of hydrogen is $-Rh\frac{1}{n^2}$ and, if the electron falls from the n_2th orbit to the n_1th orbit, the difference in its energy will be $Rh\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$. This energy is radiated as light whose frequency is given by

$$\text{Energy quantum} = h\nu = Rh\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

and hence

$$\nu = R\left(\frac{1}{{n_1}^2} - \frac{1}{{n^2}_2}\right) \tag{26}$$

This is the general series relation for the hydrogen spectrum—the generalized Balmer formula. And, the most remarkable circumstance, R, which can be computed from the e, m, and h is exactly (within experimental error) equal to the Rydberg constant.

Orbital Transitions and Spectrum Lines.—When electrons jump back from any other into the lowest energy level (quantum number 1), a line of the Lyman series is emitted, the first line if

the transition is from the second level, the second line if from the third, etc. The Balmer series is due to electrons falling down into the second level from the third, fourth, fifth, etc. The Paschen series is due to transitions down to the third, the Brackett series to transitions down into the fourth, etc. The lines of any one series are characterized by a common terminal level. It is clear enough from this picture of Bohr's why the frequency difference between the first and second lines of the Lyman series gives the first Balmer line. As the quantum number increases, the energy levels (Fig. 61) differ less and less between successive orbits and the lines in the series get closer and closer together. The limit of the series of lines corresponds to a transition from the zero energy level itself into the appropriate final level. The quantum for the limiting frequency of the series ($h\nu_{\text{lim}}$) is exactly equal to the energy of the terminal orbit.

Ionization Energy.—The energy of the innermost orbit of hydrogen is $-Rh$ and equals -1305 atomic ergs. It is h times the limiting frequency (329) of the Lyman series. This is the energy which must be given to an atom of hydrogen to ionize it. When an electron is accelerated through a potential difference of 1 volt, it acquires an energy of 96.4 atomic ergs. The ionizing potential of hydrogen is $1305/96.4 = 13.5$ volts. The energies of the atomic levels are often conveniently expressed in electron-volts. Such a scale is given in Fig. 61.

Intraatomic Motion.—Now for some comparisons. The molecules in a gas under standard conditions are on the average about 30 angstroms apart; the atoms in a solid are usually several angstroms apart. The diameter of the normal orbit of the hydrogen atom is 1.06 angstroms by the Bohr theory. (How does this compare with the sphere of influence of the hydrogen molecule?)

The outer, virtual orbits are larger. Thirty-one lines of the Balmer series have been measured. The last of these observed lines corresponds to a transition from the thirty-third orbit. Its diameter is more than a thousand times (33 squared) that of the normal orbit—over a thousand angstroms large. Such an atom can exist only in a well-nigh perfect vacuum—the spectrum is observed in nebulae.

The electrons in the normal orbit travel 2200 km. (almost 1,500 miles) a second. This is almost the distance between Chicago and San Francisco in a second. (How does this compare

with the speed of a molecule or free electron at room temperature?) Taking the diameter as 1 angstrom and the circumference as $3\frac{1}{7}$ angstroms, the electron must make $2200/3\frac{1}{7}$ or 700 revolutions per subsecond. Notice that the frequency of the radiation (Lyman series, Table 23) is quite different from the electron's frequency of rotation.

This theory of Bohr's has been surprisingly transformed in recent years. This velocity of revolution has nearly dropped out of the picture (Chap. XXVII). The heart of Bohr's model is in the different energy states which he discovered. The average molecule has translatory kinetic energy $\frac{3}{2}\kappa T$ or about 4 atomic ergs at room temperature. It takes about 1300 atomic ergs completely to ionize a hydrogen atom and three-quarters as much energy to raise the electron from the first to the second orbit. (How much to raise it to the third? To the fourth?) When one contemplates Maxwell's distribution law and sees how small is the chance of having even three times the average velocity, he realizes that the chance of a gas molecule's having sufficient energy to ionize an atom by collision is very remote indeed! Even a displacement to the nearest orbit ($n = 2$) requires a thousand atomic ergs. The atom acts as a rigid, unalterable particle during molecular collisions.

The Correspondence Principle.—The strange procedure of Bohr was to accept the ordinary laws of electricity in Eq. (21), limit their validity in Eq. (22), and finally, in computing the frequency of emission, to neglect ordinary electrodynamics entirely and to use Planck's quantum law [Eq. (17)]. The earlier physicists, thinking of an atom as a simple vibrating system, expected to find in the spectrum fundamentals and overtones, to find a fundamental frequency and harmonics with double, triple, quadruple, etc., frequencies. Instead of which they found the relations described by Balmer.

Now while Bohr insisted that the emitted frequencies of the light wave were not the rotational frequencies of the electron in the atom, there was yet a certain relation between the rotational and radiated frequencies. So when an electron jumped from the third to the second orbit, the H_α line was emitted with a frequency of 46; this frequency appeared to be a kind of mean between the rotational frequency (33) in the third orbit and that in the second orbit (110). By the classical theory, while the electron was going from one orbit to the other, the radius of

the path of the electron would have gradually decreased and the frequency increased and a continuous band of different frequencies between these values, 33 and 110 per subsecond, would have been emitted; actually one single mean frequency was emitted. The second line of the Balmer series with frequency 62 corresponded roughly to the first overtone of this, and so on (page 172). The correspondence here is rather rough. It becomes better in the Paschen and Brackett series and, as we go to the outer levels where the rotational frequencies become slower and slower, the correspondence becomes very close. The case is analogous to that of black-body radiation where the classical theory is correct for low frequencies.

The classical theory is never exactly the equivalent of the quantum theory but there is always a correspondence between them which becomes more and more exact as the frequencies become lower. It was on the basis of this correspondence principle, loose as it is, that Bohr originally developed his theory and many of the more important later results have been developed from this principle.

Elliptical Orbits.—For simplicity we have supposed that the electron moved in a circular orbit; Bohr originally made the same assumption. A planetary orbit in general is an ellipse; it is a circle only in case the major and minor axes of the ellipse happen to be equal. So it is for the electron. It was Sommerfeld who first investigated these elliptical orbits. His results are (1) that only certain discrete states of elliptical motion are possible and (2) that, as far as energies are concerned, the shape of the orbit (in the case of hydrogen) makes little difference—but that little difference is of unusual interest.

We cannot give the solution of this problem in detail but the general method is straightforward. In addition to rotary motion and angular momentum and angular action, the electron in the ellipse will have radial velocity and radial momentum and radial action. That is, except when the orbit is circular, the electron will have one component of its velocity along the line toward the nucleus. The momentum to and fro along this radial direction times the radial distance traversed to and fro in the course of a revolution gives the radial action. There are now two quantum conditions:

$$\begin{aligned} &\text{Angular action equals } kh \\ &\text{Radial action equals } n'h \end{aligned} \qquad (27)$$

The integers k and n' are called *angular*[1] and *radial quantum numbers;* $k + n' = n$ is the total or *principal quantum number.* If n' is zero, there is no radial motion and the orbit is a circle. If k were zero, the motion would be directly toward the nucleus and there would be a collision. Such motion is not allowable—k cannot be zero. (We are here following the argument as it was spun by Bohr, Sommerfeld, and their followers.)

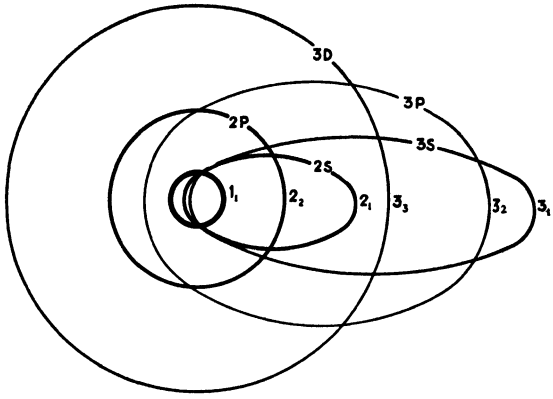


FIG. 56.—Elliptical orbits of hydrogen.

The major axis of the ellipse is determined by the principal quantum number n, the minor axis by the angular quantum number k as shown in the table.

TABLE 28

n	k	n'	(n_k)	Major axis	Minor axis	Type
1	1	0	(1_1)	1	1	S
2	2	0	(2_2)	4	4	P
	1	1	(2_1)	4	2	S
3	3	0	(3_3)	9	9	D
	2	1	(3_2)	9	6	P
	1	2	(3_1)	9	3	S

The orbits are often represented with the angular numbers as subscripts. The circular orbits 1_1, 2_2, 3_3, with diameters 1, 4, 9 angstroms, respectively, have already been considered. The

[1] "Azimuthal quantum number" describes this more exactly.

other orbits have the minor axis reduced in proportion to k as shown in Fig. 56. The orbits are often classed by their radial numbers as S, P, D, and (for $k = 4$) F types.[1]

We shall usually not be greatly concerned with the exact size or position of the orbits. It may be convenient to represent them as concentric rather than confocal. It is also convenient to draw the larger orbits in reduced scale, so that the major axes are as 1:2:3, etc., rather than 1:4:9, etc. On this scale all the S orbits will have a common minor axis of 1, the P orbits a minor axis of 2, the D orbits a minor axis of 3, etc. It is understood that this is an arbitrary distortion, used in Fig. 57 for convenience in representation.

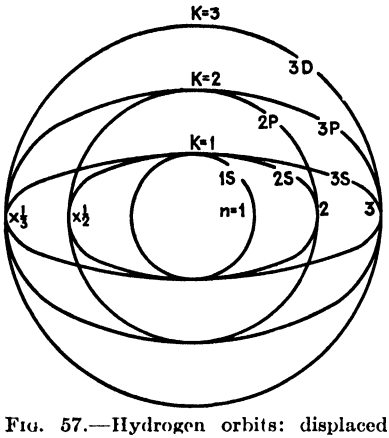


FIG. 57.—Hydrogen orbits: displaced and on reduced scale.

Energy of Elliptical Orbits, without Relativity.—There is but one orbit with $n = 1$, two with $n = 2$, three with $n = 3$, etc. This multiplicity of orbits should presumably add greatly to the complexity of the spectrum. But, as Sommerfeld remarked, *the energy of an orbit* (according to ordinary mechanics) *depends only on its major axis and hence only upon the principal quantum number.* The energy is equal to $2\pi^2e^4m/n^2h^2$ and hence the consideration of the possible ellipticity seems rather superfluous. Several distinct orbits of a common major axis (as $3S$, $3P$, $3D$) degenerate into a single one as far as energy is concerned; the system is said to be *degenerate.*[2]

This is all just as it is in the motion in the solar system. The astronomer needs only the major axis of the orbit to determine

[1] One of my students reminded me that S stands for *slim*, P stands for *phatter*, D for *decidedly phat* and F for *fery decidedly phat*—which may or may not be a memory aid. Actually the letters are derived from the old designations of *sharp, principal, diffuse,* and *fundamental* series.

[2] A familiar example of degeneracy is of a pendulum—a ball on the end of a string. To specify its state of vibration completely, we must know its greatest x extension and greatest y extension; but the energy depends on its amplitude alone: $\sqrt{x^2 + y^2}$; *i.e.*, upon the amplitude but not on the angle of the line of vibration.

the energy, kinetic and potential, of a planet of given mass; he needs the minor axis as well to determine the angular momentum. In our Fig. 57 with its reduced scale, all ellipses meeting with common major axes are alike in energy; all those with common minor axes are alike in angular momentum [Eq. (27)].

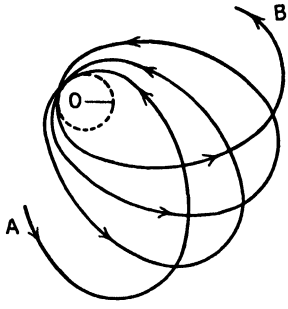


FIG. 58.

The Relativity Correction.—The degeneracy of this system is complete, however, only as long as we use ordinary mechanics and neglect relativity. The electron speeds up as it approaches the nucleus in the elliptical orbit, there is a corresponding increase in mass which at these speeds is not to be neglected, and as a consequence there is a precession of the orbit (just as is the case of the planet Mercury).[1] The orbit is not exactly a closed ellipse and the rates of precession and the energies of the orbits of different eccentricity differ somewhat one from the other. The energy of the orbit still depends primarily upon the principal quantum number; but when relativity is considered, it depends to a slight extent upon the angular number.

The effect is very small. There is only a single precession in some tens of thousands of revolutions; the actual frequency difference introduced in the Balmer lines is no more than a single vibration in a thousand subseconds! Each line of the Balmer series should

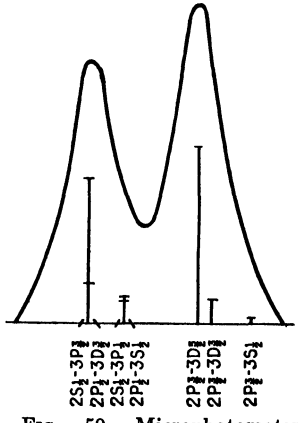


FIG. 59.—Microphotometer curve showing fine structure of *Hα*. (*Kent.*) Theoretical values shown by vertical lines. The complete theory involves corrections not only for relativity but for electron spin and for the new quantum mechanics.

[1] The precession, however, in this atomic case is not due to *general* relativity. For comparison it may be remarked that for Mercury the precession is 1 complete precession in 120,000 revolutions. The exact value for the energy of the orbit with quantum numbers n and k is

$$W(n, k) = -\frac{RZ^2}{n^2}\left[1 + \frac{Z^2\alpha^2}{n^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right]$$

where $\alpha = 2\pi e^2/hc$ is the "fine-structure constant." The value of α (in any units) is 0.00728.

appear as a doublet with a separation about one-fiftieth that of the sodium doublet. While this is a very small frequency difference, instruments of highest resolving power have shown that it certainly exists.[1] This result confirms at once the theory we are developing of the atom and the theory of relativity as applied to the atomic world.

Spark Spectrum of Helium.—Helium has a nuclear charge (e^*) of $2e$, lithium of $3e$. In general, the charge on the nucleus can be expressed as Ze where Z is the atomic number. If now all the electrons save one are stripped from one of these heavier atoms, this residual electron will travel about the nucleus *in an orbit almost exactly like that of the hydrogen electron except smaller.* The radii of the orbits will be.

$$r = \frac{n^2h^2}{4\pi^2me^2Z} \tag{23'}$$

and the energies will be

$$W = \frac{2\pi^2me^4Z^2}{n^2h^2} \quad \text{or} \quad \frac{Z^2Rh}{n^2} \tag{25'}$$

and the spectrum formula will be

$$\nu = \frac{2\pi^2me^4Z^2}{h^2}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

or

$$\nu = Z^2R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \tag{26'}$$

The radii of orbits of the same quantum number n decrease as the atomic number (Z) increases. They are inversely proportional to Z. The negative energies of the orbits and the frequencies of corresponding series are proportional to Z^2.

Spectra of such atoms stripped down to a single electron have been observed only in the case of helium. This "spark spectrum" due to the He^+ ion is well-known.[2] Z is here equal to 2. The radius of the normal orbit of this helium ion is by Eq. (23')

[1] The upper level energy is also split, the electron spin has its influence, and the new quantum mechanics has modified the theory. The effect is more pronounced in ionized helium. In so far as the necessary resolution can be obtained, the experiment agrees with the theory.

[2] The strong lines of the spark spectra of Li and Be, etc., are displaced farther into the ultra-violet; possibly this is the reason that these have not been observed.

¼ angstrom; each virtual orbit is half as large as the corresponding one of hydrogen. By Eq. (25′) the ionization potential of the helium ion is four times as great as that of hydrogen. This spark spectrum, by Eq. (26′), is similar to the spectrum of hydrogen except that each series in He^+ has a fourfold greater frequency. The limit of the shortest hydrogen spectrum is 912 angstroms, of the shortest He^+ spectrum 228 angstroms. The series formula is

$$\nu = 4R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right)$$

It is the hydrogen formula with a series constant $4R$ instead of R.

The story of the discovery of these spark spectra of helium is interesting. It is evident that the "Balmer like" spectrum of He^+ should have alternate lines identical with the Lyman spectrum of hydrogen. For when n has an even value (n = 4, 6, 8, etc.), the expression

$$4R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

can be written as

$$R\left(\frac{1}{1^2} - \frac{1}{m^2}\right) \qquad m = 2, 3, 4, \text{ etc.}$$

It was early found that, whenever the spark spectrum of helium was excited, the "lines of hydrogen appeared." Hence before the time of Bohr it was supposed that hydrogen was always present in the helium! It was not thought likely that the two elements could have these lines in common.

Reaction of the Nucleus.—Actually the He^+ spectra have frequencies about 1/20 per cent greater than those predicted above, and the correspondence between the helium spark lines and the hydrogen lines differs by this amount. This difference[1] is due to the reaction of the nucleus. In our solar system it is not quite exact to speak of our earth as rotating about the sun; actually both earth and sun rotate about their common center of gravity. So it is with the electron in the hydrogen atom.

[1] The effect is exactly allowed for if, instead of m, the mass of the electron, in all formulas $\mu = \frac{M}{M+m}m$ is used as an effective mass. (Here M represents the mass of the nucleus.) Using this in Eq. (25′) introduces a factor $\frac{M}{M+m} = \frac{1840}{1841}$ for hydrogen and $\frac{7360}{7361}$ for helium. μ is called the reduced mass and is quite generally employed in atomic formulas instead of m.

Since the mass of the hydrogen nucleus is 1840 times greater than that of the electron, the common center of gravity is only $\frac{1}{1841}$ removed from the nucleus. The difference introduced is, however, not negligible. It reduces the energy of the system in this same proportion. And so it is with the electron in the helium ion except that here the nucleus is 7360 times heavier than the electron, the center of gravity is four times closer to the He nucleus, and the energy reduction is four times less than in the case of hydrogen. There is then a displacement in the ratio of $\frac{3}{4} \times \frac{1}{1840}$ (*i.e.*, 1 part in 2450) between the lines of hydrogen and the almost identical helium lines mentioned above.

Were the Li^{++} or the Be^{+++} spectra observable, the correction for nuclear motion would be even less important than in the case of helium. In very heavy atoms the nucleus remains at rest and no correction is required. The effect of the nuclear motion is to reduce R by 1 part in 7360 for helium. The values of the constant for hydrogen, helium, and heavy atoms as determined from the spectra are

R_H	329.0331 (109,677.7 in c.g.s. wave numbers)
R_{He}	329.1663 (109,722.1 in c.g.s. wave numbers)
R_∞	329.1993 (109,733.1 in c.g.s. wave numbers)

The spectroscopic results have given an independent method—and one of the best—of determining the ratio of the mass of the electron to that of the hydrogen atom. The exact value found by comparing R_H and R_{He} is $\frac{1}{1846}$.

Summary.—Bohr's theory is of the greatest importance. It is the gateway through which we enter into the world of the atom. Its success meant the general acceptance of Planck's quantum theory. Out of (*a*) the classical equation: $e^*e/r^2 = mv^2/r$; and (*b*) the quantum equation: action $= nh$, the simple circular orbits were derived. With (*c*) the radiation formula: energy $= h\nu$, the spectrum of hydrogen was explained, including the evaluation of Rydberg's constant. The spark spectrum of helium is also completely explained. Elaboration of the simple theory led to the consideration of the mutual motion of the nucleus (with a slight alternation in Rydberg's constant) and the consideration of elliptical orbits. The latter together with the theory of relativity explains the fine structure of hydrogen lines; elliptic orbits are of great importance in more complicated spectra.



BOHR

Niels Bohr, Danish physicist. After getting his doctor's degree in Copenhagen he went to England and at the University of Manchester came into intimate contact with Rutherford. He was twenty-eight years of age when, in 1913, *he proposed his model of the hydrogen atom. In* 1921 *he investigated the structure of the atomic kernel and explained the periodicity of the elements* (*page* 274). *The Institute of Theoretical Physics was established at the University of Copenhagen in* 1916 *with Bohr as its head; the institute has been one of the great intellectual centers of Europe.*

Bohr has keen physical instinct and he has had a profound influence on the more recent developments of atomic physics.

CHAPTER XVI

OUTER SHELLS

Exposed electrons are valence electrons; they rotate about the kernel. But the kernel does not act entirely like a point charge—hence the S, P, D, and F defects. The electron spins—and hence the multiplets. Spectra of stripped atoms.

The Bohr theory is a key to the atomic world. It was fashioned to open a single room—to open to us the secrets of the hydrogen atom. But the key proved to be a master key; without much difficulty other doors were opened. After Bohr pictured the hydrogen atom, models of other atoms immediately suggested themselves. These more complicated atoms are "solar systems" with not one but many electronic "planets" rotating about the nuclear "sun." Many of the orbits of Bohr in these heavier atoms become populated with electrons; they are no longer merely virtual orbits. Depending upon the number of electrons in the atom, the first quantum orbit, the second quantum orbit, the third orbit, perhaps others, may become populated. Only the outer orbits are left unoccupied and virtual.

The "solar system" of helium has two electronic "planets" both in the first quantum orbit; the next element (lithium) has 3 electrons, 2 in the first and 1 in the second orbit[1] (Fig. 53). The following elements (beryllium, boron, carbon, nitrogen, etc.) add other electrons to this second orbit until, at the tenth element neon, it is "full." The eleventh element sodium has 11 electrons: 2 in the first, 8 in the second, and 1 in the third quantum state. Like hydrogen and like lithium it has a single electron in the outer orbit. It is this single outer electron which makes of it an alkali.

Beyond the outermost electron in the atom are always virtual orbits to which the electron can be displaced. It is the play of the outer electron among these virtual orbits which gives rise to the visible spectrum. Transitions between the interior (normally occupied) orbits are betrayed by x-rays. Among the atoms

[1] By "first," "second," etc., orbits are meant the orbits with principal quantum number $n = 1, 2$, etc.

hydrogen is peculiar; it has but one electron, which is at the same time the "outermost" and the "innermost" electron. Its spectrum closely resembles both the x-ray spectra and the optical spectra of other elements.

In this and succeeding chapters we must recount something of what is known of these electrons in the atom. We can but sketch the broader features, only so much as is absolutely necessary to comprehend what is meant by man's discovery of the atom. Yet even this barest outline will occupy the next seven chapters.

The Kernel.—Let us look to the outer atom and optical spectra.

We have seen that it is possible to take Millikan's e and Thomson's m and Planck's h and Michelson's c and compute from them exactly the wave lengths emitted by the hydrogen atom or the helium ion. We can do this with a precision as great as the precision with which these atomic constants have been determined (a few tenths per cent). The *relative* values of the different wave lengths are given within $\frac{1}{1500}$ of 1 per cent! The same kind of computation can be made for the two electrons of neutral helium, although this is a much more difficult task.[1] But beyond this we cannot go. It is too complicated a problem to attempt to compute exactly the orbits of each of the 11 electrons in sodium or of the 92 electrons in uranium. Each is attracted to the center by the large nuclear charge, each electron repels the others, each has its magnetic field interacting with all others. But although we cannot solve the problem exactly, we can readily understand the general situation.

In the case of the alkalis there is one electron in the outermost shell; these alkalis have a close optical and chemical similarity to hydrogen. We shall not look closely at the other electrons, those in the inner orbits; we may think of them as a cloud surrounding the nucleus. The nucleus and the surrounding cloud of inner electrons is called the "kernel" of the atom. The positive charge on the nucleus is (in terms of the protonic charge) equal to the atomic number; the number of electrons in the kernel is one less than this. Outside the kernel, the Z units of positive charge on the nucleus are nearly neutralized by the $Z - 1$ negative electrons; the whole kernel acts as a particle with a

[1] And unfortunately does not give the exact values for the energy levels which are observed spectroscopically (see Chap. XXVII).

single positive charge. The kernel for the alkalis takes the place of the nucleus in hydrogen. It has effectively a single positive charge and attracts a single outer (valence) electron. Hence the spectrum constant is R itself, not a multiple of R as in spark spectra.

Shielding Defects.—Did the $Z - 1$ electrons of the kernel exactly compensate for an equivalent number of nuclear charges, an alkali spectrum would be identical with the spectrum of hydrogen. We should have for the spectrum of an alkali the generalized Balmer formula $\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$. Actually the shielding is not perfect; it is especially imperfect at points near the kernel. The kernel cannot be considered as a point charge and the electric field is not exactly proportional to $1/r^2$. In consequence of this departure from the inverse square law of force, the elliptical orbits precess much as they do in hydrogen (where the effect is due to the relativistic variation in mass). In this case, however, the precession is of much more importance. Owing to this imperfect shielding and to the resultant precession, the energy of the orbit will depend markedly upon its shape. The energy will still probably be determined chiefly by the major axis and by the principal quantum number (n) but yet in large part it will depend on the minor axis and the angular quantum number (k). The energy levels of the valence electron will have values $Rh/(n + \epsilon)^2$ where n is the principal quantum number 1, 2, 3, 4, etc., and ϵ is a fractional constant whose value will depend upon whether the orbit is of the S, P, D, F, etc., type. The constant ϵ is called the shielding defect. $(n + \epsilon)$ is called the effective quantum number (Chap. XIV).

In the case of sodium ϵ is about 0.65 for the most elongated type of orbit (S orbits; $k = 1$), 0.13 for the rounder P orbits, -0.01 for D orbits, and -0.001 for F orbits. For example, for the S levels, the energies are given approximately[1] by

$$\frac{Rh}{1.65^2}; \frac{Rh}{2.65^2}; \frac{Rh}{3.65^2}; \text{ etc.};$$

the series of P energy levels is

$$\frac{Rh}{2.13^2}; \frac{Rh}{3.13^2}; \text{ etc.}$$

[1] More accurate values of the defects are given in Table 26.

Penetrating and Nonpenetrating Orbits.—These orbits all resemble those of hydrogen with a difference; the difference is represented by the defect. The defects for the *D* and *F* orbits are quite small and these two orbits are very much *hydrogen-like.* Hydrogen-like orbits are found in every spectrum and justify our picture of the electron attracted by a singly charged kernel.

The large *F* orbits are far removed from the kernel; they lie in a region where the field is not greatly different from the inverse-square type. Here the orbits will be nearly true ellipses; the

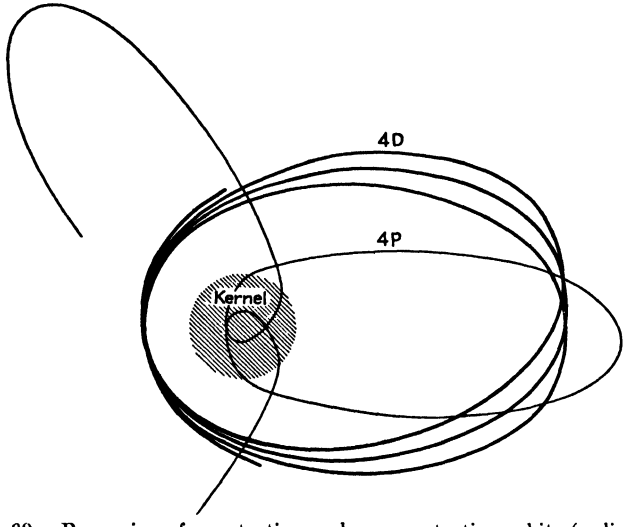


FIG. 60.—Precession of penetrating and nonpenetrating orbits (sodium).

precession may amount to only a few minutes of arc in a revolution. In the *D* orbits the precession may amount to a number of degrees. The precession of a 4*D* orbit in the sodium is represented in Fig. 60.

The *P* orbits and *S* orbits actually penetrate within the kernels. Here all resemblance to the hydrogen orbit is lost—effectively this penetration results in a very great precession as shown in the 4*P* orbit of Fig. 60.[1] These *P* and *S* orbits have large shielding defects.

[1] This is the third of the *P* orbits. It is known that the principal quantum number of this 4*P* orbit shown is not 4 but 5. Its angular quantum number (k) is 2 but its radial number (n') is not 2 but 3; the radial action is not $2h$ but $3h$. About 1 unit of this radial action, however, occurs within the kernel. The larger part of the path outside the kernel resembles in shape, size, energy, and action the 4_2 orbit of hydrogen so greatly that we cannot

Ionization Potentials of Alkalis.—Of all atoms it is in the alkalis that the outer electron is most loosely bound and of the alkalis the binding is least in caesium. The normal orbit occupied by the outer electron is $1s$ ($n = 1$, $k = 1$). The energies of these smallest circular orbits are given in Table 29.

TABLE 29.—1S STATES OF ALKALIS

	Li	Na	K	Rb	Cs
Effective quantum number	1.59	1.63	1.77	1.80	1.87
Term	130	124	105	101	94
Atomic ergs	518	494	417	401	374
Ionizing potential volts	5.4	5.1	4.4	4.2	3.9
Principal quantum number (p. 277)	2	3	4	5	6

These ionizing potentials are very low in comparison with that of hydrogen (13.5 volts). The electron is readily removed. It is because of this that alkalis are so very active chemically. The alkali is very apt to give up an electron and form a positive ion. Common salt (Na^+Cl^-) is composed of positive sodium and negative chlorine ions; the chlorine atom is as apt in capturing as sodium is in losing an electron. In solution the opposite ions in the salt dissociate—the solution becomes a conductor. The alkaline character is strongest in caesium; this is obvious from the ionizing potentials.

The Selection Principle (Angular Number k).—An electron cannot jump from a D type orbit or from an F type orbit into an S orbit. Series of the type $1S - nD$ are not found. Nor are transitions between orbits of the same type found. *In any transition an electron must change its angular quantum number by one.* Transitions from P to S or S to P or from D to P or from F to D are permitted. In Fig. 57 (with reduced scale) the minor axis must become one greater or one smaller in each transition.

$$\Delta k = \pm 1$$

The theoretical foundation for this rule is found in the conservation of angular momentum. This angular momentum of the electron ($\hbar$, $2\hbar$, etc.)

resist calling this the $4P$ orbit. The smallest p orbit we call $2P$. The integer 2 here may be considered either entirely formal or as marking roughly the action (angular plus radial) in the exterior part of the orbit. For the present, however, we shall treat it as simply the principal quantum number (see p. 277).

in its orbital motion about the nucleus is not the total momentum of the atom. We shall give the theoretical basis for a similar selection principle on page 204 after we have introduced the inner quantum number j.

Transitions to the Most Eccentric (S) Orbits.—The energy levels of sodium are shown in Fig. 61. The lowest and normal

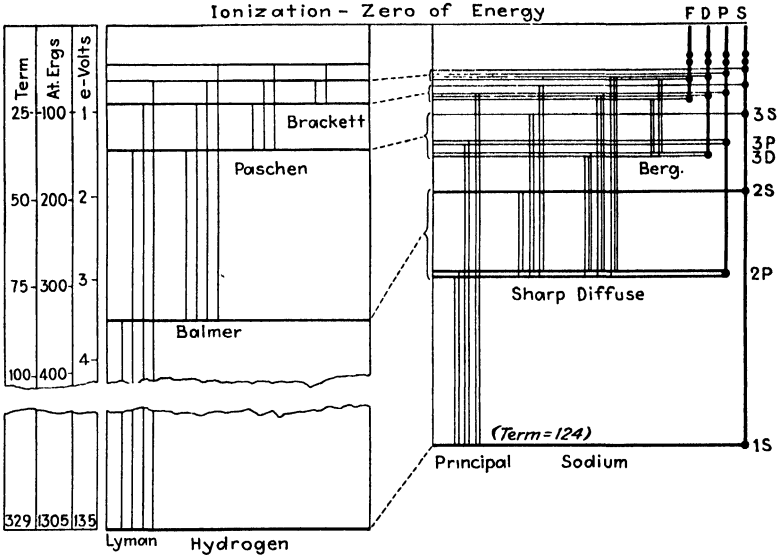


FIG. 61.—Energy levels.

orbit of the alkalis is the $1S$ orbit. For sodium the energy in this orbit is -496 atomic ergs, and the frequency number is

$$1S = 124$$

Electrons can drop into this state from the $2P$, $3P$, $4P$, etc., levels and give the lines of the principal series.

$$\nu = 1S - nP \text{ (principal series)} \qquad (28')$$

The P terms and the effective quantum numbers $(n + \epsilon)$ for sodium are

	$2P$	$3P$	$4P$
Effective quantum number	2.12	3.13	4.14
Term	74.8	34	19

This gives for frequencies of the earlier lines of the principal series: 50, 90, 105 vibrations per subsecond, etc.

Other series of this same type occur with the formulas

$$\nu = 2S - nP \text{ or } \nu = 3S - nP$$

but such series lie in the infra-red and are not easily observable.

Transitions to the P Orbits.—Transitions to the $2P$ orbit can occur from higher S or D orbits

$$\begin{aligned} \nu &= 2P - nS \text{ (sharp series)} \\ \nu &= 2P - nD \text{ (diffuse series)} \end{aligned} \qquad (28'')$$

These two are sometimes grouped as the two subordinate series. Less important subordinate series are of the types

$$\nu = 3P - nS \text{ or } 4P - nS \text{ and } \nu = 3P - nD \text{ or } 4P - nD$$

Transitions to the D Orbits.—The possible transitions to the $3D$ orbits are

$$\begin{aligned} \nu &= 3D - nP \\ \nu &= 3D - nF \text{ (Bergmann series)} \end{aligned} \qquad (28''')$$

In the Bergmann series both terms ($3D$, nF) are hydrogen-like; consequently the wave lengths of the lines differ little from the Paschen series of hydrogen

$$\nu = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

For this reason the series, though comparatively weak, was once supposed to be of fundamental importance and is sometimes called the "fundamental" series (hence the letter F).

The elliptical orbits of Sommerfeld (together with the selection principle) give exactly these series which have been experimentally found. To explain the doublet character of the lines a new quantum number must be introduced.

Doublets.—It has been said that each line in the alkali spectrum is double. The yellow line of sodium is really two lines with wave lengths 5890 and 5896 angstroms. These doublets are shown somewhat exaggerated in Figs. 52 and 61. The spectrum Fig. 52 is represented on a frequency scale; the frequency interval in this 5890 to 5896 doublet is 0.05 vibration per subsecond or a fifth of an atomic erg difference in energy. The same doublet interval is found whenever a $2P$ term occurs, as throughout the sharp and diffuse series and the first member of the principal series (see Figs. 52 and 61). Clearly there are two $2P$ terms differing by 0.05 in vibration number. (These two terms are

denoted by $2^2P_{3/2}$ and $2^2P_{1/2}$.) The doublet separation decreases as we go from $2P$ to $3P$, $4P$, etc. This is shown in the principal series.

The D orbits are likewise double. This results in three lines for each member of the diffuse series. (In sodium the D doublet interval is too small to be detected; it is represented in Figs. 52 and 61 to indicate the characteristics of the heavier alkalis.) Undoubtedly the less eccentric (F, G, H, etc.) orbits likewise are double although such doublets cannot be resolved.

Electron Spin.—The Bohr atom has been compared with a solar system. One feature of planetary motion has, however, been left out of the picture: in addition to the orbital revolution about the sun a planet rotates on its axis. If this spin is in the same sense as the orbital motion (for instance, if both are clockwise), the angular momentum and kinetic energy of the planet are increased by the spin, if in the opposite sense decreased. So it is with the atom. Every electron is not only an elementary charge, it is as well an elementary magnet with a north and south pole. As the electron goes about the kernel, let us say in the $2P$ orbit, the electron spins and this spin is either exactly parallel or exactly antiparallel to the orbital motion. And the spin is quantized. The action of the spin of the electron is a constant and its value is $\frac{1}{2}h$. The angular momentum of the electron as it spins on its own axis is $\frac{1}{2}\hbar$. ($\hbar = h/2\pi$.)

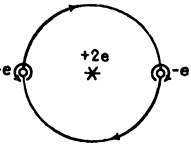


FIG. 62.—Orbital motion and spin in helium.[1] Shows two opposite spins: $s = 0$.

The story is the same with higher P orbits or with a D orbit or an F orbit. For any P orbit k is 2; adding or subtracting the spin gives angular momentum of $\frac{5}{2}$ or $\frac{3}{2}$ (times $\hbar$). For the D orbits k is 3; spin produces two states, one with momentum $\frac{7}{2}$, one with $\frac{5}{2}$. The F doublets have angular momentum $\frac{9}{2}$ or $\frac{7}{2}$. These are the values given by the Bohr theory. However, it appears that these values are in error.

A Dilemma.—S orbits are always single. This means that the momentum of electron spin does not in this case subtract from the angular momentum of the orbital motion. P orbits and D

[1] The new quantum mechanics does not permit such concrete representation of orbits; it considers the angular momentum as zero, not one, in the $1S$ state; it regards the two spins as much more closely coupled than this figure would indicate.

orbits are double but every S orbit is single. If the angular momentum of these S orbits, these thinnest of orbits, is indeed one unit (in terms of $\hbar$) as we have supposed, we should then expect that the spin could either add or subtract a half unit to this. Actually it only adds. We have, following Bohr and Sommerfeld, taken the angular action in the S orbits, neglecting spin, as h. But why this behavior? It would be explicable if all our angular momenta were one unit too large. This would make the atom in the S state devoid of revolutionary motion and naturally the spin could only add. *Such an assumption is impossible on the Bohr theory. Yet we are forced to take the total angular momentum of the atom as given by the vector combination of the spin* $\frac{1}{2}\hbar$ and $(k-1)\hbar$.

We shall find the answer to this paradox; for some pages it must remain for us (as for many years it did for all scientists) a mystery.

Quantum Numbers.—Corresponding to this total angular momentum, to this combination of $k-1$ and spin, another quantum number j is introduced. It is called the *inner quantum* number and its value is taken as one less than the half-integral momentum numbers found above. For instance, the inner quantum number of the P states is either $\frac{1}{2}$ or $\frac{3}{2}$. l is usually introduced for $k-1$.

$$j = (k-1) \pm \tfrac{1}{2} = l \pm \tfrac{1}{2} \qquad (29)$$

j is a measure of the total angular momentum of the atom. Angular momentum $= j\hbar$. (See Fig. 64.)

A doublet term such as those above is often represented as ^2S, ^2P, ^2D. The S term is represented similarly to the others to show that it belongs to a doublet system, although it is understood that no actual doubling can ever occur in an S term. To distinguish between the two terms of a doublet, the inner quantum number is added in the nomenclature as $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$.

Below are given the doublet intervals for the P doublets of the alkalis (ΔW in atomic ergs):

Li 0.004; Na 0.2; K 0.7; Rb 2.9; Cs 6.8

(The doublet separation of lithium is extremely small; it is about the same size as the relativity doublet of hydrogen.)

In Table 30 are given the terms for caesium.

Résumé—Alkali Spectra.—There is a single valence-electron outside the kernel in the alkalis. As in hydrogen, it has its

principal quantum number $n = 1, 2, 3, 4$, etc. (In view of the penetrating orbits the numbers here given are not always correct but this need not concern us at this point.) These numbers represent, in terms of h, the action, angular and radial combined, of the atom. But unlike hydrogen the energies of the different states are far from depending on this principal number alone. Hence the different series of levels S, P, D, F, G, etc.

TABLE 30.—DOUBLETS IN LOWER ENERGY LEVELS OF CAESIUM

	Spin and orbital motion	Term	Doublet separation	
			Frequency	Energy
$1^2S_{1/2}$	.....	104.2		
$2^2P_{3/2}$	Parallel	59.0	1.7	6.8
$2^2P_{1/2}$	Anti-parallel	60.7		
$3^2D_{5/2}$	Parallel	50.4	0.3	1.2
$3^2D_{3/2}$	Anti-parallel	50.7		

In the Bohr theory the angular quantum number k gives the angular action or (in terms of $\hbar$) the angular momentum. When $n = 2$, k can equal either 2 or 1 (the Bohr circle and ellipse) when $n = 3$, k can equal 3 or 2 or 1. The S states are the most elongated, with $k = 1$; we have the $1S$, $2S$, $3S$, etc., states. The P states have $k = 2$; the D states $k = 3$. For the same principal quantum number, the most eccentric (S) states have the highest energies; the $3S$ state lies above the $3P$ and this above the $3D$ in the energy-level diagram.

Bohr's exact interpretation of these states as definite circles and ellipses while very useful is not entirely correct. The wave theory of the atom is discussed briefly in Chap. XXVII. Actually the angular momentum of the electron in its orbit must be taken as given by $l = k - 1$. Despite Bohr, there is no angular momentum in the S states—the motion is entirely radial. In the P states the angular momentum is $\hbar$, in the D states $2\hbar$.

The foregoing is quite general and holds for any atom. An alkali spectrum, however, is characterized by consisting of doublets. Each level, except those of the S type, is split into two, differing comparatively little in energy. To explain this we introduce the spin of the electron. The angular momentum of the spin of a single electron is always equal to $\frac{1}{2}\hbar$ (quantum number $\frac{1}{2}$). The total angular momentum is represented by j

(inner quantum number). According as this spin is in the same sense or opposite to the orbital motion j is $\frac{1}{2}$ greater or less than l. So for the P orbits j is $\frac{3}{2}$ or $\frac{1}{2}$; for the D orbits j is $\frac{5}{2}$ or $\frac{3}{2}$. The nomenclature ($3^2D_{3/2}$, $3^2D_{5/2}$, $4^2P_{1/2}$, etc.) gives in compact form all of these orbital characteristics, n, l, j, and s. (s is the spin quantum number. The superscript 2 indicates a doublet which in turn means a single electron with $s = \frac{1}{2}$.)

The electron transitions between these energy levels are limited by the orbital selection rule: $\Delta l = \pm 1$.

Selection Principle for j and the Angular Momentum of the Photon.—*j can change by ± 1 or (unlike l) by 0. (Except that the transition $0 \rightarrow 0$ is barred.)*

This selection principle follows from the conservation of angular momentum. $j\hbar$ is the total angular momentum of the atom.[1] This angular momentum cannot change without a compensating (opposite) momentum change elsewhere.

Light has momentum. The quantum of light given out by a single transition also often has angular momentum. The light quantum is then circularly polarized and the angular momentum of the single photon is equal to $\hbar$. Or in other cases the emitted light quantum (in the single photon) may be linearly polarized, as if emitted from a small vibrating charge. Its angular momentum is then zero. But no single photon can have angular momentum greater than $\hbar$. This can be demonstrated from the classical theory of radiation; its proof lies outside our scope (see Sommerfeld, page 257).

Since the angular momentum of the photon is not greater than $\hbar$, it follows from the conservation of momentum that in emitting a quantum of light the angular momentum of the atom must change by $\pm\hbar$ or remain unchanged. This gives the selection rule.

Angular momentum is a vector. The selection rule limits the change in the direction of the axis of rotation of the atom (as given by the selection rule for m, page 230) as well as the magnitude of its angular momentum. The selection rule for the orbital momentum (l) (page 198) is based on similar considerations.

The selection principle was also derived by Bohr as a special application of his correspondence principle. It is easy to follow the application in the special case of circular orbits. An electron in a circular orbit cannot change its quantum number (in this

[1] This neglects *nuclear moment* (p. 235).

case $n = k$) by more than 1. For in these circular orbits the projected motion is simple harmonic. *There are no overtones.* Hence in the correspondence which exists between classical and quantum mechanics, where overtones correspond to double or greater electron jumps, *there must be no* Δn *greater than unity.*

Two Valence Electrons—the Mercury Spectrum.—All elements give spectra which are basically the same as those of the alkalis. The most important difference is in the multiplicity of the lines. Mercury may be considered as typical of the elements of the second group of the periodic table. Its spectrum is shown in Fig. 68. Instead of doublets there are here singlets and triplets.

The mercury nucleus has 80 positive charges. The kernel has 78 electrons; there are two outer, valence electrons. It is the presence of these *two* outer electrons which introduces the chief difference between the mercury spectrum with its singlets and triplets and the doublet spectrum of sodium or caesium. These outer electrons are normally in a $1S$ orbit. One of them may be displaced to one of the many virtual orbits of the S, P, D, etc., type. This displaced electron will be attracted now by approximately a single positive charge, the 79 electrons neutralizing all but one of the 80 nuclear charges. The screening is not perfect, of course, and the defect term ϵ appears. The general form of the term is as before $R/(n - \epsilon)^2$. Both electrons may be displaced; usually, however, only one is displaced from the $1S$ orbit, and this is the only case which will be considered.

The Spin Quantum Number.—When the total spin momentum of the atom is considered, account must be taken of the spins ($\frac{1}{2}\hbar$) of each of these outer electrons. These electrons may be spinning oppositely and the spin momenta cancel; they may be spinning similarly and the two spin actions add up to h. We speak of a spin quantum number s; for a single electron s is $\frac{1}{2}$; for two electrons it may be either zero or 1. When these combined spins are zero, no multiplicity of levels can occur. Such singlet orbits are indicated as ^1S, ^1P, ^1D, ^1F, etc. (or rather with the principal and inner quantum numbers included as 4^1S_0, 2^1P_1, etc.).

When the combined spins are equal to $\hbar$ (*i.e.*, $s = 1$) the P, D, F levels are triple. We have the $^3S_1$ level and the $^3P_0$, $^3P_1$, $^3P_2$, levels and similarly for the D and F types.

Singlet Levels of Mercury.—The terms as usual are represented by $R/(n+\epsilon)^2$ where the defect ϵ depends primarily upon the angular quantum number. The value of the defect and the terms of the singlet system of mercury are given below. Compare these values with the corresponding hydrogen terms.

TABLE 31.—SINGLET TERMS OF MERCURY

S Terms

	1^1S_0	2^1S_0	3^1S_0	4^1S_0
$n+\epsilon$	1.14	2.33	3.35	4.38
Term	252.5	60.8	29.3	17.3

P Terms

		2^1P_1	3^1P_1	4^1P_1
$n+\epsilon$	.....	1.91	2.92	3.87
Term	.....	90.3	38.7	22.0

D Terms

			3^1D_2	4^1D_2
$n+\epsilon$	.....	.....	2.92	3.93
Term	.....	.....	38.5	21.4

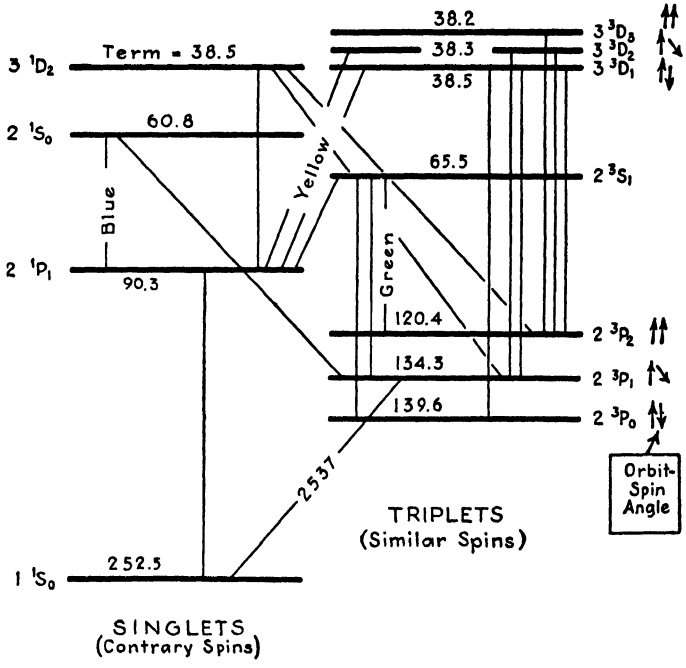
Each of these energy levels is here evaluated in vibration number.

Singlet Spectrum Lines.—Out of these levels arise the singlet series of lines which are given (in frequency and wave length) in Table 32.

Triplet Levels of Mercury.—In each of the states above enumerated the two valence electrons are spinning oppositely; the combined spin is zero. Below are listed the triplet states of mercury, due to electrons spinning in the same direction.

The most important triplet series are

1. Principal: $2^3S_1 - n^3P_{0,1,2}$ (three lines; common limit)
2. Sharp: $2^3P_{0,1,2} - n^3S_1$ (three lines; common differences)
3. Diffuse: $2^3P_0 - n^3D_1$, $2^3P_1 - n^3D_{1,2}$, $2^3P_2 - n^3D_{1,2,3}$ } (six lines)



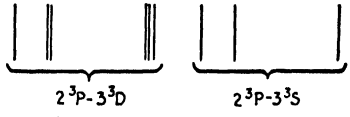


FIG. 63.—The lower energy levels of mercury.

TABLE 32.—SINGLET SERIES IN MERCURY

Series				Limit
Principal: $1^1S_0 - n^1P_1$.....	162.2 1,850	213.8 1,403	230.5 1,269	252.5 1,189
Sharp: $2^1P_1 - n^1S_0$.....	29.6 10,140	61.0 4,916	73.0 4,108	90.3 3,310
Diffuse: $2^1P_1 - n^1D_2$.....	51.7 5,790	68.9 4,348	....	90.3 3,310

TABLE 33.—TRIPLET TERMS OF MERCURY

n =	2	3	4
$^3S_1$	65.5	30.8	17.9
$^3P_0$	139.6	44.0	23.2
$^3P_1$	134.2	43.5	23.1
$^3P_2$	120.3	38.9	22.1
$^3D_1$	.....	38.5	21.0
$^3D_2$	.....	38.3	21.0
$^3D_3$	.....	38.2	21.0

Lines such as $2^3P_0 - n^3D_2$, etc., are ruled out by the selection principle for the inner quantum number.

Combination Series.—The first principal series of triplets does not occur, owing to the absence of the 1^3S term.[1] However, electrons may fall from the $^3P_1$ levels into the 1^3S_0 level, giving a *combination* series. (Transitions from $^3P_0$ or $^3P_2$ levels are barred by the selection principle.) This falling from a triplet to a singlet level is a rather complicated process for the atom; not only does the electron change orbits but the electron must reverse its direction of spin. Nevertheless, the series is quite strong. The first line of the principal combination series of mercury $1^1S_0 - 2^3P_1$ with wave length 2537 is the best known of all ultra-violet lines.

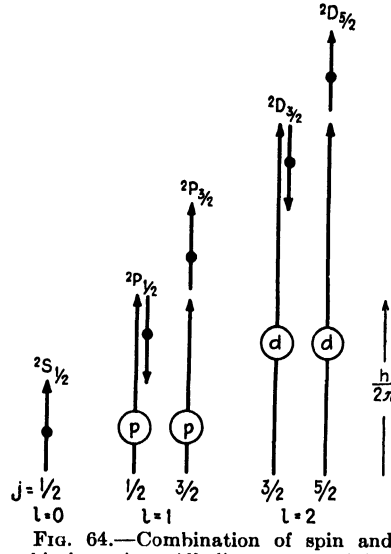


FIG. 64.—Combination of spin and orbital motion: Alkalis; $s = \frac{1}{2}$, giving doublets. Shows several values of l.

Formation of Multiplets.—The interpretation of the multiplet structure of lines in terms of the reduced angular momentum l and the spin s is beautiful because of its simplicity. We have seen how each individual electron has a spin of $\frac{1}{2}\hbar$. For the alkalis this is the total spin of the atom ($s = \frac{1}{2}$). When two electrons are present, according as they are parallel or

[1] The higher principal series $2^3S - n^3P_{0,1,2}$, etc., of course, occur but are in the infra-red.

anti-parallel, the total spin will be $\hbar$ or 0. If there are three electrons as in the third periodic group, the spin can be $\frac{3}{2}\hbar$ (if all electrons spin alike); of $\frac{1}{2}\hbar$ (if only two spin alike). With four electrons the spins can total 0 or 1 or 2. So the spin quantum number s is $\frac{1}{2}$ for the alkalis, 0 or 1 for the alkali earths, $\frac{1}{2}$ or $\frac{3}{2}$ for the earths, and so on.

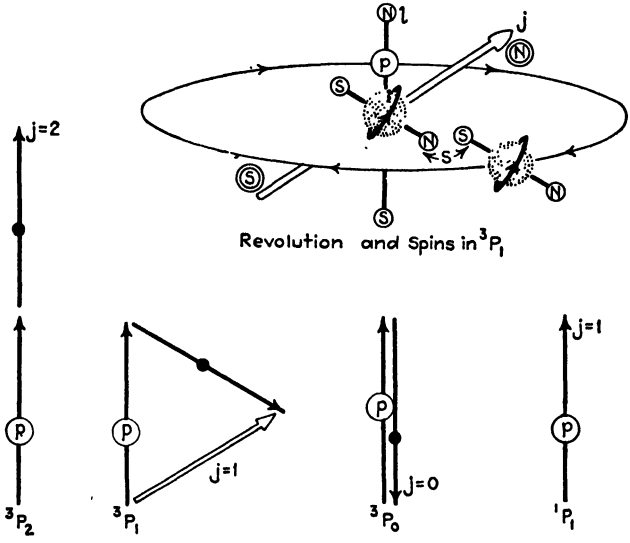


FIG. 65.—Combination of spin and orbital motion: Alkali earths; $s = 0$ or 1, giving singlets or triplets. Shows only $l = 1$. Concerning the pictorial representation of $^3P_1$, see note on Fig. 62.

Singlets, doublets, triplets, and other multiplets are formed because of the combination of the spin with the orbital motion of the electron. Just as the *orbital momentum* and the *spin* are quantized separately, so the combined *total angular momentum* of the atom is quantized and it is represented by the inner quantum number j. If s is an integer, j is an integer; if s is $\frac{1}{2}$ or $\frac{3}{2}$ or $\frac{5}{2}$, j is also a half number. Figure 64 shows the angular momenta in the alkali doublets. The largest value which j can have is $l + s$; the smallest value (when spin and revolution are opposite) is $l - s$. In higher multiplets the two vectors representing spin and revolution can also be at an angle, giving other values differing by h, $2h$, $3h$, etc. from these extremes. So the triplet levels of mercury shown in Fig. 65 have j equal to 2, 1, and 0. In thallium s may be $\frac{3}{2}$ and the quadruplet D levels have $j = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$.

TABLE 34

Group	I	II	III	IV	V	VI	VII	0
Valence electrons	1	2	3	4	5	6	7	8
Typical element	Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulphur	Chlorine	Neon
s	½	0, 1	½, 3/2	0, 1, 2	½, 3/2, 5/2	0, 1, 2, 3	½, 3/2, 5/2, 7/2	0, 1, 2, 3, 4
Multiplets	Doublets	Singlets	Doublets	Singlets	Doublets	Singlets	Doublets	Singlets
		Triplets	Quartets	Triplets	Quartets	Triplets	Quartets	Triplets
				Quintets	Sextets	Quintets	Sextets	Quintets
						Septets	Octets	Septets
								Nonets

The multiplicities found in the different groups of the periodic table are shown in Table 34.

Spark Spectra.—Confirmation of this explanation of multiplet structure is found when spark ("enhanced") spectra are studied. When the electric field of a discharge is especially strong as in the electric spark or in the negative glow, additional lines appear in the spectrum. These lines are due to the exciting of an electron in a positive ion. After one or more electrons are lost to an atom, the remaining valence electrons are bound more tightly and the energy required for optical excitation is greater in the ion than in the neutral molecule.

Now these spark lines show no resemblance to the ordinary arc spectrum of the element in question but the spectrum of a singly ionized atom is very similar to the arc spectrum of the element preceding in the periodic table. The arc spectrum of magnesium consists of singlets and triplets but the spark spectrum consists of doublets similar to the doublets of sodium. In other cases a similar change in multiplicity is found. This is quite what is expected by theory. The spark spectrum of magnesium (Mg^+) must be of the one-electron type. The spark spectrum of singly ionized aluminum (Al^+) must be of the two-electron, singlet-triplet type.

Spark spectra of higher order are also known. When two electrons are stripped from aluminum, the ion (Al^{++}) has the alkaline type of spectrum. The elements silicon, phosphorus, and sulphur have been stripped of all their valence electrons down to the alkaline state. The spectra of Na and Mg^{+} and Al^{++}, Si^{+++}, P^{++++}, and S^{+++++} are remarkably similar except that the spectrum is displaced further into the ultra-violet as the degree of ionization is increased. The wave length is shortened because of a change in the value of the series constant. The Rydberg constant is multiplied by 4, 9, 16, etc., according as the ion is singly, doubly, triply, etc., charged. This is all in accord with the theory. Equation (25′) shows that the energy of hydrogen-like orbits equals $Z^2Rh(1/n^2)$ where Z represents the number of charges on the nucleus. The valence electron, as it is displaced into the various optical orbits in the normal atom, finds itself attracted by a single positive charge, since here the other electrons (in the kernel) are one less than the positive nuclear charges. The orbits are then like those of hydrogen. In Mg^{+} the valence electron is attracted by 2 charges; the analogue is the spark spectrum of helium. Z is taken as 2 and the series constant is $4R$. And so Z_e (the effective value of Z) increases until, when in sulphur five of the six valence electrons are removed, the series constant is $25R$. The shielding defect varies somewhat among the stripped atoms so that the energies of the levels are only rather roughly proportional to 1, 4, 16, 25. In illustration, the energies of the $1S$ levels (in terms of ionization potentials) for the sodium-like ions are shown in Table 35.

TABLE 35.—1S TERMS IN IONS WITH A SINGLE VALENCE ELECTRON

	Volts
Na	5.1
Mg^{+}	15
Al^{++}	28.3
Si^{+++}	45
P^{++++}	64.8
S^{+++++}	88

Similar results are found for elements in other rows of the periodic table. Ca^{+} resembles potassium; Hg^{+} resembles gold. The spark spectrum of the alkalis is harder to obtain since this involves disrupting the kernel itself. The first spark spectrum of the alkalis, of course, resembles the spectrum of the noble gases. Such relations as these show in a beautiful way the

fundamental unity of the chemical elements. In the periodic table the elements in a single vertical group have similar spectra, and elements in the same row in the table show even closer similarities when the elements are ionized so as to have equal numbers of outer electrons. These relations show the underlying unity which Prout suspected but could not prove.

The familiar yellow doublet of sodium ($1^2S_{1/2} - 2^2P_{1/2,3/2}$) appears again and again in the spark spectra of the succeeding elements of the same row of the table. In sodium the wave lengths are 5890, 5896 angstroms; in Mg^+ 2795, 2802 angstroms; in Al^{++} 1854, 1862 angstroms; in Si^{+++} 1394, 1403 angstroms; in P^{++++} 1118, 1128 angstroms; and in S^{+++++} 933 and 944 angstroms.[1] So each of the other lines of sodium finds its corresponding lines in the spectra of these stripped atoms. A beautiful regularity of nature!

Fourth-power Law.—The doublet interval increases as the fourth power of Z_e. The same relation recurs among x-ray doublets; this was indeed the clue which enabled the physicist to distinguish the spin doublets from the screening doublets.

Stripped Atoms in the Stars.—The scientist knows the nature of the gaseous atmosphere about the sun and other stars from their absorption spectra. In the case of the sun most of the atoms appear to be in their normal states, as witness the spectrum of hydrogen and iron and the other normal arc spectra. A few easily ionized atoms (like calcium) show the spark spectrum. On hotter stars, stripped atoms, singly, doubly ionized become quite prominent. Indeed the astronomer has used the degree of ionization found in spectra as a temperature scale for the classification of stars.

All of the valence electrons are removed at a temperature of a few hundred thousand degrees. But in the interior of the stars temperatures are much greater, running up to perhaps some 50 million degrees. Here all of the electrons even in the kernel itself may be stripped from the atom—the atom reduced to the bare nucleus. Such a completely stripped atom may occupy a volume some ten thousand times less than the normal atom and the density of the star may be as much as 60,000 gm. per cubic

[1] Most of these lines are in the far ultra-violet and are only observable in the vacuum spectrograph. Wave lengths below about 2000 angstroms are absorbed by air.

centimeter. Such an instance of a hot dwarf, tremendously heavy, is found in the celebrated companion of Sirius (page 31).

Summary.—The spectrum gives us our fullest information about the nature of the exterior of the atom. Spectra usually contain multiplets; the number of components in a multiplet term depends on the number of outer electrons in the atom. The way in which electron spin combines with the orbital motion to give the total angular momentum (inner quantum number j) is indicated in the chapter.

In every case the outer orbits are of the S, P, D, and F, etc., type. In the first and second groups of the periodic table the $1S$ orbit (never a multiplet) is occupied; the other orbits are virtual. The screening defects, due to imperfect shielding of the nucleus, are largest in the S and P type orbits, comparatively small in the D and F types—these are "hydrogen-like."

In addition to the normal arc spectrum, attention is called to the "spark" spectrum, the spectrum appearing in stronger fields due to the atom which has sloughed off one or more of the valence electrons. Such spectra show great similarities to those of the preceding elements in the atomic table.

CHAPTER XVII

ELECTRON COLLISIONS

An atom resembles an egg: it is elastic unless it is hit too hard. Direct proof of energy levels. Step-by-step excitation of spectra.

It is the method of physics, as of the other natural sciences, to invite critical tests of its theories. The physicist approaches his inquiry without prejudice—he asks only for the truth. One sometimes hears of the "scientific method." There is no method except observation, analysis, common sense, ingenuity, and perfect fairness. (And unfortunately this "method" cannot be learned by conversing about it.)

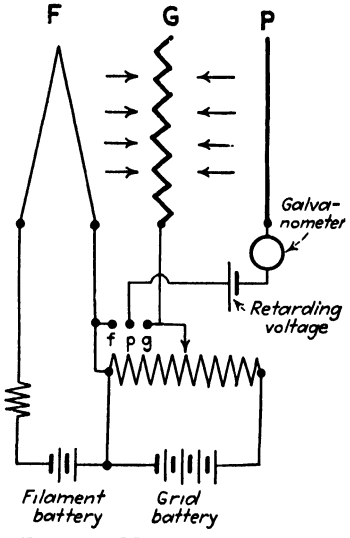


FIG. 66.—Measurement of ionization and resonance potentials; *f-p* connected for ionization, *p-g* for resonance.

No theory is true until as far as possible it has been checked and cross checked and proved right in its every implication. Our detailed theory of spectra would not be accepted without the converging confirmation of many experiments. We now present some phenomena which seem to give the most direct confirmation of Bohr's energy levels.[1]

The best proof of Planck's theory would be to measure the energy of the individual photon and the best proof of Bohr's postulated energy states would be to measure directly the energies of those states. This latter was done in a celebrated experiment by Franck and Hertz.

Franck and Hertz were trying to measure ionization of gases. The apparatus which they used we should recognize today as an

[1] But not necessarily of the orbits which Bohr assumed to account for these states of energy.

ordinary three-element radio tube. In Fig. 66 the plate P is to be considered at present as connected through the switch pf to the filament F. A dry cell keeps the potential of the plate slightly below that of the filament.

Electrons leave the filament, are accelerated to the grid, and are retarded from the plate. Relative to the filament the grid is positive and the plate negative. No electron can reach the plate since its potential is lower than that of the filament; the acceleration which the electron experiences in the region F-G is more than balanced by the deceleration in G-P. No electrons can reach the plate but any positive ions formed in the region G-P will be collected. The current to the plate is measured on a galvanometer.

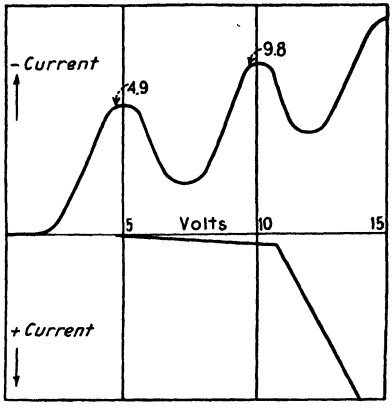


FIG. 67.—Ionization and inelastic impacts.

Just such a tube as this is used today to measure low gas pressures (the ionization gage page 50). No current can be collected by P in perfect vacuum. The ionization current is a measure of the gas present.

With such a tube Franck and Hertz attempted to measure the ionization potential of gases. They first tried mercury vapor. A drop of mercury placed in the tube produced the necessary vapor pressure.[1] The potential on the grid was gradually raised and a very small *positive* current to the plate was detected when this grid voltage reached 4.9 volts. A much larger current was obtained at 10.4 volts. This is shown in the lower curve in Fig. 67. When it has a velocity corresponding to a potential difference of 10.4 volts, the impinging electron can strike an electron loose from the atom. It can ionize the atom with which it collides. Beginning at this voltage a positive-ion current is collected by the plate (P). (The small current beginning at 4.9 volts is due to the photoelectric effect as explained later.)

[1] Mercury has a pressure of about a thousandth of a millimeter of mercury at room temperature and about a quarter millimeter at 100°C. This latter is a suitable pressure.

Other gases were similarly studied by Franck and Hertz and their successors. Typical values of ionizing potentials are given in Table 36.

TABLE 36.—CRITICAL POTENTIALS OF GASES

Gas	Ionizing potential, volts	Resonance potential, volts	Limit principal series	
			Wave length, angstroms	Frequency, vibrations per subsecond
Hydrogen	13.5	10.3	913	329
Helium	24.8	21.4	504	595
Sodium vapor	5.2	2 1	2412	124
Potassium vapor	4.4	1.6	2857	105
Cadmium vapor	9.0	3 8	1379	217
Mercury vapor	10.4	4.9	1188	252

Inelastic Collisions.—In a variation of this experiment Franck and Hertz measured the energy losses suffered by electrons when they collide with a mercury atom. The connection is now made in Fig. 66 between p and g; the plate P is now maintained by the cell 1½ volts lower than the *grid*. As the potential of the grid is raised, the voltage of the plate will likewise be raised. The electrons will be accelerated in the region F-G and decelerated, but only slightly, in the region G-P. Electrons can now reach the plate P unless their velocity has been reduced by collision to less than 1½ e-volts.

The current received by the plate in this experiment is negative. When the grid is raised to 1½ volts, the plate voltage rises above zero, and electrons begin to be received by the plate. The current then increases, at 4.9 volts it falls, rises again after about 1½ volts more, falls again at 9.8 volts and again at 14.7 volts (Fig. 67). Below 4.9 volts the collision of an electron with a mercury atom is elastic; above that potential the electron can lose 4.9 e-volts of energy and, if the original energy of the electron was less than 6.4 volts, the residual energy after collision will be less than the 1½ volts required to reach the plate. The decrease of the current in this part of the curve is a measure of the number of electrons which have lost their energy. An electron can lose 4.9 e-volts in one collision, or 9.8 e-volts in two inelastic collisions,

or 14.7 *e*-volts in three collisions. These experiments of Franck and Hertz showed two types of inelastic collisions: one the ionizing type requiring at least 10.4 volts in mercury, and one an excitation collision[1] involving an energy loss of exactly 4.9 *e*-volts. Values of excitation voltage for several other elements are given in Table 36.

Single-line Spectrum.—But this is not the end of the story. Franck and Hertz showed that the complete arc spectrum of mercury appeared at 10.4 volts. Below that voltage and above 4.9 volts they observed the single line λ2537! Below 4.9 volts nothing. Thus this single-line spectrum of mercury was correllated with this 4.9-volt energy loss.

The Test of the Bohr Theory.—This was in 1914. These discoveries with galvanometer and spectrometer came very happily for the newly proposed theory of Bohr. The newly born theory furnished an exact explanation of these experimental results.

1. *Ionization.*—We have shown in Tables 31 and 33 the vibration numbers of the more important virtual orbits of mercury. The electron is normally in the 1^1S_0 state. The limit of the principal series of mercury has a frequency of 252.5 vibrations per subsecond. This corresponds to an energy quantum of 1000 atomic ergs. Such is the energy of the quantum of light given out when an electron falls into this orbit from the periphery of the atom; such is the energy which must be acquired to remove the electron to the periphery. In terms of our atomic units (96½ atomic ergs = 1 electron-volt), an electron traveling with 10.4 volts should be able to ionize the atom. This is in exact agreement with Franck and Hertz.

2. *Inelastic Collisions.*—Next beyond the 1^1S_0 base level come the triplet levels; $2^3P_{2,1,\text{or}0}$. But a free transition to the base level, emitting light, can occur only from the 2^3P_1 level (page 204). (This single transition, in the reverse sense, also occurs in absorption.) The line emitted ($1^1S_0 - 2^3P_1$) has a wave length 2537 angstroms, and a frequency 118 vibrations per subsecond. In the inelastic collision observed by Franck and Hertz the valence electron in mercury was displaced to this 2^3P_1 level; the line 2537 angstroms, and this alone, appeared in the spectrum at 4.9 volts. The photon of this 2537 line has an energy of 470

[1] This is also called a *resonance* collision. We speak of resonance potential and (in the single line spectrum) of the resonance line.

atomic ergs or 4.9 electron-volts. Again an exact agreement between theory and experiment. If V_c represents the critical potential for inelastic collision and ν the emitted frequency, we have

$$eV_c = h\nu$$

This experiment is a direct measurement of the energy in a single quantum of radiated energy, shows definitely the existence of energy states, and is the clearest demonstration of the reality of Planck's quantum of energy ($h\nu$).

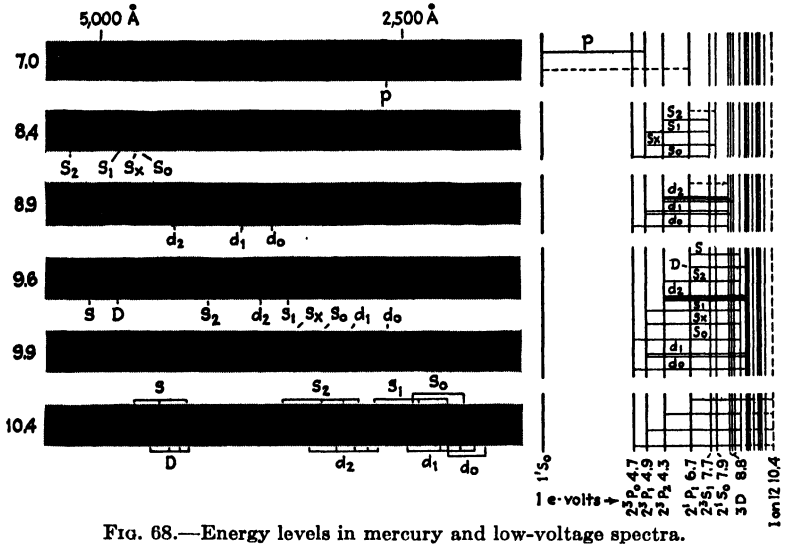


FIG. 68.—Energy levels in mercury and low-voltage spectra.

The small positive current which Franck and Hertz observed coming to their plate at 4.9 volts (Fig. 67, lower curve) is due to the photoelectric effect. The line λ2537 coming in at this voltage excites the plate photoelectrically. The electrons leaving the plate produce the positive current which Franck and Hertz at first attributed to positive ions.

Step-by-step Excitation of Spectra.—But why (it may well be asked) only this single line (λ2537) below the ionizing potential? Others asked this question but not for a decade was the question answered. It was then shown that in fact each line of the spectrum appears below ionization as soon as the voltage is sufficient to displace the valence electron to the appropriate outer level. Above 6.7 volts the electron may be displaced

to the 2^1P level and we get the line λ1850 angstroms. (This is so far in the ultra-violet that it is not usually observed.) Above 7.9 volts the electron can be displaced to the $2S$ levels (either 2^1S or 2^3S)—lines of the sharp series appear. Above 8.8 volts the first lines of the diffuse series appear. The spectrograms in Fig. 68 show the step-by-step excitation of this spectrum. All this is an exact confirmation of the Bohr energy levels.

The Scientist at Work.—In the earlier chapters the successive scenes of our panorama have passed quickly before our view. We have hardly had time to see the men who have done these things. Yet there is hardly a page of this book the writing of which has not cost the labors of many men—many men perhaps for years. There is no fascination in the bare picture of this atomic world; the fascination is in the memories associated with each detail, memories of failure and of success. It is all an entrancing story of the solving of mystery.

The men who do these things—physicists—are primarily artists. They are not usually inventors or public benefactors or wizards—perhaps they are prophets—but, most generally, they are artists. They enjoy an unexplained phenomenon as Sherlock Holmes enjoyed a clever crime and often care no more, I suspect, for "progress" then he did for "law and order." But out of their work has come, for better or worse, the basis of our modern civilization.

Let us pause here and see the physicist at work. Let us see how this art of measuring critical potentials gradually developed.

A decade or so before Franck and Hertz, Lenard (like J. J. Thomson a great pioneer in electronics) first measured the ionizing potentials of gases. He was before his time; his results were bare facts without theoretical setting. Men cannot digest very much of such. Theory or a law of nature or an atomic model—call it what you will—acts as a cement, binding apparently unrelated parts together. Hence the peculiar beauty of physics; each of the truths of physics forms a part delicately fitted into its place in one vast whole.

Lenard's results were just brutal unalleviated facts. Incomplete, suggestive, they were buried in the files of the *Annalen der Physik*. But his method of attack lived on; it was his method which was used by Franck and Hertz in 1914. They were looking

for ionizing potentials just as Lenard had been before them; they stumbled upon resonance potentials and, of course, did not recognize them at first. But now in 1914 there was a theory to guide and direct the experimenter. Before long, Franck and Hertz recognized the 4.9-volt collision in mercury as an inelastic collision. Very opportune was all of this for the new Bohr theory —and *vice versa.*

Others followed this trail. War halted science in Europe; American scientists came to the front. Other gases were studied, particularly the metal vapors. Then diatomic gases were investigated—more complicated results now, since dissociation of the molecule must first occur before the simple energy states of the atom appear. Hydrogen was investigated in vacuum furnaces at white heat, at such temperature that the diatomic molecules were mostly dissociated. Its 13.5-volt ionizing potential, its 10-volt resonance potential was observed—also at lower temperatures the energy states of the hydrogen molecule. Just after the war American, German, English physicists, united in the common task, produced a wealth of quantitative confirmation of the objective reality of the Bohr energy states.

In all of this earlier work on electron collisions very little that was really new developed. Time after time the predictions of the Bohr theory were confirmed. These energy levels can, granting the theory, be more accurately computed from spectroscopic data than by such direct measurement. But these experiments with resonance potentials strengthened this platform upon which future physics was to build. Much in the Bohr theory is superfluous, some inconsistent; but these energy levels certainly exist. Only by having a prodigality of proof, by having support from every side, by the cumulative support of a great quantity of detail does a theory become a fact, established forever. Such a fact is, I believe, the existence of this table upon which I write; such a fact is, I believe, the existence of energy levels in atoms. This is the meaning of all of those papers on critical potentials which a decade ago appeared in our *Physical Review* and in the English *Proceedings of the Philosophical Society* and in the *Zeitschift für Physik.* They were building up *truth.*

The investigations of these electron collisions have been very extensive. We have mentioned only the most elementary question: how much energy is lost? Other questions which have

been studied extensively are the nature of the scattering of electrons when they collide with atoms, the nature of collision producing multiple ionization and "spark lines," and ionization by collision of positive ions. Sometimes an already excited atom strikes another particle; instead of absorbing energy from the particle it may then give energy up to it. This is called a *collision of the second kind.* All these experiments are fascinating because of the directness of the interpretations we can usually make. They have contributed greatly to our understanding of atomic and molecular physics. It is to be regretted that we cannot in this chapter present more from the wealth of experimentation in this field.

The Ionizing Potentials of the Atoms.—From spectroscopy the energies of the normal states of the atom have been deter-

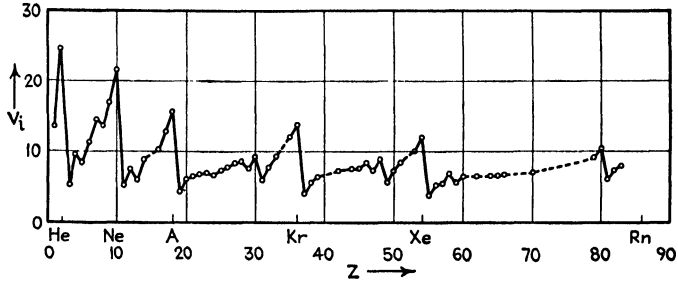


FIG. 69.—Ionizing potentials of the elements. (*Ruark and Urey.*)

mined. In many cases the results have been confirmed by the electrical methods just described. These results are summarized in Fig. 69.

Perhaps this summary of the binding force of the valence electrons in the different atoms represents the most notable single result of spectroscopy. The weak binding in the alkalis, the strong binding in the halogens and in the completed rare-gas shells, this explains to us the fundamental chemical differences of these elements. Now we see what is meant by the alkalis, the electron losers, and halogens, the electron capturers. Minor periodicities are shown in the figure. But at present we need notice only the increasing affinity for electrons as we go from light to heavy element within any period, the similarity of potentials among the transition elements of the long periods, and, as between elements of the same group, the weakening of the binding with increasing weight of the element.

CHAPTER XVIII

IN A MAGNETIC FIELD

The atom is a magnet and the magnet is a gyroscope. In a magnetic field everything is one large merry-go-round. But only quantized orientations occur: proof, the Zeeman effect. Thus is completed our description of quantum state. Nuclear spin and fine structure.

Magnetic Moment and Mechanical Moment.—The electron moving about its orbit acts as an electric current; in consequence, except when j is zero, the atom acts as a small electromagnet. This electric current bounds a *magnetic shell* and the magnetic moment (M) of this shell is $\frac{1}{2}\frac{e}{c}vr$. This is the strength of this atomic magnet.[1]

But also, in virtue of the mass of the revolving electron, the atom acts as a small flywheel. Its angular momentum (J) is, as we know, mvr. The ratio of the magnetic moment to this

[1] The reader should be familiar with magnetic moment. It is the fundamental quantity in magnetism, more fundamental than the rather fictitious "poles" in terms of which it is usually defined. A current in a single loop of wire is equivalent to a flat magnet, a "magnetic shell." The moment of this disk-shaped electromagnet equals the current (in e.m.u.) times the disk area; the corresponding value for the orbital electron is given above. The potential energy of any magnet in a field H equals $M'H$, where M' is the component part of the magnetic moment in the direction of H. Considerable familiarity with these concepts will be desirable before this chapter is read. References are Starling, "Electricity and Magnetism," p. 225, or any book on intermediate electricity.

Magnetic Units.—We shall continue to use atomic units. A unit magnetic pole is one which will repel another like pole 1 angstrom away with a force of 1 atomic dyne (1.65×10^{-6} dyne). Hence from the equation $F = m_1m_2/r^2$ we have $1.65 \times 10^{-6} = m^2/10^{-16}$ giving $m = 1.285 \times 10^{-11}$ c.g.s. unit for the *unit pole.*

The unit of *magnetic moment*, the moment of a magnet 1 angstrom long with unit poles, is 1.285×10^{-19} c.g.s. unit. This unit is about fourteen times as large as the magneton (the natural unit of magnetism).

The corresponding atomic unit for *magnetic field* is 128,500 gauss. This is a rather large unit. Actually the strongest fields usually obtainable are some 40,000 gauss, about one-third of an atomic unit.

mechanical moment is therefore $\frac{1}{2c}\frac{e}{m}$. For an electron this ratio M/J is about $\frac{1}{9}$ (exactly 0.113).[1]

$$(\text{Orbital})\ \frac{M}{J} = \frac{1}{2c}\frac{e}{m} = (\text{approx.})\ \frac{1}{9} \qquad (30')$$

This result is for a charged mass, not spinning but moving in an orbit. When a charged mass is spinning on its own axis, the distribution of charge and mass at varied distances from the center must be considered and the problem is somewhat altered. For the spin of the electron the ratio of magnetic to mechanical moment M/J is e/mc.

$$(\text{Spin})\ \frac{M}{J} = \frac{1}{c}\frac{e}{m} = (\text{approx.})\ \frac{2}{9} \qquad (30'')$$

This fundamental difference between the orbital and spin motions introduces a complication; to avoid this, let us at present consider only cases (such as the singlet states) where the spin may be neglected.

The Gyrating Atom.—Despite the magnetic force, these atomic magnets when free (as in a gas) cannot turn themselves parallel to the magnetic field. Because of its rotating mass, each atom must act as a gyroscope and precess about the direction of the magnetic field (H). If its axis of rotation is oblique to the field, that axis turns about, keeping the same obliquity, like the precession of a top. If its axis is parallel to the field, the orbital motion is slightly accelerated. We shall show that the precession in any case is $\frac{1}{9}H$ radians per subsecond.

Larmor Precession.—This is but a special case of a general principle. A magnetic field causes the paths of all moving electrons to precess slowly. We have seen in Fig. 40 the straight path of the cathode ray twisted through several degrees. An oscillating electron in a magnetic field finds its line of vibration gradually rotated. And now we find that a charge revolving in its orbit acts like a gyroscope, the axis of revolution precessing in the magnetic field. The paths of all electrons are turned about the magnetic field as if the world were one large merry-go-round.

[1] $\dfrac{37.1}{2 \times \frac{1}{1830} \times 300000} = 0.113$ (in atomic units).

This general rotary motion induced by the magnetic field is called the "Larmor precession." The angular velocity of this general precession is[1]

$$\Omega = \frac{M}{J}H \text{ radians per subsecond}$$

or

$$\nu = \frac{1}{2\pi}\frac{M}{J}H \text{ revolutions per subsecond} \qquad (31)$$

In a field (impracticably great) of 1 atomic unit the frequency is $1/2\pi \times 0.113$, or 0.018 per subsecond. In a field of 1 gauss (1/128,500th of our unit) the system makes one complete turn in about 7 million subseconds; or, in other words, its frequency of precession is 1.4×10^6 revolutions per second.[2]

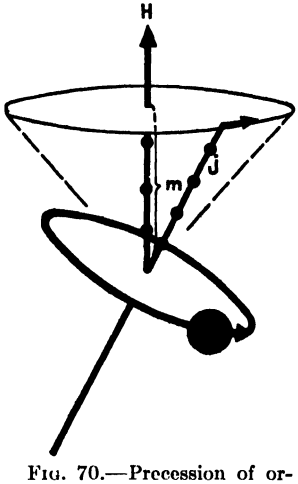


FIG. 70.—Precession of orbit in magnetic field. The precession is $\frac{1}{2\pi}\frac{M}{J}H$ cycles per subsecond. This is 1.4 million per second with a field of 1 gauss. The figure also shows the relation between the inner and the axial quantum numbers.

Depolarization of Resonance Radiation in a Magnetic Field.—A beautiful illustration of this Larmor precession is found in an experiment performed by Wood and Ellett. The resonance line of mercury (λ2537) was first polarized and then entered a tube containing mercury vapor. The classical picture of the atom can be used to explain the broader aspects of the observed phenomenon. We can think of the atom as a tuned oscillator, a minute radio station. This atomic oscillator would absorb the polarized light, would oscillate in the plane of polarization, and later would reemit light polarized in the same plane. This is substantially

[1] This comes from the formula for precession of a gyroscope. $\Omega = L/J$. Closely analogous to the equation for centripetal force (which may be written as $F = mv\omega$ or $\omega = F/mv$) is the equation which mechanics gives for gyroscopic precession: $\Omega = L/I\omega$ where ω represents the rotational velocity, I the moment of inertia, and L the torque. Now the torque on a magnet in a cross field is MH; $I\omega$ is J. Hence $\Omega = \frac{M}{J}H$ as above.

[2] $T = 2\pi \cdot \frac{J}{M} \cdot \frac{1}{H} = 2\pi \times 9 \times 128{,}500$.

what Wood and Ellett found when the experiment was performed without a magnetic field.[1] But when a magnetic field was applied to the resonance tube the secondary light could be completely depolarized. In this magnetic field the atomic oscillator precesses between the time of its excitation and the time of reemission. Only a gauss or two was required to nearly depolarize the secondary emission.

Ellett has used the method to determine the mean life of the excited state of the atom. He finds that for mercury this

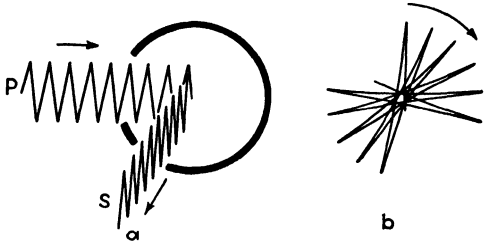


FIG. 71.—(*a*) Polarized primary and fluorescent radiation, without field (*b*) Precession of electron vibrator in magnetic field, destroying polarization (field inward toward page).

excited life is 10^{-7} sec. During that time a field of 1 gauss would rotate the plane of polarization through one-seventh of a revolution—enough to give considerable reduction in polarization; 2 gauss would cause a precession of more than 90° and completely depolarize the light.

The Element of Magnetism.—Let us consider singlet states, where the spin of the electron can be neglected. In earlier chapters it has been shown that the angular momentum of the atom is equal to $j\hbar$. $\hbar$ (*i.e.*, $h/2\pi$ or 0.632 atomic unit) is Nature's unit of angular momentum. This natural unit of angular momentum we may call (inventing the name) a Bohr "momenton."

The electron (without spin) having mechanical moment of j momentons acts as a magnet with magnetic moment of $j \cdot \frac{1}{2}\hbar$ [see Eq. (30′)]; $\frac{1}{2}\hbar(= 0.0714)$ is the natural unit of magnetic moment and is called the *Bohr magneton.* The magneton is practically one-fourteenth of an atomic unit. This natural element of magnetism is usually represented by μ.

$$\mu = \frac{M}{J}\hbar = 0.0714 \text{ atomic unit} \qquad (31')$$

[1] The polarization was only 80 per cent complete—the full explanation of the phenomenon cannot be given on this classical basis.

The free electron (although its spin is only a half momenton) has, because of its greater M/J value, a magnetic moment of 1 Bohr magneton. An electron is at the same time a charge e and a magnet of strength μ.

The magnetic moments for several atomic states are shown in Table 37. In the singlet states the magnetic moment is simply equal to $j\mu$; in the other cases the relation is more complicated (page 232).

TABLE 37

State	l	s	Mechanical moment		Magnetic moment	
			Momentons (j)	Atomic units	Magnetons	Atomic units
$^1S_0$	0	0	0	0	0	0
$^1P_1$	1	0	1	0.63	1	0.07
$^1D_2$	2	0	2	1.26	2	0.14
$^2S_{1/2}$	0	½	½	0.32	1	0.07
$^2P_{3/2}$	1	½	⅔	0.95	2	0.14
$^2P_{1/2}$	1	½	½	0.32	⅓	0.02
$^3S_1$	0	1	1	0.63	2	0.14
$^3P_2$	1	1	2	1.26	3	0.21
$^3P_1$	1	1	1	0.63	⅔	0.10
$^3P_0$	1	1	0	0	0	0

Ferromagnetism.—The theory of the free gyroscopic motion of the elementary magnet in the magnetic field is more directly applicable to gases than to solids. In solids frictional forces come into play; the precession of the gyroscope is damped out, and the rotating atom is brought more or less into alignment with the field.

In metals, the outer electrons have become free electrons. The magnetic character of iron and nickel and cobalt is due to the magnetic moment of the uncompleted kernels of these atoms. But here we shall be interested only in the much simpler effects shown by the free gas molecule or atom.

Magnetic Energy.—A magnet tends to point along the direction of the magnetic field. It requires work to turn it into any other direction. Its energy may be taken as zero when it is transverse to the field. Then its potential energy is $-HM$

when pointing along the field, $+HM$ when pointing opposite to it. The potential energy in any intermediate position is given by HM' where M' represents the projection of M in the direction of $-H$. (This is from the most elementary theory of magnetism.)

The magnetic energy of an atom is always relatively very small. Pointing against the extremely strong field of 1 atomic unit a Bohr magneton will have energy (HM) of $\frac{1}{14}$th of atomic erg, much smaller than the kinetic energy of gas molecules at normal temperatures, only about $\frac{1}{1400}$th of an electron-volt.

Résumé.—Let us summarize here the important magnetic relations which have been deduced.

a. The ratio of the magnetic moment to the angular momentum of an orbital electron is

$$\frac{M}{J} = \frac{e}{2mc} = \frac{1}{9} \text{ atomic unit}$$

b. For the spinning electron the ratio is $\frac{2}{9}$.

c. The Larmor precession of the orbit (in revolutions per subsecond)

$$\nu = \frac{1}{2\pi}\Omega = \frac{1}{2\pi}\frac{1}{9}H \text{ revolutions per subsecond}$$

d. The elemental magnet has a moment

$$\mu = \text{Bohr magneton} = \tfrac{1}{9}\hbar = \tfrac{1}{14} \text{ atomic unit}$$

e. Energy of magnet in magnetic field

$$W = M'H$$

Atomic units:

$$\text{Magnetic field} = 128{,}500 \text{ gauss}$$
$$\text{Magnetic moment} = 1.285 \times 10^{-19} \text{ c.g.s.}$$

Quantized Orientation.—All of this has been quite straightforward. The atoms can be pictured each as a small magnet, as a small compass needle. These minute magnets vary in strength in proportion to the angular momentum of the atom; they are 0, 1, 2, 3 magnetons strong in the ^1S, ^1P, ^1D, ^1F state. But now we meet with a fact more disconcerting to our usual forms of thought than any which the quantum theory has so far given us. These magnetic compasses can be inclined only at certain favored angles from the magnetic field!

In the singlet states M is equal to j magnetons. M' must obviously be between $+M$ and $-M$; in other words M' is equal to m magnetons where m lies between $+j$ and $-j$. The energy in the magnetic field is $Hm\mu$.

The remarkable fact now is that m (like j) can (for these singlets) have only integral values. The values of m for the $^1D_1$ orbits might have been supposed to have been anything between $+2$ and -2. Actually only five values are found: 2, 1, 0, -1, -2. This means that the revolving atom can have its axis of revolution in only five favored directions. Not only is j itself integral but only certain values for the projection of j (*i.e.*, m) are possible. The energy difference in the atom in virtue of its position in the field is

$$\Delta W = Hm\mu \ (m \text{ between } \pm j) \qquad (32)$$

This is called "quantization in space." The atom precesses in the field like a spinning top—but here the top can assume only a certain few definite inclinations. The proof of space quantization is found in the Zeeman effect.

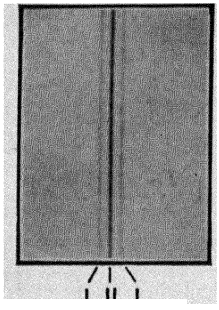


FIG. 72.—Normal Zeeman splitting (H_α of hydrogen). Magnetic field 39,000 gauss. Fourth order of diffraction grating. (*Back.*)

Zeeman Effect.—In 1896 Zeeman noticed that, when a strong magnetic field was applied to an atom which was emitting a line spectrum, each spectrum line was split. If a sodium flame is between the poles of a strong electromagnet the yellow lines are no longer simply two but the 5890 line is split into four parts, the 5896 line into six parts. In the simplest cases, in hydrogen and in singlets, the lines are split into three parts; one part is shifted a little toward the red, one toward the violet, and one is left undisturbed. These components are each polarized; the undisturbed part is always vibrating parallel to the magnetic field, the others perpendicular thereto. In the strongest available fields (about $\frac{1}{3}$ atomic unit) the separation in this *normal triplet* is 0.006 vibration per subsecond. This is about a tenthousandth part of the usual optical frequencies; the wave length shift is about a tenth the distance between the lines in the sodium doublet.

Classical Theory.—Lorentz interpreted these results of Zeeman in terms of the Larmor precession. Actually the frequency of the Larmor precession ($\frac{1}{2}\pi \cdot M/J \cdot H$) is exactly equal to the

frequency shift observed in this normal Zeeman effect. (On page 224 it was shown that the precessional frequency was 0.018 revolution per subsecond in unit field.) Such a precession would leave a vibration along the axis of precession unaffected; a transverse vibration must be split with its frequency increased and decreased by the precessional frequency. So the classical theory explained the polarization and frequency change in the normal effect. It was one of the triumphs of the older electron theory. It afforded one of the earlier methods of evaluating e/m [see Eq. (30′)].

Bohr Theory of the Zeeman Effect.—This is one point of view. But in many cases the effect is not so simple as has been described. The field may break the line up into more than three components. We know today that this "anomalous Zeeman effect" is found in cases where the electron spin must be reckoned with. The prequantum theory could not explain this anomalous effect. Bohr found in the classical explanation of Lorentz only an approximation to the truth. To explain the Zeeman effect by the quantum theory he assumed space quantization. Not only must the atoms be quantized with a principal quantum number n and an angular quantum number l and an inner quantum number j, but, whenever a magnetic field is present, the *axial* quantum number m (representing the projection of j in the direction of the field) must also be known.

Usually the exact plane in which the rotational motion of the electron takes place is immaterial. However, when the magnetic field is applied, there is the slight energy difference mentioned above between an atom revolving with the field, transverse to the field, or against the field. When the electron makes a transition from one orbit to another, these energy differences will affect the frequency of the emitted light.

We take, for example, the Zeeman effect in a $2^1P_1 - 3^1D_2$ line. Figure 73 shows the energy levels (A) without and (B) with a magnetic field. The P level is broken into three, the D level into five levels. The smallest energy is, of course, found in the case where the atomic magnet is pointed exactly along the field. For the D orbit m is then -2. There are four other D states. The atomic axis can point 60° away from the field ($m = -1$) or point at right angles ($m = 0$) or it can have similar positions against the field. As long as no election spin is involved, *consecutive levels always differ in energy by* μH.

Selection Rule.—Fifteen types of transitions might be expected here; the spectrum line resulting from a transition from an $m = +2$ level to an $m = -1$ level would differ by $3\mu H$ from the normal line. But this transition is impossible. A selection rule again enters here. m can change only by ± 1 or 0. The types of transition to the P levels which are shown in the figure are the only ones permitted. In view of this selection principle *the transitions in the magnetic field can differ in energy only by* $\pm\mu H$ *or by* 0 *from those in the absence of the field.* From the quantum relation $W = h\nu$ and by using the value of the magneton it

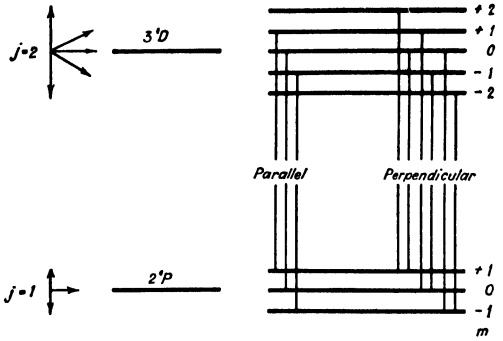


FIG. 73.—Normal Zeeman effect of the $2^1P - 3^1D$ line. Normal energy levels and the same levels with increments in magnetic field. Separation between energy levels is μH.

follows that the Zeeman frequency change is $\Delta\nu = \pm\frac{\mu}{h}H$ or 0. μ/h equals 0.018—the normal Zeeman interval in unit field.

In this normal Zeeman effect the intervals between every pair of adjacent energy levels are the same; the same line, with increased frequency, results whether the displacement is from $+2 \rightarrow -1$ or $+1 \rightarrow 0$ or $0 \rightarrow -1$; transitions from $-2 \rightarrow +1$; from $-1 \rightarrow 0$; from $0 \rightarrow +1$ all give a single line displaced toward the red. These displaced lines are polarized $\perp$. Transitions from $1 \rightarrow 1$, from $0 \rightarrow 0$, from $-1 \rightarrow -1$ give the unmodified line. Whenever m is unchanged, the polarization is $\parallel$.

The selection rule governing the axial quantum number is: m can change only by ± 1 or 0. An electron rotating in a D orbit parallel to H ($m = +2$) can, by retarding its motion (as light is emitted), go to a similarly rotating P orbit ($m = +1$). It cannot, however, reverse the direction of its motion (*i.e.*, it cannot go into the P orbit with $m = -1$). *Whenever the value*

of m changes, the light emitted is polarized perpendicular to the field. When m is not changed, the polarization is parallel. Hence the $\perp$ components are displaced by $\frac{\mu}{h}H$ (*i.e.*, $0.018H$); the $\parallel$ components are not displaced. (Our discussion here is limited to the normal effect.)

Experiment of Stern and Gerlach.—An experiment of Stern and Gerlach gives incontrovertible proof of this space quantization. A fine beam of silver atoms was defined by appropriate slits, passed between the poles of a powerful magnet, and then formed a deposit on a glass plate. The poles of the magnet were

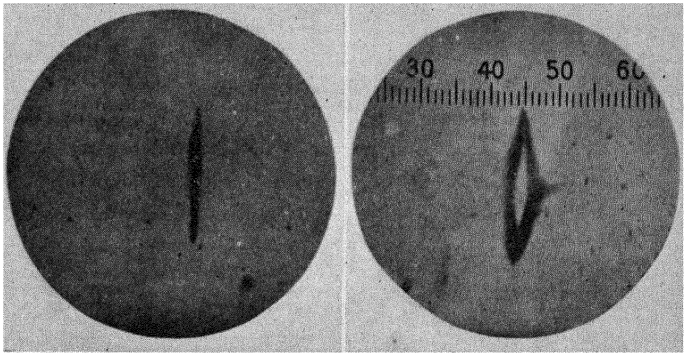


FIG. 74.—The Stern-Gerlach experiment.

designed to produce a very intense, nonuniform divergent field which would strongly attract or repel a magnetic element passing through it. Without a field the deposited silver image was slit shaped; with the field this slit-shaped image was pulled into two parts, especially in the center where the field was strongest. This showed that the silver atoms were magnetic and were pointing half with the field (attracted) and half pointing against it (repelled).

This is a direct proof of the orientation of atoms. The deflection observed corresponded to a magnet with moment just equal to μ and is in exact agreement with the theory. Silver atoms are (like sodium) in the $1^2S_{1/2}$ state. j equals $\frac{1}{2}$, entirely due to spin. The value of m is $+\frac{1}{2}$ or $-\frac{1}{2}$. This means that in silver atoms the electrons spin, some clockwise, some counterclockwise, about an axis parallel to H. Since this magnetism is entirely due to s rather than l, the magnetic moment is equal

to $2m\mu$. m equals $\pm\frac{1}{2}$, giving a magnetic moment of $M = \pm\mu$. (The factor 2 here introduced is the Landé splitting factor discussed in the following section.)

Other elements were investigated; each showed the expected magnetic moment. Copper and gold are like silver (moment equals μ); lead (like mercury in the $^1S_0$ state) showed no moment. Thallium has an electron in the 2^2P_0 state and showed (in agreement with theory) a magnetic moment of $\frac{1}{3}\mu$.

It should not be overlooked that this space quantization is a very subtle thing. We can, of course, have space quantization along only one axis at a time. What axis? In the absence of a field (degeneracy) we cannot say; and by the same token it makes no difference. Whenever a field is applied or some condition of symmetry enters sufficient to determine such space quantization along some axis, along that axis will be space quantization! It is there whenever you look for it. A very subtle thing.

Anomalous Zeeman Effect.—When both rotation and spin (l and s) enter into the inner quantum number, the Zeeman effect is not so simple as this. There is a splitting into many components rather than into the normal triplet.

As an example, the line λ5896 of sodium is split into four components.

Two $\perp$	$\Delta\nu = \frac{4}{3}$ normal separation
Two $\parallel$	$\Delta\nu = \frac{2}{3}$ normal separation

The stronger line of the doublet, λ5890, is split into six components:

Two $\perp$	$\Delta\nu = \frac{5}{3}$ normal separation
Two $\perp$	$\Delta\nu =$ normal separation
Two $\parallel$	$\Delta\nu = \frac{1}{3}$ normal separation

In these cases the direction of the magnetic moment often does not coincide with the direction of the mechanical moment. (This is illustrated in the drawing of the orbit and spins in the $^3P_1$ state of Fig. 65. The atomic poles are represented slightly off the j axis.)

We shall not give here the detailed explanation of this anomalous effect. Suffice to say that because of the doubling of the magnetic-moment mechanical-moment ratio, whenever the moment is due to spin, the effective value of the magnetic moment is no longer simply j but is given by gj where g is the *Landé splitting factor*. It is little more than a matter of trigo-

nometry to show that the value of this factor as it follows from the Bohr theory is

$$g' = 1 + \frac{j^2 + s^2 - l^2}{2j^2} \tag{33'}$$

(When there is no spin $j = l$ and $g' = 1$; no correction is necessary. When l is zero, $j = s$ and $g' = 2$; the magnetic moment is doubled since it is entirely due to spin. When both s and l are present, the result is more complicated.)

Now as a matter of fact this formula which was derived from the Bohr theory by simple vector addition is not quite correct. The question might arise whether we should not use here

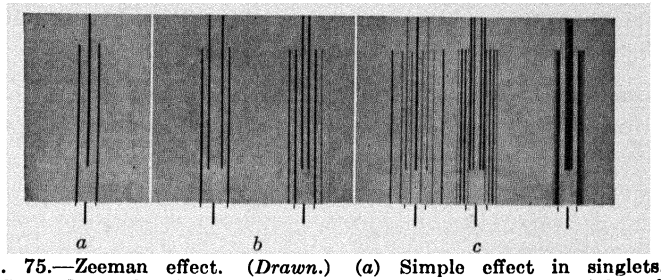


FIG. 75.—Zeeman effect. (*Drawn.*) (*a*) Simple effect in singlets. (*b*) In $1^2S - 2^2P_{½,3/2}$ doublet of sodium. (*c*) In $2^3P_2 - 3^3D_{1,2,3}$ triplet of cadmium.

k $(=l + 1)$ rather than l. We must then similarly increase j and perhaps s, giving

$$g'' = 1 + \frac{(j+1)^2 + (s+1)^2 - (l+1)^2}{2(j+1)^2} \tag{33''}$$

But this overcorrects the value of g. *The value of g which is in exact agreement with the observations of the Zeeman effect is a mean between these formulas.*

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \tag{33}$$

This result, undoubtedly correct, is not, however, to be derived from the Bohr theory. Here is a second instance where the Bohr planetary theory of the atom has been found wanting. The first instance was when that theory took k to be the angular momentum of the atom; we have usually used $l(= k - 1)$ instead.

In conclusion, then, the Bohr theory explains the normal Zeeman effect and gives approximately—but only approximately—the solution for the anomalous effect. The Zeeman effect shows that the molecule must be quantized in space. There is introduced a new quantum number (m) the value of which varies by integral steps between $+j$ and $-j$.

Stark Effect.—In strong electric fields a somewhat similar splitting of energy levels occurs. This is the Stark effect. The multiplicity of the Stark energy levels is equal to that in the magnetic field ($2j + 1$) but the energy values are different. The electric field causes a distortion of the orbits rather than a precession. The Stark effect for the third line of the Balmer series is shown in Fig. 76. In contrast with the Zeeman effect, which for hydrogen degenerates into the normal triplet, the Stark effect here shows 14 components parallel to the field (above) and 13 perpendicular components (below). The pear-shaped appearance is due to the variation of the electric field (near the cathode of a discharge tube where the spectrograms were taken).

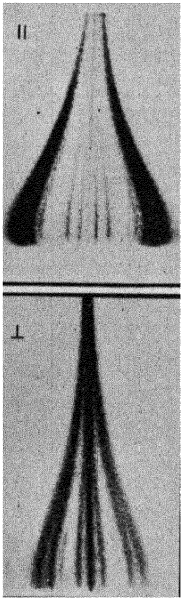


FIG. 76.—Stark effect of $H\gamma$. (*Foster.*)

Complete Description of State.—An electron, considered for the moment as a mere point charge, has three degrees of freedom. Hence it requires three quantum numbers to specify its state. These may be taken as the principal number n, the angular number k or l, and the *axial* or magnetic number m. Without spin, j is not to be distinguished from l. In the hydrogen atom it was found that the energy was dependent almost entirely upon the first of these numbers. It is almost superfluous in this case to describe the shape of the orbit (by k or l) or the particular plane in space in which it lies (by m). The system is said to be "degenerate."

Actually, in view of relativity the minor axis of the orbit (as determined by k) does affect the energy slightly. But in the absence of outer fields, the orientation in space is quite immaterial and m cannot conceivably be determined. If a magnetic field exists, the energy does depend upon the direction of the orbit in space. In a magnetic field all degeneracy is removed; the energy depends upon n and l and m.

Actually the single electron is something more than a point charge. It has spin ($\frac{1}{2}\hbar$) either parallel or antiparallel to l. Either the spin quantum number ($\pm\frac{1}{2}$) or alternatively j, its combination with l, must be considered in addition to the other three numbers.

Now for the first time we have before us the picture of the electron in the atom in all its dimensions (n; k or l; m; and s or j). It is the magnetic field which has completed the scheme for us. The picture now has much more detail than that first simple picture of Bohr.

Consider an electron in the third orbit of Bohr (Fig. 54): $n = 3$. But this is not a single state—there are three possible substates: $l = 0$ or 1 or 2 (Fig. 57). And the state $l = 2$ contains within itself five substates with different orientations ($m = \pm 2, \pm 1$, or 0); and $l = 1$ contains three substates ($m = \pm 1$ or 0); the state $l = 0$ has but one orientation (Fig. 73). In all there are here nine states (each specified by its n, l, and m). And in each of these states of rotation the spin (s) can be either parallel or antiparallel—18 states, differing little, sometimes not at all in energy, within the third orbit of Bohr.

Hyperfine Structure.—Like the electron the proton has spin. Its angular momentum is equal to that of the electron: $j = \frac{1}{2}\hbar$; but its magnetic moment is of an order 1840 times smaller. (If a proton is to be treated like an electron: $\frac{M}{J} = \frac{1}{c}\frac{e}{m}$. However, the value of the magnetic moment as determined by experiment appears to be several times larger than this.) Each heavier atomic nucleus, composed as it is of electrons and protons, has its characteristic spin value. Just as the electron spin, combining in various ways with the orbital motion, produces the multiplets, so within each multiplet there is a much finer multiplicity which has its root in the coupling between this weak nuclear magnet and the orbital motion. This is the "hyperfine structure" of the line. The study of hyperfine structure leads to the values of the spins of the various nuclei, is one of the most promising methods of unraveling the secret of the nucleus, and is one of the outstanding current problems of spectroscopy. Only in a few cases can this structure be resolved in the spectroscope. The precessional method of Ellett (page 224), although less direct in its interpretation, distinguishes between energy states which differ by only a single vibration in the duration of the state (1 in 100 million for 2^1P_1 of mercury). This is unparalleled resolution. It is a promising mode of attack.

The helium nucleus (the α particle) has no spin. The two neutrons and two protons which enter into its composition are so balanced as to cancel out the angular moment. Similarly the oxygen nucleus, which must be composed of four α particles, is without spin.

Summary.—For the singlets the ratio M/J is about one-ninth. Since the "momenton" ($\hbar$) is 0.632, the magneton is about $\frac{1}{14}$ atomic unit. The atom in a magnetic field is limited to orientations in which m, the projection of j along the field, is integral (or half-integral if j itself is half-integral). The energies in these different orientations of this atomic magnet differ slightly; in this subdivision of energy states lies the explanation of the Zeeman effect. The state of an electron is exactly specified by its four quantum numbers.

The consideration of the magnetic behavior of the electron can grow quite involved. What is essential for the further understanding of the atom is this: For any atomic state with inner quantum number j there are $2j + 1$ substates, differing only in orientation in space. They are characterized by different values of the axial quantum number m extending from $-j$ to $+j$.

CHAPTER XIX

X-RAYS

What happened when x-rays passed through a crystal. How crystals analyze x-rays and x-rays analyze crystals. Ionic sizes affect chemical action.

X-rays were discovered by Roentgen in 1895. For seventeen years it was not definitely known whether they were electromagnetic waves or particles. X-rays differed from light in apparently not being refracted when they passed through a material medium; the phenomenon of interference is the crucial test of a wave motion and interference had not been observed for x-rays. So much could be said against the wave theory. On the other hand, if x-rays were particles, they were not charged particles like cathode or canal rays; x-rays are not deflected in a magnetic field. Two strongly developed schools of thought arose to support the opposing views.

Absorption of X-rays.—In the intervening seventeen years before the nature of x-rays was definitely known, experiments dealt mostly with absorption. The English physicist Barkla was foremost in these early investigations. A tube excited with a hundred thousand volts emitted very penetrating radiation ("hard" rays); at lower voltages the radiation was more readily absorbed; with the voltage below 10,000 volts the rays were so soft as to be absorbed by the glass walls of the tube and even by the air. The intensity I of any homogeneous beam of rays must obey the simple exponential law of absorption: $I = I_0 e^{-\mu x}$, where x is the thickness of the material and μ the absorption constant. This law did not hold. It was evident that x-rays were not homogeneous. Hard rays and soft rays with different values of μ were mixed in the emitted radiation.

As the absorbing properties of matter were investigated, two remarkable facts developed: (1) x-ray absorption depends only upon the atom in the absorbing medium, not at all upon its state of chemical combination; (2) x-ray absorption is proportional (except for certain discontinuities) to the fourth power of the atomic number. Here no sign of the periodicity of the elements.

It was fairly clear that x-rays would tell of the nature of the kernel itself rather than of the superficial characteristics of the atom. But up to the day when x-ray wave lengths were measured the results were more often qualitative than quantitative.

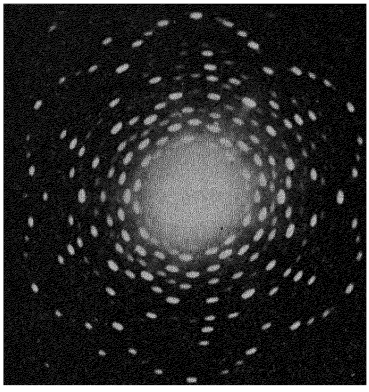


FIG. 77.—Laue pattern from quartz crystal. (*Wyckoff.*)

X-rays as a Wave Motion.—In 1912 x-ray diffraction in crystals was observed. If x-rays were indeed a form of wave motion, these waves must unquestionably be of very short wave length. It occurred to the German physicist Laue that the regularly spaced atoms in a crystal could be used as a diffraction grating. These rows of atoms in a crystal are about ten thousand times closer together than are the lines in an ordinary diffraction grating. It was a fruitful suggestion. A beam of x-rays sent through a crystal of zinc sulphide was diffracted into a pattern of regularly spaced spots. From the spacing Laue was able to compute the wave length of x-rays and the wave theory was at once established.

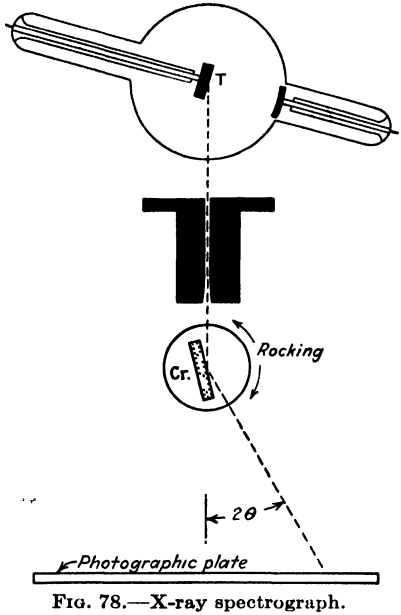


FIG. 78.—X-ray spectrograph.

William Bragg had been a staunch upholder of the particle theory. He at once accepted the fundamental significance of the new discovery and (with his son) began a program of investigation into the nature of solids for which in 1915 they were awarded the Nobel prize.[1] Laue had observed the selective

[1] Laue had received the prize in 1914. Barkla received it in 1917.

scattering of x-rays as they passed through the crystal. Bragg observed the selective reflection from the crystal face. We shall describe his results before explaining the formation of Laue spots.

Reflection from a Crystal Face.—A narrow beam of x-rays from the target T (Fig. 78) is defined by the slit in a lead block and falls upon the face of a crystal (Cr). The crystal is rotated so that the glancing angle (θ) varies through a suitable range. The reflected x-rays are photographed on the plate, the different wave lengths being reflected at different times and at different angles as the crystal rocks back and forth. This gives the x-ray spectrogram. If the x-rays are homogeneous in frequency, a single line will be photographed (see Fig. 88 showing several such lines). Usually a wide range of frequencies will be present and there will be a continuous spectrum in addition to the characteristic lines.

Laws of a Space Grating.—Suppose that a homogeneous beam of wave length λ falls upon the crystal. It is found that reflection occurs under the following conditions:

1. The angle of reflection equals the angle of incidence (law of optical reflection).
2. The glancing angle of incidence (and hence of reflection) must be such that $2d \sin\theta = n\lambda$, where d is the distance between the adjacent atomic planes in the crystal and n is an integer.

The plane diffraction grating is a number of closely ruled *lines* on a plane; the crystal is a number of closely spaced *planes* of atoms. In order to have x-ray reflection from such a "space grating," every atom in every plane must conspire to produce constructive interference. (1) For every atom in a single plane to do this, it suffices that the angle of incidence equals the angle of reflection. The path of each incident-reflected ray is then the same; there is zero retardation. (2) At normal incidence a ray reflected from the second plane of atoms travels a distance $2d$ farther than one reflected from the first. At oblique incidence the additional path (retardation) is $2d \sin\theta$. For constructive interference this retardation must exactly equal 1 wave length or (for higher order reflections) 2, 3, 4, etc., wave lengths.

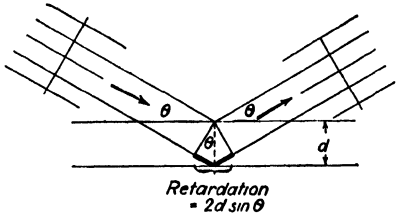


FIG. 79.

$$n\lambda = 2d \sin\theta \text{ (Bragg's law)} \qquad (34)$$

This is precisely the law of reflection from thin films in optics (Newton's rings).

Summarizing: Because of interference within a plane and between different planes, x-rays can be reflected only for equal incident and reflecting angles and even so (for a given λ) only when these angles are such as to obey Bragg's law.

In illustration consider the reflection from calcite where the grating space d is 3 angstroms. The angles of reflection for three particular lines are given below.

TABLE 38

	Angstroms	Degrees	sin θ	Exciting voltage
K_α line of phosphorus	6	90	1	2,000
K_α line of bromine	1	10	0.17	12,000
K_α line of uranium	0.1	1	0.017	120,000

The very soft line of phosphorus is the longest observable with a crystal of this grating space. The K line of uranium, deviated only 1°, is the shortest of all characteristic x-ray lines.

The selective reflection of x-rays of different wave lengths at different angles is exactly analogous to the reflection of light from a thin soap film or from a thin piece of mica. If a piece of mica thin enough to show interference color is rotated, the color of the reflected light changes toward the blue and violet as the glancing angle is decreased. The difference in x-ray reflection is one of resolution (page 109). Because there are many thousands of equally spaced planes in the crystal (as contrasted with the two surfaces of the mica), a single very sharply defined x-ray frequency is reflected at any given angle.

The Powder Method.—The Bragg method of x-ray spectroscopy requires a large crystal. The crystal is rocked. But instead of rotating the crystal, it can be used in the pulverized state. Some few crystals in the powder will always be tilted in the proper direction for x-ray reflection. Thus this powder method of spectroscopy is not different in principle from the Bragg rotating-crystal method. Since, in the powder, crystals are tipped in all directions, the spectrogram shows a *ring* of constant x-ray deviation instead of the lines obtained by Bragg

when he rotated his crystal in the horizontal plane. (Figure 134, which in fact represents a very different phenomenon, nevertheless resembles closely these x-ray powder spectrograms.)

This is a favorite method of analysis. It is not confined to powders; the many small crystals in metals, in textiles, in ceramics, etc., can be studied in this way.[1]

A Cubic Crystal.—X-rays have provided a most powerful tool for analyzing the structure of crystals. By using a ray of known wave length, the distance *d* between various crystal planes can be found. Even among the chemical elements the crystal forms are many; copper is cubic, zinc is hexagonal, sulphur rhombic.

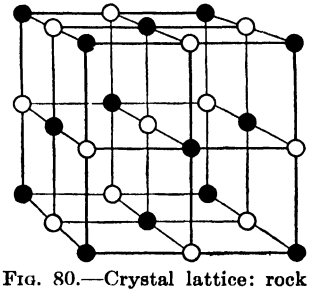


FIG. 80.—Crystal lattice: rock salt.

Common salt has one of the simplest of structures; it is shown in Fig. 80. Here the sodium ions (Na^+) and the chlorine ions (Cl^-) are arranged alternately so that each ion of one type has six neighbors of the other. The sodium atoms alone (•) form a *face-centered* cube. The chlorine atoms (o) have a similar structure. With both kinds of atoms considered together, this crystal is made of simple cubical cells. The faces of these cubes define what are called the 100 (and 010 and 001) planes of the crystal. These planes are 2.8 angstroms apart. Each plane consists of sodium and chlorine atoms in equal numbers. These faces are again shown in the larger crystal of Fig. 29.

In a cornfield many different systems of rows can be found; direct, transverse, and in diagonal directions. As we look through the diagonal rows we find them closer together and perhaps less well defined. So with crystals there are many systems of planes of atoms. The more important planes are illustrated in Fig. 29. The edges to this crystal are cut to represent the 110, 101, and 011 planes. The planes represented

[1] X-ray analysis is used in regulating heat treatment of metals. The size of the metal crystals increases with annealing. When the crystals are very small, the diffraction circles lose their sharpness as in well-pulverized powders. Rolling tends to orient the crystals, with the result that the circles are strengthened along certain axes, weakened along others. With a coarser grained metal, sets of Laue spots are found (like the Laue spots from a single crystal), instead of the continuous circles. (See "Encyclopaedia Britannica," X-rays, Plate II.)

as cut through the corners are the 111 planes.[1] These 111 planes each pass through atoms of a single type, the first a plane through sodium atoms, then 1.6 angstroms below this a plane through chlorine; the spacing between similar planes is 3.2 angstroms.[2] There are many other crystal planes at intermediate angles. They become of less importance in x-ray reflection as the number of atoms making up the plane becomes smaller.

We are using here to designate planes the *Miller indices*. A plane can be designated by its intercepts along the three crystal edges. But the Miller indices are the reciprocals or rather are the simplest whole numbers proportional to the reciprocals of these intercept numbers. So in Fig. 81 the plane passing through atoms 1 and 2 and 3 along the three respective axes (reciprocals 1, ½, and ⅓) is designated as 6, 3, 2. A zero index means an intercept at infinity, *i.e.*, parallelism.

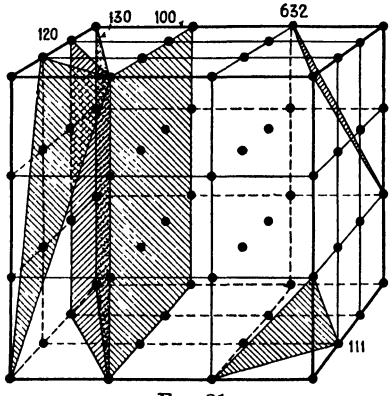


FIG. 81.

Absolute Measurement of Wave Lengths.—In order to measure x-ray wave lengths it is necessary to know the crystal spacing (d). Once the structural type of the crystal is known, this spacing can be found from the density of the substance. For instance, consider rock salt. Its weight per cubic centimeter is 2.16 gm. This is $\frac{1}{27}$ of a mole (58.5 gm.) and hence 1 c.c. contains $6.06 \times 10^{23}/27 = 22.5 \times 10^{21}$ atoms of sodium and atoms of chlorine. This is 45×10^{21} atoms in all in a centimeter cube, arranged in simple cubic array. The number of atoms along one edge is the cube root of this or 3.55×10^{7}. Hence the grating space between neighboring atoms is $1 \div 3.55 \times 10^{7} = 2.82$ angstroms.

[1] The 110 planes are 2 angstroms apart; the 111 planes are 1.6 angstroms apart. It is easy to show that the 110 and 111 spacings are reduced from the principal grating space (2.8 angstroms) in the ratio $1/\sqrt{2}$ and $1/\sqrt{3}$.

[2] In common salt these successive planes are quite different since each sodium ion contains 10, each chlorine ion 18, electrons. But in sylvite (KCl) the potassium planes contain the same number of electrons as the chlorine; the successive planes act almost exactly alike as far as x-ray scattering is concerned.

The limit of accuracy of *absolute* x-ray measurements is limited by the accuracy of Avogadro's number (1 part in a 1000). For relative measurements of different lines the accuracy is very much greater. X-ray wave lengths are given to six significant figures.

Theory of Laue Spots.—In the Bragg method the image is usually reflected from the 100 planes, parallel to the cleavage surface. But any of the other planes with its own grating space may serve to reflect x-rays. The Laue spots are due to rays reflected from different surfaces of this sort.

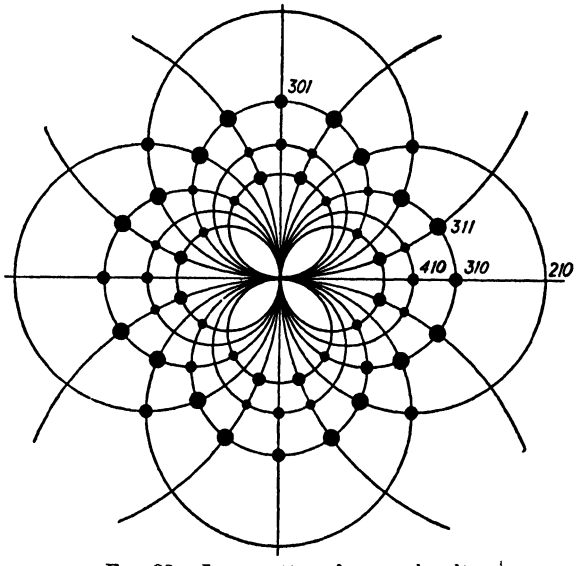


FIG. 82.—Laue pattern from rock salt.

Figure 82 shows the symmetrical arrangement of the Laue spots when a beam of continuous x-rays pass through a rock salt crystal. Each spot is due to reflection from a different plane of atoms. For simplicity let us consider in only two dimensions the tilt of the various reflecting planes such as 210, 310, 410 (Fig. 83). To explain the spots reflected from the 311, 321, and other such planes the analysis would have to be slightly extended. In Fig. 83 a narrow beam of x-rays is supposed to strike the crystal from above (for convenience the direction of the ray is shown at the left). The 100 planes are those which are perpendicular to this beam, the 010 plane is parallel to it; between

these are other planes of atoms which are represented by the dotted lines.

The x-ray beam if reflected from the 100 planes will be reversed in direction; from the 120 planes it will be deviated by 128°; from the 110 planes by 90°. None of these rays can play a part in the Laue spectrograms. The 210, 310, 410 planes are inclined at angles of 26°, 19°, 14°. The rays from these planes emerge deviated by 52°, 38°, and 28° and form the spots (210, 310, 410) indicated in Fig. 82.

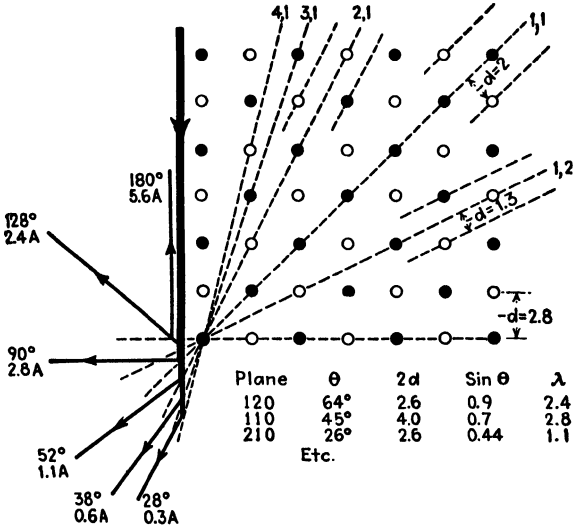


FIG. 83.—Theory of Laue spots: in two dimensions.

So far the story for these Laue spots has been one of pure reflection—no mention of wave length and no proof of the wave theory. However, it is true that each of these spots is caused by x-rays of different wave length and, unless this wave length is present, in the primary radiation that spot will be missing.[1] Here is the proof of the wave theory.

The frequencies reflected from the various planes can be computed. The separation of the 100 planes is 2.8 angstroms, of the 110 planes 2 angstroms, of the 120 and 210 planes 1.8 angstroms, etc. Bragg's law gives the wave lengths reflected for the corre-

[1] The Bragg spectrograms (Fig. 88) were taken with homogeneous x-rays; only two frequencies were prominent; for Laue spots a continuous range of frequencies must be present.

sponding glancing angles. These results are summarized in the table in Fig. 83.

The Laue spots give directly the angles of the various reflecting planes in the crystal and the separations of the planes can be found by measuring the wave length of the radiation; the powder or rotation method is often more convenient.

Results of Crystal Analysis.—Only a few of the crystal structures which have been evolved as a result of x-ray analysis will be mentioned. Similar to NaCl (but with larger grating space as the ions increase in size) are the crystals of KCl, KBr, KI, PbS, and CaS. Calcite ($CaCO_3$) is well-known. Its structure is shown in Fig. 84*a*. It resembles the rock-salt structure if we imagine two opposite corners of the salt crystal pushed together so as to form a rhombohedron from the cube. CaS has a structure similar to NaCl; calcite is formed from this if for each sulphur atom the CO_3 group is substituted. In this group the carbon atom may be supposed to be surrounded by three oxygens in a ring (horizontal in Fig. 84) about it. The presence of these rather flat CO_3 groups causes an enlargement of the crystal in this plane giving the rhombohedral shape.

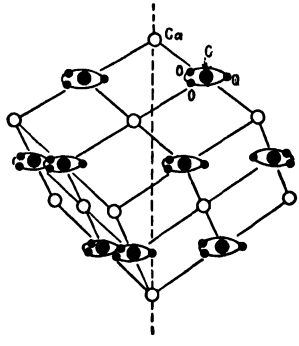


FIG. 84-*a*.

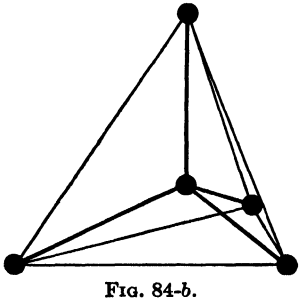


FIG. 84-*b*.

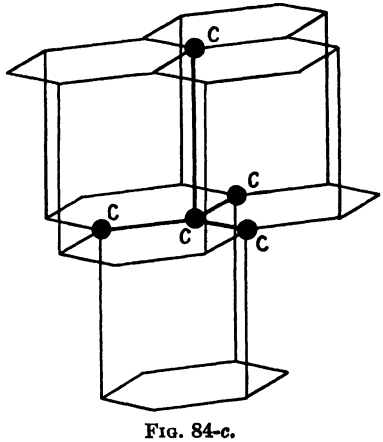


FIG. 84-*c*.

The dotted line is the "principal axis"; the closer packing in this direction affects the optical properties and gives the crystal its well-known double

refraction. Light which is vibrating parallel to this axis travels with a speed of 125,000 miles per second; light vibrating at right angles thereto travels 110,000 miles a second. Hence double refraction.

Many of the metallic elements crystallize in *face-centered* cubic array. Such elements are Cu, Ag, Au, Al, Ni, Pb. Other common metals (Na, Fe, Cr, W, etc.) have a *body-centered* cubic structure. Here the atoms are found on the corners and in the center of the elementary cube but not in the face centers. Still others—Be, Zn, and Mg—have a hexagonal structure, much like the array of shot piled in a pyramid of triangular base.

Figures 84*b* and *c* show two structures for carbon, the first as it is found in diamond, the second less closely packed as in graphite. In each the tetravalence of carbon is indicated by the four bonds and in graphite the benzene ring structure appears continually repeating in all directions throughout the cleavage planes of the crystal.

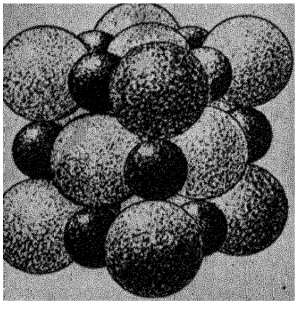


FIG. 85.—Atomic spheres of influence: NaCl. (*Wyckoff.*)

From x-ray analysis we have learned not only the positions of the atoms in the crystal but the sizes of the atoms or ions and even something of the distribution of electrons within them. Some crystals are made of ions as in the salts, in some a neutral atom or group forms the crystal element, and in metals it would seem that a free electron must take the place of a larger ion. The field of investigation is very large. Some of the results are summarized by Bragg's article in the "Encyclopaedia Britannica" (X-rays and Crystal Structure).

Ionic Size and Chemical Action.—From the x-ray analysis of ionic crystals the crystallographer can determine the distance of nearest approach for the various ions and hence can be derived an effective ionic radius. As might be expected as we go from one period of elements to the next and shell after shell is added to the atom (Chap. XXII), this ionic radius increases. A given shell shrinks as the nuclear charge increases. The ions from C^{4-} to Cl^{7+} all have two completed shells (like neon) and the radius shrinks from 2.3 to 0.25 angstrom as the atomic number increases from 6 to 17.

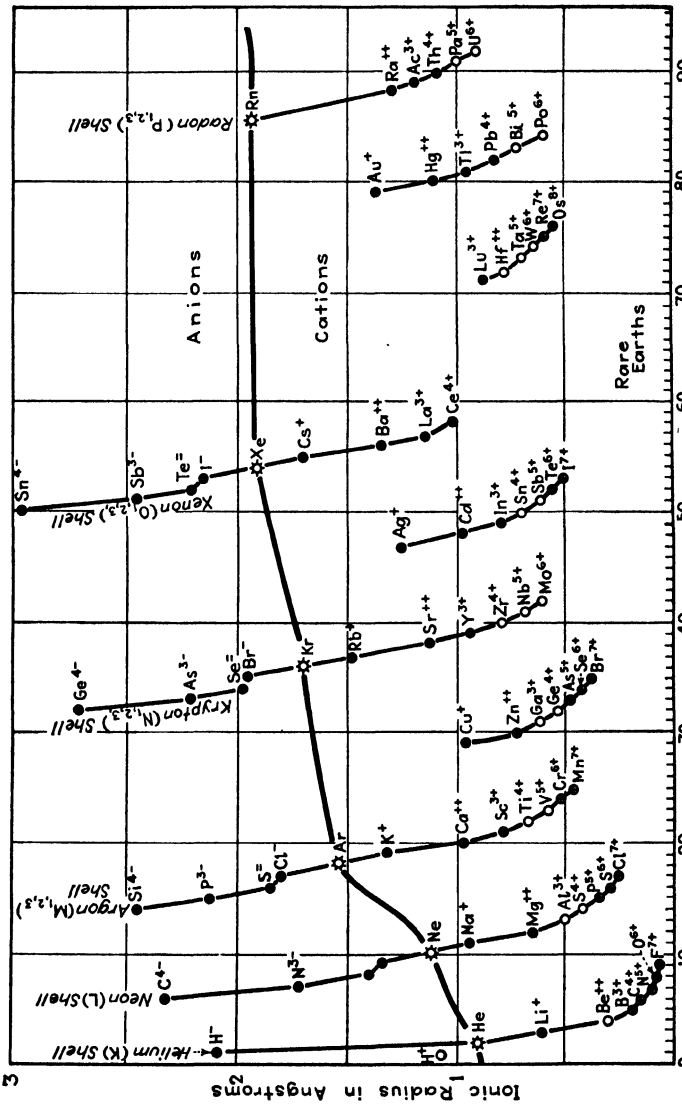


FIG. 86.—Ionic sizes. The figure shows the formation of the atom shell by shell and the gradual shrinking of the shell with increasing nuclear charge.

Suppose we think of the ion as a charged sphere. The capacity of a sphere is equal to its radius (r). If the ion is considered as a charged sphere, its potential is proportional to n/r where n is the number of charges upon it, *i.e.*, the degree of ionization. The chemical action of the ion depends largely upon this ionic potential. For positive ions such as Na^+, K^+, Cu^+, Mg^{++}, Ca^{++}, where the ionic potential is less than 5, the ion is basic in water solution; it releases negative ions readily. So NaOH is dissociated at the sodium-oxygen bond. There are no free H^+ ions in sodium hydroxide solutions. When the ionic potential lies above 10, the ion is acidic. For example, Cl^{7+} takes oxygen atoms from water.[1] H^+ ions are released in dissociation. With ionic potentials between these limits the ion is amphoteric. The ionic potential of H^- is 9; acidity or basicity depends on whether the potential of the cation is notably higher or notably lower than this value.

[1] Making $HClO_4$.

CHAPTER XX

THE HIGH-FREQUENCY SPECTRA OF THE ELEMENTS

The spectrum constant for hydrogen was R; for He^+ it was 4R. This chapter continues the story.

A new era in physics began in 1912–1913 with Bohr's theory of the atom and with the discovery by Laue and Bragg of x-ray diffraction and with Moseley's discovery of characteristic x-ray spectra. It is difficult to say whether the discovery of the mathematical physicist or those of the experimenters were the more important.

Moseley had worked with Rutherford on radioactivity. After Laue's discovery he investigated the wave lengths of the characteristic radiation emitted by different substances and in 1913 published a paper whose title is that of this chapter. He was only twenty-six. Two years later he was killed in the World War. "Some day," says Millikan, "a poet will arise who will make an epic for the ages out of young Moseley's discovery."

X-ray Lines and Atomic Number.—Moseley made up x-ray tubes with targets of different elements; Bragg's rotating-crystal method was used for determining the wave lengths of the emitted radiation. The spectrograms always showed a background of continuous radiation the high-frequency limit of which depended upon the voltage of the tube. But far more intense than this continuous radiation, each element had a line spectrum. Moseley found two lines for each element. The frequency of these lines depended on the element itself, not upon its state of chemical combination; the frequency increased regularly as he went from one element to the next in the periodic table.

Figure 87 shows his spectrograms for the first transition group of elements. These lines are known as the alpha and beta lines of the K series. Between calcium and titanium the element scandium is missing from the series. Then the others follow in regular sequence. The elements iron, cobalt, nickel are chemically quite similar and the complete separation of them is difficult; the cobalt used by Moseley was evidently contaminated with

both iron and nickel. The alloy brass reveals the lines of both its constituents, copper and zinc.

It had long been known that the heaviest elements had the hardest characteristic radiation. Moseley wished to decide whether this depended upon the atomic weight or (as Rutherford contended) upon the atomic number. Cobalt is one of the paradoxes of the Mendeleef scheme; it has slightly greater atomic weight than nickel but in other properties resembles iron more closely than does nickel and it is placed between iron and nickel in the table. But before Moseley's time one could never feel quite justified in so violating the rule on which the table was built. In view of Fig. 87, however, the arrangement is not to be questioned. Atomic weight as such has little to do with x-ray emission. There is a very intimate relation with atomic number.

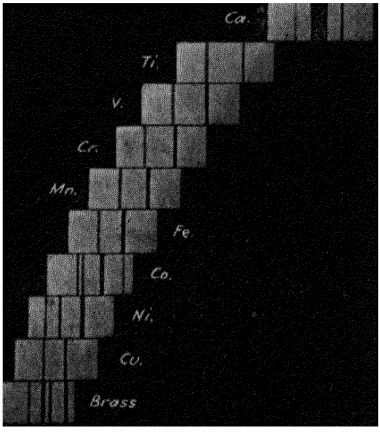


FIG. 87.—Characteristic emission. (*Moseley.*)

Mendeleef was forced to leave many places vacant in the periodic table. X-ray spectrograms show unmistakably where such elements are missing. The omission of scandium between calcium and titanium is evident from the irregularity in the sequence of lines here. The characteristic lines serve to detect and identify the elements and have been the means of discovery of several of the missing elements which have been found in recent years.

X-rays from the Fourth Period.—Moseley's sequence stops with zinc (30). Figure 88 continues the sequence from arsenic (33) to rhodium (45). The noble gas krypton (36) is omitted between bromine and rubidium; rare elements are omitted between strontium and niobium and rhodium. All such omissions are apparent in the sequence of the lines. Figure 88 is due to Siegbahn. Here four lines of the *K* series are shown: the alpha doublet and beta and gamma. In Moseley's pictures the closer lines are not resolved.

X-ray Wave Lengths—K Series.—Siegbahn's spectrograms were taken with a calcite crystal. The glancing angle (half the observed deviation angle) is shown and from this the wave lengths and frequencies can be computed. Take, for example, bromine:

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

Calcite grating space: 3.028 angstroms

$\theta(K_\alpha$ bromine$) = 9° 50'$; $\sin \theta = 0.171$

$\lambda = 2 \cdot 3.028 \cdot 0.171 = 1.035$ angstroms

$\nu(= c/\lambda) = 290{,}000$ vibrations per subsecond.

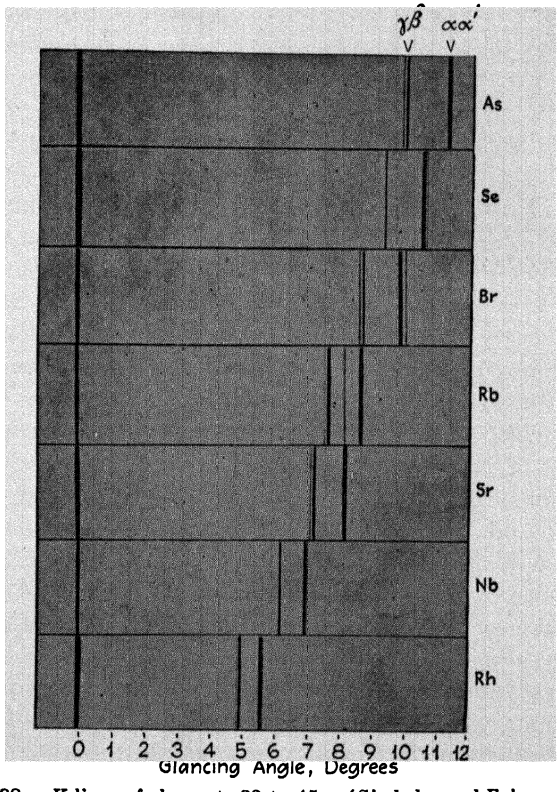


FIG. 88.—*K* lines of elements 33 to 45. (*Siegbahn and Friman.*)

The wave length is about 1 angstrom—some five thousand times shorter than visible light—300,000 vibrations per subsecond as compared with 60. This is about the average of the wave lengths which have been measured. Most of the measured

characteristic lines have had frequencies between a hundred thousand and a million per subsecond. These are high frequencies—as many per subsecond as in radio broadcasting there

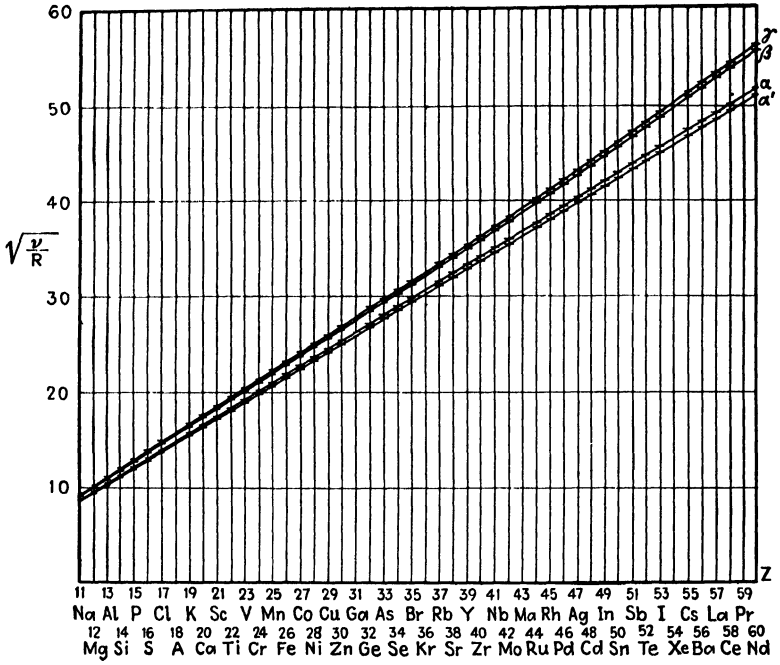


FIG. 89.—Atomic number and frequency (Moseley's law).

are vibrations per second! Table 39 gives the frequencies of the K_α line for several elements.

TABLE 39.—FREQUENCY AND ATOMIC NUMBER: K_α

Z		λ	ν	$\sqrt{\nu}$	$Z-1$
11	Sodium	11.883	25,000	159	10
20	Calcium	3.352	89,000	298	19
22	Titanium	2.742	109,000	330	21
24	Chromium	2.285	131,000	362	23
26	Iron	1.932	155,000	394	25
28	Nickel	1.655	181,000	425	27
30	Zinc	1.433	209,000	456	29
35	Bromine	1.035	290,000	539	34
38	Strontium	0.871	344,000	586	37
50	Tin	0.487	616,000	785	49
74	Tungsten	0.209	1,435,000	1,196	73

The Moseley Law.—A remarkable relation exists between the frequency and the atomic number. In going from the eleventh to the seventy-fourth element, the frequency has increased from 25,000 to 1,435,000. The square root of the frequency has been computed in the table; it is nearly proportional to the atomic number (Z). Actually, except for some of the heavier elements, $\sqrt{\nu}$ is almost exactly proportional to $Z - 1$; the proportionality constant is 16.0. This proportion will become evident if the last two columns are carefully compared.

This simple relation is the substance of Moseley's law: The square root of frequency is proportional (except for a constant s) to the atomic number.

$$\sqrt{\nu} = C(Z - s)$$

The constant s is called the screening constant. This same law holds for the other lines of the K series and, with different values for the screening constant, for the other series. The linear relation is shown for the four lines of the K series in Fig. 89 where $\sqrt{\nu/R}$ is plotted against the atomic number. The lines are almost straight and, extended, they all intersect the axis at atomic number 1.

Bohr's Theory and X-rays. No other physical property of the several elements exhibits any such simple relationship as that expressed in this law; its significance becomes much greater when we attempt to interpret characteristic x-ray emission in the light of the Bohr theory. Just as an optical series is due to transitions of electrons between outer orbits of the atom, so these characteristic x-ray lines are due to transitions between orbits within the kernel. Within as without the kernel, electrons move in quantized orbits. The innermost (K) orbit is circular, with principal quantum number 1; the next (L) orbits, either elliptical or circular, have principal quantum number 2; the next (M) orbits

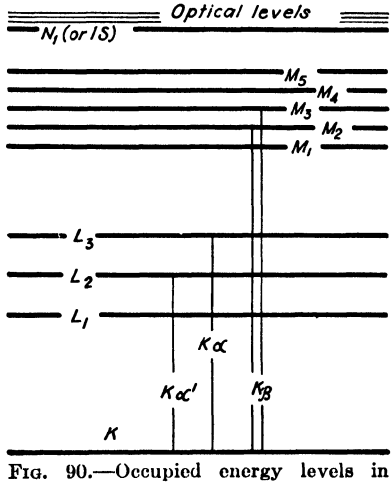


FIG. 90.—Occupied energy levels in copper.

have quantum number 3, and so on. The K series which has been described is the series of shortest wave length and is due to transitions from L, M, etc., levels into the inner (K) level. In fact the alpha, beta, gamma lines of the K series are quite analogous to the Lyman lines of hydrogen.

Bohr saw that the theory which he had applied to hydrogen and ionized helium was directly applicable to x-ray spectra of heavier elements by using the appropriate value of Z. The diameter of the inner orbit of hydrogen was 1 angstrom, for helium $\frac{1}{2}$ angstrom. By Eq. (23′) it is inversely proportional to Z (or better to Z_e, the effective atomic number). The diameter of the K orbit of sodium is $\frac{1}{10}$ angstrom; of tungsten $\frac{1}{73}$ angstrom. The next circular orbit in the tungsten kernel (an L orbit) is four times as large.

The energies of the orbits are given by[1]

$$W = -Z_e^2 Rh\left(\frac{1}{n^2}\right) \qquad (25'')$$

For the inner orbit of hydrogen W was found to be -1300 atomic ergs, for helium ion -5200 atomic ergs. For tungsten it is a negative number 73^2 times larger than the value in hydrogen.

The frequency of the emitted radiation is given by

$$\nu = \frac{W}{h} = Z_2{}^e R\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right) \qquad (26'')$$

This is the generalized Balmer formula, with the series constant $Z_e^2 R$ instead of R. If we let $n_1 = 1$ to give the energy and vibration number of the K orbit and $n_2 = 2$ for the L orbit, we have

$$\nu_{K\alpha} = Z_e^2 R\frac{3}{4}$$

for the frequencies of the K_α lines; for the K_β lines

$$\nu_{K_\beta} = Z_e^2 R\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = Z_2{}^e R\frac{8}{9} \text{ (roughly approximate)}$$

For the L_α line (due to transition $M \rightarrow L$)

$$\nu_{L_\alpha} = Z_e^2 R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = Z_e^2 R\frac{5}{36} \text{ (roughly approximate)}$$

[1] See energy levels for uranium in Fig. 97.

This and other lines of the L series are analogous to the Balmer series of hydrogen.

From Eq. (26″) the frequency is proportional to Z_e^2; for K_α

$$\nu_{K_\alpha} = \frac{3}{4}RZ_e^2; \qquad \text{or } \sqrt{\nu_{K_\alpha}} = \sqrt{\frac{3}{4}R}(Z - s)$$

which is Moseley's formula. The proportionally constant $\sqrt{\frac{3}{4}R} = 15.7$, in close agreement with the results of Moseley!

Such a result is not short of amazing; this confirmation came as an unexpected present to the Bohr theory before its first birthday. The hydrogen spectrum was related to other optical spectra; we have remarked on that. But that relation is not so close as the relation between the spectrum of hydrogen and the x-ray spectra of the heavier elements. The visible spectrum of hydrogen indeed appeared to be essentially the x-ray spectrum of the element of atomic number 1; the Lyman series can be considered as the K series, the Balmer as the L series, the Paschen as the M series of hydrogen. K_α for uranium is about 0.1 angstrom, for tungsten 0.2 angstrom, for bromine 1 angstrom, for iron 2 angstroms, for sodium about 12 angstroms; if we extrapolate backwards to hydrogen 1200 angstrom does not seem unreasonable for the K_α of hydrogen, the first line of the Lyman series. The Bohr theory connected by one law the spectra of all these elements, elements some 90-fold different in atomic number and 10,000-fold different in frequencies!

The Screening Constant.—The result is surprising since the Bohr theory treats of a single electron and attracting nucleus; any effect due to other electrons we have so far largely ignored. Elementary electrical experiments show that the charge on the surface of a conducting sphere produces an external but no internal force field. Hence the effect of any shell of electrons upon an electron placed *within* it can be largely neglected. There are two electrons in the K shell; the electrons in the L shells or M shells or still larger shells of the kernel will have no appreciable influence upon these. But when one of these K electrons is displaced, the other electron still shields the nucleus. The effective attracting charge is now not Z but $Z - 1$. For this reason it is appropriate to take $Z_e = Z - 1$, with a shielding constant (s) of unity. This for the innermost, the K, shell.

The effect of the shielding on other shells is more serious and the theory less simple. In a rough way one may write as we have written above the frequencies of the lines K_β and K_γ as

$$\nu_{K_\beta} = (Z - 1)^2 R\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = \frac{8}{9}R(Z - 1)^2$$

and

$$\nu_{K_\gamma} = (Z - 1)^2 R\left(\frac{1}{1^2} - \frac{1}{4^2}\right) = \frac{15}{16}R(Z - 1)^2$$

This, however, implies the same Z_c for the third and fourth shells as for the inner ones which is far from true.

The L Series.—Electrons falling into the L shells from M, N, etc., levels give lines of the L series. There are three distinct L

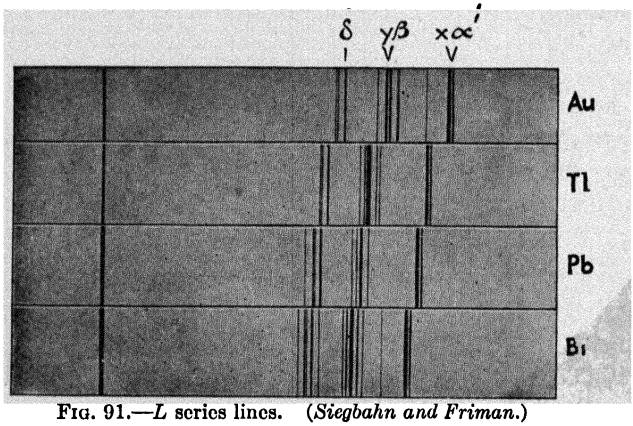


FIG. 91.—L series lines. (*Siegbahn and Friman.*)

shells and three distinct L series. The L shells are usually six or seven times less deeply buried than the K shell and the wave lengths of the more important lines are some six or seven times greater. The majority of these wave lengths are greater than 1 angstrom. L_α of uranium (92) has about the same frequency as K_α of rubidium (37).

These L series lines clearly correspond to the Balmer series of hydrogen. The electrons return to an orbit of principal quantum number 2. The frequencies are greater than those found in hydrogen in proportion to the square of the effective atomic number. Again we have the Moseley law of proportion.

$$\nu \propto (Z - s)^2$$

That the frequencies are some six or seven times smaller than in the K series rather than four times smaller as in hydrogen is due to the influence of the screening constant, which is much larger here than it is in the K shell. The value of s is about 3.5 for these L levels.

M and N Series.—When electrons fall into the third (M) shells, the M series is emitted. There are five M levels and hence five M series. The wave lengths are usually some four or five times greater than those of the L series. The M radiation is so soft that it will not penetrate the glass walls of a tube; and it is even absorbed by air at ordinary pressure. Even for the heaviest elements only a few thousand volts are required to excite the M radiation.

N radiation has been observed for thorium and uranium.

Summary.—In the kernel are orbits corresponding to the first, second, third, etc., orbits of hydrogen. These orbits are normally occupied; but in case a vacancy is created, an electron can fall into it from an outer orbit. So transitions into the inner K orbit produce the K series, into the second group (L orbits) the L series, into the third (M orbits) the M series. These are analogous to the Lyman, Balmer, and Paschen series. By the Bohr theory the series constant should be RZ_e^2 and hence the square root of the frequency be proportional to Z_e. This is Moseley's famous law. The agreement with Bohr's theory is a great success for atomic theory.

CHAPTER XXI

PROPERTIES OF X-RAYS

Line emission and continuous emission; Einstein's photoelectric law again and the inverse effect. Absorption edges and series limits—there are no absorption lines.

In medical practice x-ray tubes are usually operated at voltages between 30,000 and 300,000. The kinetic energy of the electron in atomic ergs is directly computed from the relation: 1 electron-volt equals 96.4 atomic ergs. X-rays are emitted when the fast-moving electrons are suddenly stopped by the target.

According to the classical theory, whenever an electron is accelerated an electromagnetic wave is given off (page 103). When an electron is stopped very suddenly a very short pulse, a *continuous* spectrum of very short wave lengths should be emitted. This is the classical explanation of x-rays. According to Bohr's theory, the impinging electron displaces an electron from one of the inner shells of an atom in the target of the tube (a type of ionization). Then an electron falls into this vacated orbit from some other orbit less deeply buried and gives off a characteristic x-ray line. When it is the innermost orbit which has the vacancy, one of the K lines is emitted.

There is truth in each of these points of view. We have seen something of the line spectrum which is characteristic of the material of the target. Always as a background to this there is the continuous spectrum which is nearly independent of the nature of the target; its range of wave lengths depends upon the speed of the bombarding electrons.

Ionization Spectrometer.—For direct measurements of the x-ray intensities an ionization chamber is often substituted for the photographic film in the Bragg spectrometer. The ionization chamber travels on a circular track about the crystal; a narrow slit allows the reflected beam to enter the chamber, where it renders the gas conducting. The crystal must rotate just half as fast as does the ionization chamber so that the chamber

will at all times be in a position (angle 2θ) to receive the directly reflected beam.

The ionization current is measured by the rate of leak of a sensitive electrometer. For exact measurement of deflection angle the photographic method is probably superior; the ionization method has an advantage when intensity measurements are desired.

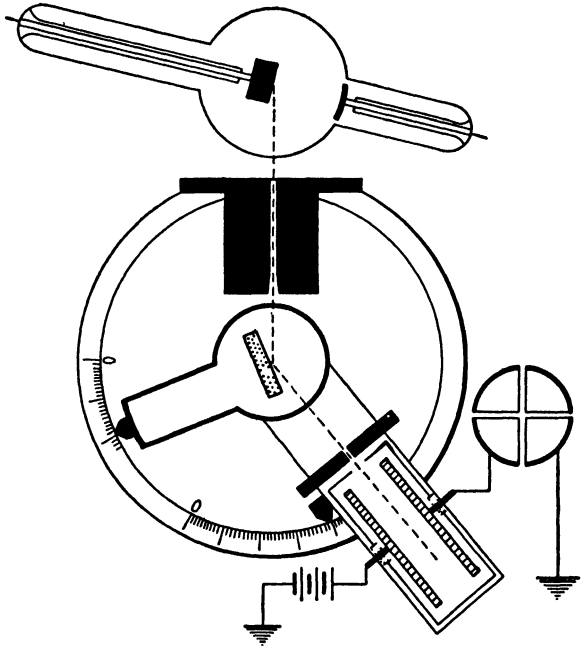


FIG. 92.—Ionization spectrometer.

Figure 93 shows the record of such an ionization spectrometer. The emission in this case was from a tube with a rhodium target (with a slight trace of ruthenium). The upper curve shows the spectrum when the exciting potential on the tube was 40 kv.; other curves show the spectrum for lower voltages. At 23.2 kv. only the continuous spectrum appears (minimum deviation 5° corresponding to 0.53 angstrom). At higher voltages this continuous spectrum is stronger, extends to shorter wave lengths, and upon i_v is superposed the K spectrum of rhodium—K_α, K_β, and K_γ being resolved. The K_α and K_β lines of ruthenium also appear.

The continuous spectrum extends indefinitely into the longer wave lengths; as we approach shorter wave lengths, the intensity of emission comes to a maximum and then drops to zero at a sharp limit. This continuous x-ray spectrum has a resemblance to the continuous radiation of much longer wave length emitted by a heated body. It has been shown how black-body radiation increases in intensity and extends to shorter wave lengths as the temperature is raised. The short-wave limit is here for this continuous x-ray emission much sharper than the limit found in black-body radiation.

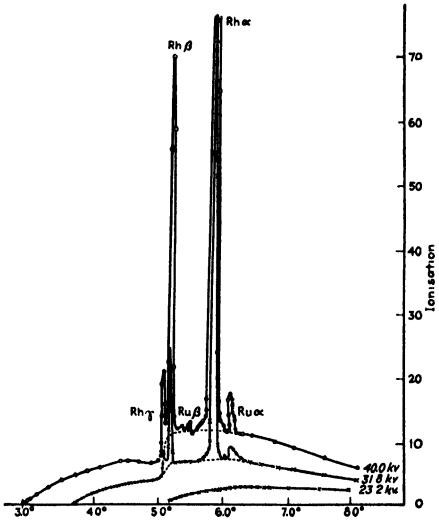


FIG. 93.—Continuous and line emission. K series of rhodium (trace of ruthenium). The lines do not appear until the critical voltage is reached.

Law of the Inverse Photoelectric Effect.—The continuous spectrum is shown to better advantage in Fig. 94 where it is not distorted by the line emission. (The K lines of tungsten have wave lengths about 0.2 angstrom). This continuous radiation is due to the stopping of the impinging electron. It is the inverse process to the photoelectric effect. When the electron stops, its kinetic energy is transformed into electromagnetic energy; in the photoelectric effect the process is the reverse. By the quantum theory the limiting frequency ν_{lim} should be proportional to the tube voltage. If the tube potential is V the energy of the impinging electron is eV (or, expressing V in volts, $96V'$). The quantum of radiated energy can be less (owing to dissipation

of energy) but not greater than this. The maximum frequency ν_{lim} then is given by[1]

$$eV = 96V' = h\nu_{\text{lim}} \tag{35}$$

This is the fundamental formula for x-ray excitation. By Eq. (35) the limiting frequency is given by

$$\nu_{\text{lim}} = 24V'$$

In laboratory practice the wave length is referred to more often than the frequency. Substituting $300{,}000/\lambda_{\text{lim}}$ for ν_{lim} and expressing V' in kilovolts, we have

$$\lambda_{\text{lim}} = \frac{12.5}{V''} \quad (V'' \text{ in kilovolts})$$

At 12.5 kv. the shortest wave length is 1 angstrom; at 25 kv. the limit is ½ angstrom; at 100 kv. it is ⅛ angstrom, and so on.

This gives one of the celebrated confirmations of the quantum theory and gives an independent method of measuring h. In Fig. 94 the 40-kv. curve has a minimum wave length slightly greater than 0.3 angstrom, corresponding to a frequency of approximately a million per subsecond. Solving the equation for h, we get

$$h = \frac{96 \cdot 40{,}000}{1{,}000{,}000} = 3.8$$

This is the approximate solution; the reader, noting the limiting wave lengths in Fig. 94 more carefully can obtain a more exact value for h.

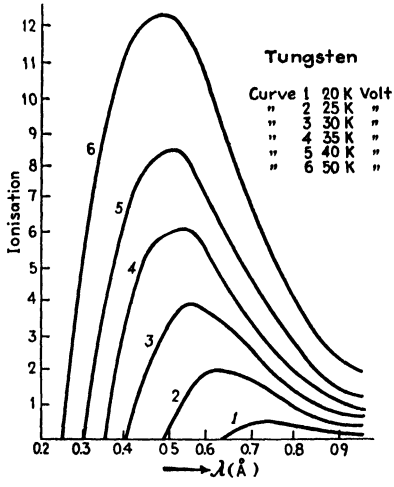


FIG. 94.—Continuous radiation from tungsten target. $eV_{\text{lim}} = h\nu_{\text{lim}}$.

Excitation of Characteristic Spectra.—The process of line excitation is less direct than this. The impinging electron in this case displaces an electron from one of the orbits in the kernel; in this case the energy of the high-speed electron has gone, momentarily at least, into the potential energy of the ionized atom instead of into radiation. After this, as a secondary process, another electron falling into the vacant place from an

[1] Compare Eq. (18); here W_0 is negligible.

outer orbit gives the characteristic emission. To excite the K emission an electron must be removed from the innermost (K) shell. One of the L-shell electrons then falls into this level, giving the K_α line, or an electron falling from an M level gives K_β or from N, K_γ, etc.

Now the critical voltage required to excite any of these K lines is equal to the ionizing potential of the K shell. The K_α line is not excited when the voltage corresponds (through the Einstein equation) to $\nu_{K\alpha}$; no line of the K series appears (Fig. 93) until the voltage corresponds to the limiting frequency of the series (slightly greater than K_γ) and then all lines of the series appear at once. Herein the case differs from that of optical spectra where at the critical potential a single line spectrum occurs. The difference is due to the fact that all orbits in the kernel normally have their full complement of electrons; the electron cannot be displaced from the K shell to the L shell, since the latter is already complete. The series from any shell appears only when the potential is sufficient to remove an electron therefrom to the periphery of the atom. All lines of the series then appear at once.

Photoelectric Effect.—When electrons are suddenly stopped, x-rays are produced; when x-rays are absorbed by matter, electrons are set free. When x-rays strike a surface, electrons are released just as in the photoelectric effect with visible and ultraviolet light; when x-rays fall upon gas molecules, these molecules may become ionized. Part of the x-ray energy will then be used in removing the electron from the atom; this will be a large loss if the electron is removed from a deep-lying shell in the atom. The remainder appears as kinetic energy of the free electron. The *fastest* electrons then will have energy

$$\tfrac{1}{2}mv^2 = eV \qquad (18')$$

The energy (W_0) which is always necessary to remove even the most loosely bound electron from the surface (or from the gas molecule) should in all strictness be subtracted from eV but, since this energy is only a matter of a few e-volts, it may be neglected.[1]

[1] The combination of the inverse and direct photoelectric effects (excitation of x-rays and ionization) explains a phenomenon observed long before it was explained. When a discharge takes place in a tube, electrons are emitted from metals in the neighborhood. The speed of the fastest of these equals the speed of the electrons in the discharge tube.

Secondary X-rays.—X-rays passing through a solid are scattered. Except for a slight shift which sometimes occurs (Compton effect), the wave lengths of the original and scattered rays are equal.[1] To be distinguished from this scattering of the primary radiation is the secondary radiation. In passing through matter, the primary x-ray may be absorbed and electrons are displaced from the inner shells of the atoms. Other electrons falling into these vacated shells again create x-rays. The frequencies of these secondary rays are always less than the frequencies of the primary rays. In fact the absorbed frequency must be equal to or greater than the limit of the series, while the secondary x-rays are the series lines.

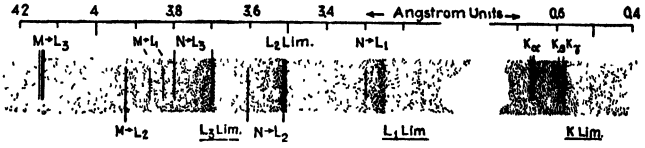


FIG. 95.—Emission lines and absorption edges in K and L regions of silver. The L_3 series of lines is shown above, the L_2 below, L_1 centered.

X-ray Absorption.—In x-rays one finds absorption edges rather than absorption lines such as are found in visible spectra. The reason for this is that electrons cannot be displaced from orbit to orbit within the kernel since all orbits are filled. X-rays can be absorbed by electrons in any shell as soon as the x-ray frequency exceeds the ionization vibration number of the shell. A sudden increase in absorption occurs whenever the frequency reaches the limiting frequency of a K, L, M, etc., series. These edges are fundamental in the interpretation of the atom, since each gives directly the energy of the level; x-ray lines give only differences between energy levels.

The drawing (Fig. 95) shows the absorption edges of silve superimposed on the line spectrum of this element. Such absorption edges could be obtained by passing a continuous spectrum through a thin piece of silver foil before being photographed. As long as the wave lengths are longer than the limit of the K series (which lies just beyond the K_γ line), the radiation is not absorbed by the K electrons and the blackening on the film is

[1] Constructive interference from crystals is in reality due to the reenforcement of scattered wavelets from the individual regularly arranged atoms.

intense. At the series limit a great diminution in blackening occurs. Similarly for the L levels three absorption edges are shown. There are in fact three L levels (L_1, L_2, L_3) and three distinct L series. One of these absorption edges marks the limit of each one of these series. These absorption edges and series limits occur at 3.25, 3.5, and 3.7 angstroms.

Absorption Coefficient.—In roentgenology penetrability is of paramount importance. A ray of wave length ½ angstrom will be half absorbed by 1 mm. of aluminum or 0.01 mm. of lead. Scattering of x-rays may contribute to the apparent absorption

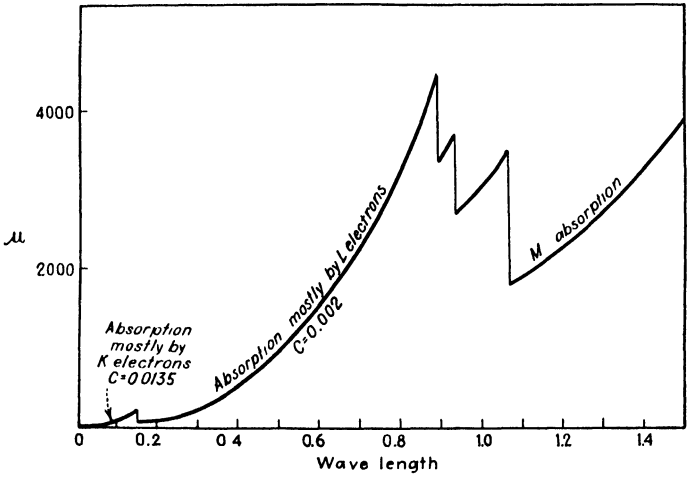


FIG. 96.—Absorption coefficient of platinum.

but, except for light elements and very short wave lengths, it is relatively unimportant.

It has been found that the absorption coefficient (μ) increases as the fourth power of the atomic number and as the cube of the wave length. The relation is complicated by the absorption edges at each of which the constant of proportionality changes.

$$\mu = C\frac{Z^4\lambda^3}{V_0}$$

where V_0 is the atomic volume (Fig. 32). In Fig. 96 the absorption coefficient for platinum is plotted. The values of the constant C given there apply to all elements.

Summary.—We have discussed (1) the emission of photons as high-speed electrons are stopped (primary excitation; inverse

photoelectric effect); (2) the emission of electrons as x-ray photons are absorbed (photoelectric effect; ionization); (3) the emission of weaker x-ray photons as stronger photons are absorbed (secondary radiation); (4) the scattering of photons; and (5) the absorption of photons, through process (2) or (3). Through all of this we are piloted by the quantum theory. The Einstein equation $\frac{1}{2}mv^2 = h\nu$ holds (for maximum ν or maximum v) in (1) and (2).

Through all of this there is a degradation of energy. A high-speed electron may give its energy to an equivalent photon; but usually several photons of lesser energy (longer wave lengths) are emitted. The photons in turn are absorbed by matter and electrons of equivalent or (more usually) of lesser energies are set free. The limiting wave length of a series is absorbed; the lines of the series of lower frequencies are emitted. The energy always tends to degrade, the energy being formed into more and more quanta (electronic or photonic) of less and less energy.



COMPTON

Arthur H. Compton—born 1892, *graduated from Wooster (Ohio)* 1913, *Ph.D. from Princeton* 1917, *graduate work in Cambridge. Since* 1923 *has been at the University of Chicago. Nobel prize in* 1927. *His major investigations have been in the fields of x-ray scattering and of cosmic rays. This work is discussed in Chap. XXVI.*

Compton's interests are not confined to the laboratory; he is alive to the human implications of science. His intellectual interests are inherited; his father has been professor of the classical subjects—Latin, mathematics, English, and eventually philosophy. His brother is a distinguished physicist, president of the Massachusetts Institute of Technology.

CHAPTER XXII

ENERGY LEVELS IN THE KERNEL

Shells and subshells! Principal and angular quantum numbers again, and selection principles. Breaks in the Moseley curves. The meaning of the periodic table. Pauli's exclusion principle.

Energy levels are given directly from the experimental absorption edges. Table 40 gives the wave length of the edges observed and the corresponding frequencies for uranium.

TABLE 40.—ABSORPTION EDGES FOR URANIUM

	λ	ν		λ	ν
K	0.107	2,800,000	M_1	2.23	131,000
L_1	0.564	532,000	M_2	2.38	126,000
L_2	0.588	510,000	M_3	2.87	106,000
L_3	0.718	418,000	M_4	3.33	90,000
			M_5	3.49	86,000

These and the higher levels are plotted in Fig. 97. The transitions corresponding to some of the stronger lines are shown. These emission lines give the differences between energy levels and all lines can be computed once the energy levels are known.[1]

Multiplicity of Levels.—The K level is single; there are three L, five M, seven N levels. According to the Bohr theory, the K level, principal quantum number 1, is necessarily circular. The L orbits, principal number 2, can have angular number $l = 1$ (circular) or $l = 0$ (elliptical)—represented as 2_1 and 2_0. The M orbits can be 3_2 (circular) or 3_1 or 3_0, the N orbits 4_3, 4_2, 4_1, 4_0.

In addition to this, each of the orbits except the narrowest ($l = 0$) is double. This multiplicity is due to the spin of the electron. The thinnest orbits ($l = 0$) have an orbital angular momentum of 0, a spin of $\frac{1}{2}$, and an inner quantum number $j = \frac{1}{2}$. The inner quantum number must be incorporated into the nomenclature. The orbit is indicated as n_{lj}. The K orbit,

[1] Actually emission lines can usually be measured with greater exactness than absorption edges and energy levels are usually computed by the use partly of absorption and partly of emission data.

K_1 is $1_{0\frac{1}{2}}$. Similarly the thinner L orbit (L_1) is represented by $2_{0\frac{1}{2}}$ ($l = 0$ and $j = \frac{1}{2}$). The other (circular) L orbits with $l = 1$ have $j = 1 \pm \frac{1}{2}$. These are represented by $2_{1\frac{1}{2}}$ and $2_{1\frac{3}{2}}$. There are thus three L orbits in all. In a similar way we account

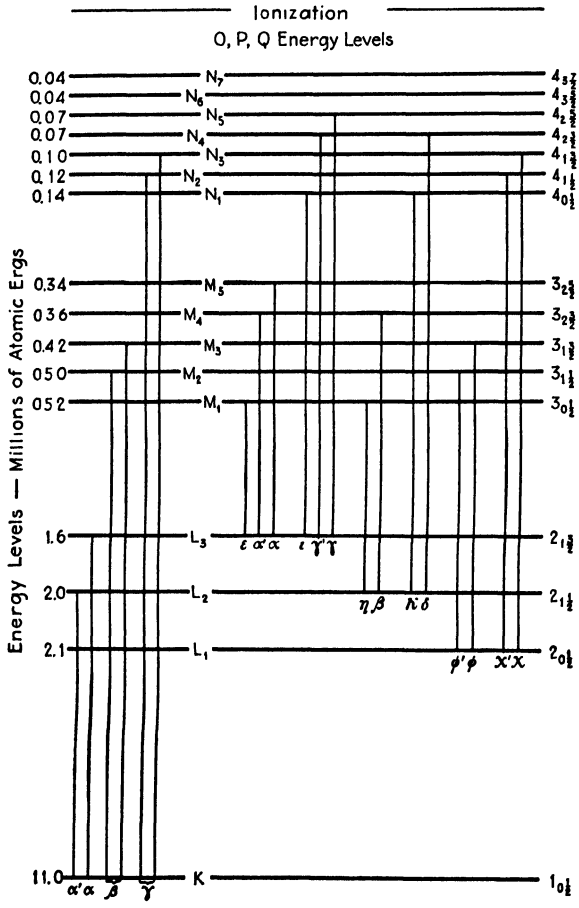


FIG. 97.—Energy levels of uranium.

for the five M orbits. (These orbits have three elliptical shapes and each value of l except $l = 0$ can occur with two opposite spins.) The orbital types are given in Table 41.

These orbital types stand in exact correspondence with those of visible alkali spectra. There the orbital shapes were distinguished by the letters S, P, D, etc. 1_0, 2_0, etc., were represented as $1S$, $2S$, etc. The three orbits of total number 3 (*i.e.*,

TABLE 41

		n	l	j			n	l	j
K_1	$1_{0\frac{1}{2}}$	1	0	$\frac{1}{2}$	M_1	$3_{0\frac{1}{2}}$	3	0	$\frac{1}{2}$
					M_2	$3_{1\frac{1}{2}}$	3	1	$\frac{1}{2}$
L_1	$2_{0\frac{1}{2}}$	2	0	$\frac{1}{2}$	M_3	$3_{1\frac{3}{2}}$	3	1	$\frac{3}{2}$
L_2	$2_{1\frac{1}{2}}$	2	1	$\frac{1}{2}$	M_4	$3_{2\frac{3}{2}}$	3	2	$\frac{3}{2}$
L_3	$2_{1\frac{3}{2}}$	2	1	$\frac{3}{2}$	M_5	$3_{2\frac{5}{2}}$	3	2	$\frac{5}{2}$

3_0; 3_1; 3_2) were represented by $3S$, $3P$, $3D$. Each orbit except the S type was a doublet (*e.g.*, $3P_{\frac{1}{2}}$; $3P_{\frac{3}{2}}$). The x-ray orbital types then can be summarized in optical nomenclature as follows:[1]

K_1:$1S$				
L_1:$2S$	L_2:$2P_{\frac{1}{2}}$	L_3:$2P_{\frac{3}{2}}$		
M_1:$3S$	M_2:$3P_{\frac{1}{2}}$	M_3:$3P_{\frac{3}{2}}$	M_4:$3D_{\frac{3}{2}}$	M_5:$3D_{\frac{5}{2}}$

L_1 and L_2 differ in shape but not in *total* angular momentum (j). The one of these orbits comes much closer to the nucleus than the other; the screening by other shells of electrons differs for the two and this accounts for the difference in the energy levels. The L_1L_2 doublet is called a *screening* doublet.

L_2 and L_3 differ in j but not in shape (l); their energy difference is due to the coupling of the spin with the magnetic field of rotation—L_2L_3 is called a *spin* doublet. For the light elements the screening effect is much the more important. But the spin doublet increases rapidly in importance among the heavier elements (Fig. 98).

Emission Lines.—The observed emission lines are in almost complete agreement with the energy levels which have been described. It will be remembered that the selection rules restrict electrons to transitions between orbits such that

$$\Delta l = \pm 1$$
$$\Delta j = \pm 1 \text{ or } 0 \text{ (except } 0 \rightarrow 0, \text{ forbidden)}$$

Two possible transitions may occur to the K level from L levels. $L_2 \rightarrow K_1$ gives $K_{\alpha'}$; $L_3 \rightarrow K_1$ gives K_α. Similarly transitions into K_1 doubtless occur from M_2 and M_3 and from N_2

[1] However, as was mentioned on p. 197, the series numeral in the optical spectra is conventional and does not always represent the actual principal quantum number.

and N_3. These doublets (spin doublets) are not resolvable; the single lines K_β and K_γ are observed.

Fifteen transitions between M and L levels might be expected if there were no selection rule—actually the number of observed lines is seven: $M_{5,4,1} \rightarrow L_3$; $M_{4,1} \rightarrow L_2$; $M_{3,2} \rightarrow L_1$. Figure 97 represents these transitions for uranium.

Doublet Intervals.—The observed lines agree exactly with the energy diagram shown. The Ritz combination formula applies to many of these lines. Several interrelations between frequencies were early observed and were of great aid in the systematization of the spectra. The following approximate relations were found:[1]

$$\begin{aligned} L_\alpha &= K_\beta - K_\alpha \\ L_\chi &= K_\gamma - K_\alpha \\ L_\beta &= K_\beta - K_{\alpha'} \\ M_\alpha &= L_\gamma - L_\alpha, \text{ etc.} \end{aligned}$$

Such relations were almost, but not exactly, correct; the reason for the discrepancy became apparent as soon as the multiplicity in the M and N levels was realized. More complicated relations hold exactly; for example, as can be seen from the diagram.[2]

$$L_\gamma - M_\gamma = K_\beta - K_\alpha$$

Most helpful in the early exploration period was the discovery of the "spin" and the "screening" doublet intervals which appeared repeatedly as an interval between the observed emission lines. For instance, the doublet interval $L_3 - L_2$ was found in at least six different places in the spectrum as shown in Table 42.

TABLE 42.—APPEARANCE OF L_3L_2 DOUBLET

K doublet	$K_\alpha - K_{\alpha'}$
L doublets	$L_\beta - L_{\alpha'}$
	$L_\eta - L_\epsilon$
	$L_\delta - L_{\gamma'}$
	$L_\chi - L_\iota'$
Absorption doublet	L_3 edge $- L_2$ edge

The reader can find similar relations for the screening doublet $L_2 - L_1$. Such interrelations as these give convincing proof of the correctness of the energy levels of atoms.

[1] We use Sommerfeld's Greek letter notation which differs from Siegbahn's.

[2] The M_α and M_γ lines are not represented in Fig. 97. They correspond, respectively, to the transitions $N_7 \rightarrow M_5$ and $N_5 \rightarrow M_3$.

It will be apparent that the screening doublets correspond to the difference between series in optical spectra (*i.e.*, to a difference in l) and that the spin doublets correspond to the multiplicity within the optical series. It may seem strange that the latter interval is the greater in the L levels shown in Fig. 97. In Fig. 98 it is apparent that this spin-doublet interval decreases as the atomic number is reduced. (Z is effectively unity in arc spectra.)

As a matter of fact, the spin-doublet interval is proportional to Z_e^4. Sommerfeld showed that this doublet interval could be accounted for as a *relativity correction*—the fourth power of Z enters into the correction term in the equation given on page 189. The subsequent history of the theory is a singular story—how Millikan observed this same fourth-power law (page 212) among the optical doublets in stripped atoms and so showed that the multiplicity must be due to spin, not to shape; and how this spin introduced a greatly different interval law from that of Sommerfeld; and then how later the new quantum mechanics brought in still another correction, so that in the end the doublet-interval law turns out to be simply that which Sommerfeld had derived long before merely from relativity considerations. These doublets are usually referred to as spin-relativity doublets. But we cannot enter further into their theory nor can we discuss the screening doublets and the screening constant.

Number of Electrons in the Shells.—The number of electrons in each shell is definitely limited. This is based on the celebrated Pauli exclusion principle, the explanation of which will be given later. The number of electrons which can enter each subshell depends on its value of j as follows:

TABLE 43

j	½	3/2	5/2	7/2
Maximum number of electrons	2	4	6	8

(The number is one greater than the numerator of j.) Hence we can at once compute the number of electrons in each type of shell.

TABLE 44

K_1	L_1	L_2	L_3	M_1	M_2	M_3	M_4	M_5	N	O
2	2	2	4	2	2	4	4	6		
2	8			18					32	50

These numbers in the shells are just twice the integral squares: 1, 4, 9, etc.

Energy Levels of the Atoms.—The x-ray energy levels of all the elements are shown in Fig. 98. For these energy levels we

are indebted to many scientists for many years of most precise work.[1] The energy levels are represented in terms of $\sqrt{\nu/R}$. The curve for the K levels, starting at $\nu = R$ for hydrogen, is nearly a straight line. This shows that Moseley's law is followed for the energy levels as well as for the lines. The K shell gets ever more deeply buried until, for the last element represented on this curve, the ionization potential is 38^2 (*i.e.*, 1400) times greater than for hydrogen. This is the type of linear progression obtained when the charge inside of the orbit considered (Z_e) increases steadily from element to element. The effective attracting charge in this case is simply the charge on the nucleus less a small screening constant.

Breaks in the Moseley Curves.—Let us consider the energy of some very large orbit. It may now happen that, as we go from one element to the next, the new electron which must go into the atomic structure will enter an orbit inside the orbit being considered. In this case Z_e does not increase. The positive charge on the nucleus increases from one element to the next but the number of negative electrons in its neighborhood likewise increases. The two charges cancel; the electron effectively shields the nucleus. In this case no change in energy of the level occurs. Z_e does not increase with Z. This situation is illustrated by the O_1 and O_{23} levels in the rare earths (Fig. 98).

An intermediate case arises when the atom is being built up by addition of electrons in the very shell whose energy level is being considered. In this case the added electron partly neutralizes the increase in nuclear charge; the Moseley curve then ascends but with a reduced slope.

Guided by these considerations one can determine exactly where each of the electrons in the kernel is placed. After element 10 (neon) the curves for the L levels ascend at nearly constant

[1] Visible spectroscopy yields results of precision almost unparalleled. The wave lengths of the stronger line of the D doublet of sodium is 5389.977 angstroms with an error of probably less than 0.002 angstrom. X-ray wave lengths are usually given in milli-angstroms or "X-units." The K_α line of iron is given as 1935.987 X-units (or 1.935987 angstroms) and, in these thousand times smaller units, the error is probably a small number in the second decimal place! The most accurate x-ray measurements are due to Siegbahn in Upsala (Sweden). The accuracy mentioned is for the *relative* values of the wave lengths. The *absolute* value depends upon the grating constant of calcite, which in turn depends upon Avogadro's constant. The probable error in this is 0.1 per cent.

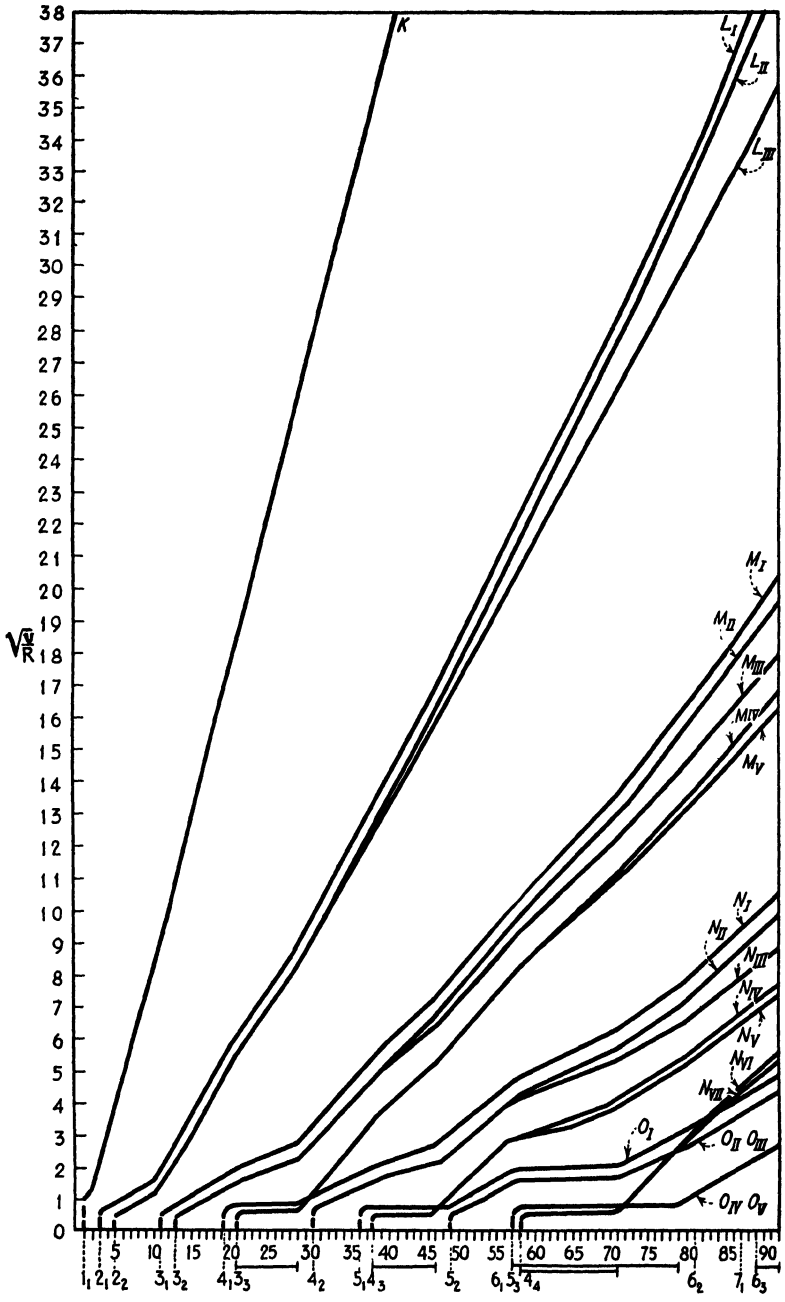


FIG. 98.—Energy levels and atomic number.

slope. A slight change in slope (much more marked in the M curves) occurs at 29 (copper); at this element the M levels are completed, and additional electrons must henceforth enter the N shell. But both M and N levels lie outside the L levels and in consequence the effect on these L levels is not very great. Below neon (10) the slope is reduced; electrons here are building up the L shell itself. It is evident from the figure that the L_1 shell is begun at 3 (lithium), the L_2 shell at 5 (boron).

The M shells are first entered at 11 (sodium)—they are finally completed with 18 electrons at 29 (copper). So, following the ever-deepening energy levels in the kernel, we can, by noting these changes from the steady progression, determine just when each successive level is entered.

Structure of the Atom. *a. The First Period.*—This description of optical and x-ray spectra has been rather long—perhaps tedious. But we now approach a climactic point in our exposition. We are now able to interpret the periodic properties of the atom, long regarded as the fundamental mystery of chemistry.

The atomic number Z is the number of charges on the nucleus. For the neutral atom the number of electrons about the nucleus also equals Z.

1. For hydrogen $Z = 1$; one electron is present; it is in the lowest (K) shell.

2. For helium $Z = 2$; two electrons are in the K shell, which is now full (Table 44).

b. The Filling of the L Shells.—3. In lithium two electrons are in the K shell, the third electron enters the L shells; this L electron is much less firmly bound than were those in the K shell—in Fig. 69 the decrease in ionizing potential is seen. Lithium, the alkali, readily gives up this single outer electron.

4. After lithium, beryllium. There are now two L electrons and the L_1 subshell is complete.

5. In boron a third electron enters the L shells, now entering the L_2 subshell. There appears to be a small energy difference between subshells. Figure 69 shows that this third L electron is less firmly held than the electrons of beryllium.

So, with the succeeding elements carbon, nitrogen, oxygen, fluorine, and neon, the L_1, L_2, L_3 subshells are built up step by step. Neon (10) has two electrons in the K and eight in the L shells—a completed structure of two shells and a stable atom, like helium chemically inactive. The magnetic moment of these

electrons in various orbits just balances. The K and L shells form an inert kernel for succeeding elements. The electrons in neon are: 2:8, in the K and L shells, respectively.

This building up of these shells can be followed in Fig. 98. L_1 is not occupied until lithium (3), L_2 at boron (5), and L_3 at nitrogen (7). These mark the theoretical beginnings of the 2_{11}, 2_{21}, and 2_{22} orbits as occupied, rather than virtual, orbits. After neon (10) the L curves are nearly straight lines; if not so closely so as the K curve it is because the outer electrons do indeed have a slight shielding effect.

c. The M Shells Entered.—The story repeats, as with sodium the M shell is begun and gradually built up, first M_1, then M_2, and then M_3, which at argon (18) is complete. We have now completed the third period of the periodic table. The M_4 and M_5 subshells are still to fill but, as it happens, actually N_1 is lower in energy level than either of these and must be filled first. The number of electrons in the shells of argon are 2:8:8.

d. Fourth Period.—The nineteenth and twentieth electrons (in potassium and calcium) enter the N_1 shell. The new shell in potassium has even lower ionizing potential than lithium and sodium—potassium is a stronger alkali (Fig. 69). But after calcium the process of building up the M shells is continued. Scandium marks the beginning of the transition elements as the M shells are filled out with 10 more electrons. From element to element the outer (N_1) shell now remains unchanged with two electrons. The valence for these elements remains 2,[1] and the chemical properties are very similar from element to element. In iron, cobalt, and nickel, we see prominently the effect of the magnetic moments of uncompleted shells. In nickel the M shell lacks but two electrons for completion; in the next element (copper) this shell is completed as one electron is added to the atom and as the N_1 shell gives up another for the sake of completeness in the M structure. Copper, unlike other transition elements, has a valence of 1 (or 2). With the next seven elements the N_1, N_2, N_3 subshells are filled with 8 electrons. These elements resemble closely the elements from 4 to 10 and from 12 to 18. Krypton is the final element in this period. Its structure is 2:8:18:8. The entering of the electrons into the M orbits is clearly shown by the change in shape in the curves for the M levels in Fig. 98.

[1] Or more, since the $M_{4,5}$ electrons are easily removed.

Orbital Models.—Figure 99 shows the assemblage of orbits in sodium and argon and copper as these elements were visualized by Bohr. Within sodium can be seen the neon structure with 10 electrons, and near the center of the neon structure (reduced in size because of the strong field, $Z = 11$) are the two electrons like those of helium, in the K shell. The single valence electron is seen in the M_1 orbit.

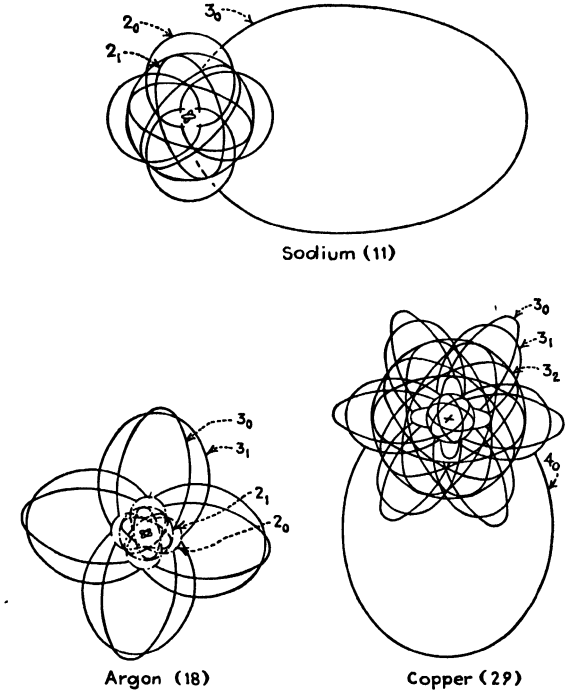


FIG. 99.—Atomic orbits according to Bohr. The new mechanics does not permit of such portrayal of orbits.

In argon the M_1, M_2, and M_3 shells are shown complete. These eight electrons have orbits about the neon structure just as in neon there were eight outer electrons about the helium structure.[1]

Finally in copper, with the addition of 10 circular M orbits (M_4 and M_5) the shells are complete and a single electron is in the N shell.

[1] In these diagrams, the M_1 and M_2 shells are together grouped as 3_0 orbits, most eccentric. This is incorrect—they are alike in j but differ in l. This is the early model of Bohr, devised before the role of spin was exactly understood.

e. Fifth Period.—At krypton with its eight N electrons the building up of the N shells is interrupted for two elements; in rubidium and strontium the O shell is begun. Thereafter comes another transition group in which 10 electrons are added, completing the N_4 and N_5 shells. Five N subshells are completed at silver, thanks to the loss of an electron from the O shell. (Compare with copper.) The N_6 and N_7 shells are still vacant. The next seven elements build up the O shell from 1 to 8 and xenon ends the period. Xenon, inert and magnetically balanced, forms the kernel for heavier elements immediately following. Structure, 2:8:18:18:8.

f. Sixth Period.—The P shells are entered at caesium and barium. The kernel of the atom is now obviously incomplete. Only five of the seven N subshells and only three of the nine O subshells are occupied. The 32 elements after barium form a transition group in which five O subshells and all of the N subshells become filled. N_6 and N_7 are filled with their 14 electrons in the rare-earth group. This is a transition group within a transition group. These N shells are two shells below the shell (P_1) of valence electrons—their effect on the chemical properties of the atom is almost negligible. The rare earths are all very similar chemically. The breaks in the curves of Fig. 98 at elements 58 and 72 mark clearly the beginning and end of this rare-earth group.

The filling of the O_4 and O_5 levels with 10 electrons gives a transition group of elements with rather similar properties but, of course, the similarity found here is nothing like so close as that found in the rare-earth group. This group resembles the earlier iron and palladium transition groups.

At gold the structure is 2:8:18:32:18:1. Seven more electrons and the period is complete. Structure of radon, 2:8:18:32:18:8.

This nearly completes the picture. In the next period a couple of electrons enter the Q shell. Then a transition group begins and the system of known elements ends.

Principal Quantum Number and Shielding Defect of Optical Orbits.—We have now, starting from the K shell of the kernel, again reached the periphery of the atom. These x-ray orbits when first entered are outer orbits, optical orbits; they contain the valence electrons.

In Chap. XVI the lowest optical orbit of sodium was designated as $1S$. In x-ray terminology it is M_1. The effective

quantum number is 1.63 (Table 29). Actually the principal quantum number (n) is not 1 with a defect 0.63. $n = 1$ gives the K shell. The true value of n is 3 and the defect is negative and quite large (-1.37). Similarly the smallest P orbit ($2P$) has a principal quantum number of 3. These true values of the principal quantum number for the s orbits are listed in the last row of Table 29.

This matter was mentioned in the note on page 197. Figure 60 shows the $4P$ orbit ($O_{2\text{ or }3}$ in x-ray terminology). The nucleus here has a charge of 11, shielded by 10 K and L electrons. The optical electron during most of its path is attracted by unit charge. But as it enters the kernel, the L shielding is lost, the value of Z_e rises from 1 to 9, its path is suddenly bent in toward the center. The electron speeds up quickly, acquires very great momentum as it approaches the nucleus, and then, like Halley's comet about our own sun, is away again and far out beyond the electrons of the kernel. (However, in terms of revolutions of the K electron, the "comet," takes some thousands instead of a mere 80 years to return.) That short incursion at such high speed into the heart of the atom adds a unit or two to the *radial action.*

Thus it is that the smallest P orbit in sodium ($2P$) has $n = 3$, yet outside the kernel closely resembles a hydrogen orbit of $n = 2.12$. Other larger defects occur for the S orbits and for heavier alkalis. For the S states of caesium the defect is greater than four units!

Table 45 gives the quantum number of the smaller orbits of the different types for the alkalis.

TABLE 45

	1S		2P		3D		4F	
	n	Defect	n	Defect	n	Defect	n	Defect
Hydrogen	1	0	2	0	3	0	4	0
Lithium	2*	−0.41	2	−0.03	3	−0.001	4	000
Sodium	3*	−1.37	3*	−0.88	3	−0.010	4	−0.001
Potassium	4*	−2.23	4*	−1.77	3	−0.15	4	−0.006
Rubidium	5*	−3.20	5*	−2.72	4*	−1.23	4	−0.011
Caesium	6*	−4.13	6*	−3.61	5*	−2.45	4	−0.023

* Penetrating orbits.

Pauli's Exclusion Principle.—In explaining our periodic table we have employed the celebrated Pauli "Verbot" or the exclusion

principle. *Two electrons cannot be in the same state.* This is the most fundamental of laws.

This law is an extension of the "common-sense" doctrine that two particles cannot occupy the same place at the same time. Illustrations of this latter are so commonplace that it is not given the dignity of a law of physics. Everyone knows it. Matter, it is said, is that which occupies (to the exclusion of all other matter) space. This common-sense law is not actually precise. Pauli's principle gives it precision and extends it in a surprising fashion.

We have found the states of the atom. We know in virtue of the M-B law how the electrons struggle for position in the lowest energy state. But why (we may ask) do not all of the electrons enter the K shell of the atom? The two electrons of helium invariably occupy the K state. The M-B law gives the chance of an electron being in the L orbit as $e^{-\frac{2000}{\kappa T}}$. (The energy of the second orbit of helium is about 2000 atomic ergs higher than the first.) Why does the third electron, in lithium, occupy this second orbit? The first orbit is clearly full. Why is it full? Pauli found here the first evidence for his exclusion principle. It is not that electrons cannot occupy exactly the same *place.* Two electrons cannot have exactly the same *action* as specified by its complete set of quantum numbers. In the K orbit, n is 1, l is zero, j is $\frac{1}{2}$; m for one electron is $+\frac{1}{2}$, for the other $-\frac{1}{2}$. Each electron here is different but there are no other possibilities.

It is just this principle which permits 2 electrons in the K shell, 8 in the L, 18 in the M, etc. An L_3 orbit has $j = \frac{3}{2}$; m can be $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$—four states. Four electrons can occupy this subshell each circulating about the nucleus in a different direction. The L_2 and L_1 orbits, each with $j = \frac{1}{2}$, have each two possible states—two electrons as given in Table 43.

"This picture suggests the analogy to a big apartment house, whose inhabitants tend to crowd into the lower floors, but are restricted in this by a law, providing that each double room should be occupied by one married couple only. The opposite sexes correspond to the opposite direction of the spins of the electrons. We should imagine the whole building to consist of such double room apartments (there can be many of them on the same floor corresponding to a given energy

level) and the number of floors to be infinite." (Frenkel: Wave Mechanics.)

But what is the fundamental meaning of this law? By what force does the "government" enforce its regulation?

Pauli extended his principle to other cases and found it apparently of universal validity as regards electrons. It also applies to protons.

In mercury the normal atom has its two electrons in the 1^1S state, but there is no 1^3S state. These two valence electrons have the same principal quantum number, and the same angular quantum number ($l = 0$). Each electron has the same spin ($\frac{1}{2}\hbar$). Such electrons can exist only if the spins are opposite in direction. Hence there is a singlet but no triplet state.

The principle could not be given until we had completed the description of "state" and discovered the four quantum numbers. A free electron has its state specified by its three momentum and position coordinates and its positive or negative spin. Two free electrons, similarly spinning, very close together in a gas must necessarily differ considerably in speed, enough to put them into different quantum states. We have been too spacially minded. We have seen that two particles could not occupy exactly the same position. Before Pauli's time it was not recognized that two similar charged particles could not have exactly the same velocity.

In terms of the new wave mechanics (Chap. XXVII) the exclusion principle means that two charged particles cannot have exactly the same wave, in length and direction of propagation.

"$h\nu$"

All black-body radiations,
All the spectrum variations,
All atomic oscillations
Vary as "$h\nu$."

(CHORUS)
Here's the right relation,
Governs radiation,
Here's the new,
And only true,
Electrodynamical equation;
Never mind your d/dt^2,
Ve or half mv^2
(if you watch the factor "c^2")
's equal to "$h\nu$."

Ultra-violet vibrations,
X- and gamma-ray pulsations,
Ordinary light sensations
All obey "$h\nu$."

Even in matters calorific,
Such things as the heat specific
Yield to treatment scientific
If you use "$h\nu$."

In all questions energetic,
Whether static or kinetic,
Or electric, or magnetic,
You must use "$h\nu$."

There has been a mighty clearance,
We are all now Planck's adherents,
Because now even in interference
We use the quant "$h\nu$."

G. S.

Adapted from the "Post-Prandial Proceedings of the Cavendish Laboratory."

CHAPTER XXIII

MOLECULAR ROTATION AND VIBRATION

Rotation and vibration—and even translation—of molecules are quantized. Specific heat of hydrogen at low temperatures. Even to even and odd to odd. Molecular spectra in absorption, emission, and in scattered light.

On page 89 we asked a question. It has taken us some time to answer it. It is now clear why the electrons in the atom do not share in the partition of energy.

The electrons in the atom can be excited; how this was done was discussed briefly in Chap. XVII. But the exciting energy must be enough to cause a transition from one quantum state to another. This is not to be found among the gas molecules under normal conditions. A thousand atomic ergs are required to raise the electron in hydrogen from the first to the second quantum state; the average energy of an impinging molecule at room temperature is 4 atomic ergs.

Let us look back again to that maelstrom, the world of the molecule. Chaotic it seems indeed, compared with this neat little world within the atom. But now that our eyes have been opened, we shall see also here the rule of quantum law. The rotation of the molecule on its axis, the vibration of the atoms within it, indeed even its translation, its every motion has its definite quantum states. But this molecular world is a world in which frequencies and energies of the quantum states are much smaller than those which belong to the electron in the atom.

Molecular and Atomic Frequencies.—The mean time of free flight of hydrogen molecules between impacts (standard conditions) is 1000 subsec. If we would speak loosely of a "period" for translation, this would be that period; the frequency would be of 0.001 vibration per subsecond. When it is in its first state of rotation, the hydrogen molecule, dumbbell shaped, rotates about 120°, ⅓ revolution, per subsecond. The bells of the dumbbell can vibrate; they make about 13 vibrations per subsecond.

Compare these values with atomic frequencies: 700 revolutions per subsecond for the hydrogen electron, 6 million per subsecond for the K electron of uranium!

Molecular and Atomic Energies.—At 50°C. the average molecule has 4 atomic ergs of kinetic energy. The first rotational state of hydrogen has 0.7 atomic erg, its lowest vibrational state has 50 atomic ergs. Compare these with atomic energies. To break the H_2 molecule in twain requires 400 atomic ergs; to excite the H atom requires 1000 atomic ergs; to ionize it, 1300 atomic ergs; to remove a K electron from uranium takes some 12 million atomic ergs.

Nature works her changes in discrete jumps. The quantum law restricts the degrees of freedom of an atom—even as the railroad track restricts the freedom of a train. The train has but one degree of freedom—unless the transverse impulse is sufficient to make it jump the track. Quantum rules furnish tracks, tracks almost imperceptible for translation, small (usually negligible) ones for rotation, larger ones for vibration and for the electron in the atom tracks which are inescapable except under extreme conditions. These "tracks" give the order to the world of the atom. In molecular motion the molecule jumps easily from one translational state to another, from one rotational state to another; we can here in this rotation and translation easily lose sight of the underlying quantum laws; the motion at first appears quite free. The hydrogen atom at normal temperature has five degrees of freedom—three translational, two rotational.

Rotary Motion.—A molecule can rotate only with such speeds as make the action a multiple of h; that is to say, the angular momentum ($I\omega$) must be a multiple of $\hbar$.

$$\text{Ang. mom.} = I\omega = l'\hbar \qquad (22'')$$

where l' is the angular quantum number for the molecule. The kinetic energy of these quantized rotational states is

$$\text{K.E.} = \frac{1}{2}I\omega^2 = \frac{\hbar^2}{2I}\cdot l'^2$$

Consider, for illustration, hydrogen (H_2). The two atoms are known (from band spectra) to be 0.76 angstrom apart and the mass is (approximately) 2 protols. Hence in atomic units the moment of inertia about the center of mass is

$$I = mr^2 = 2\cdot 0.38^2 = 0.29.$$

Dividing the angular momenta ($\hbar$, $2\hbar$, etc.), by I gives the angular velocities (ω) of the allowed rotations. The energies are given by

$$\text{K.E.} = \frac{\hbar^2}{2I} \cdot l'^2 = 0.7 \cdot l'^2$$

The angular velocities and energies of the first few states of H_2 are given below:

TABLE 46

l'	Action	ω, radians per second	$\frac{1}{2}I\omega^2$	*Energy N.Q.M.*	
0	0	0	0	*0*	Parahydrogen
1	4	2.2	0.7	*1.4*	Orthohydrogen
2	8	4.4	2.8	*4.1*	Parahydrogen
3	12	6.6	6.3	*8.2*	Orthohydrogen
4	16	8.8	11.2	*13.8*	Parahydrogen

The energy increases as the square of the quantum number. In the third state, the molecule, making three-fourths of a turn in a subsecond, has a kinetic energy about equal to the average rotational energy at room temperature (κT = 2.5 atomic ergs at 300° abs.[1]). In the next state the energy is more than twice this mean value. Practically all the hydrogen molecules are limited to the five states given in the table. We have thought of the molecules in a gas as moving helter skelter, as rotating with infinitely many different speeds. Actually the possible modes of rotation are quite restricted. And even in translatory motion we shall find the quantum law applying although the restriction here is seldom of much importance.

The lowest state (l' = 0) might be called the "normal" state and others "excited" states of the molecule if we used the language of atomic theory. But such classification has little significance here. Here the "virtual" states are almost as apt to be occupied as the normal state. Collisions with other molecules are constantly increasing the molecular rotation and as often decreasing it. The number of molecules in the first state, and the second state, and the third state of rotation are apportioned very much as in the Maxwell distribution law; for a single

[1] The reader should review the classical discussion of rotation, vibration, and heat capacity given in Chap. IV.

component of angular motion the distribution would be as in Fig. 24. The spread of the distribution, of course, depends on the temperature.

Molar Heat of Hydrogen.—At lower temperatures strongly exciting collisions become less frequent. At 60° abs. the mean rotational energy is ½ atomic erg; in the case of hydrogen most of the molecules will now be rotating in the 0 or 1 state. At still lower temperatures even the 1 quantum state is unlikely—

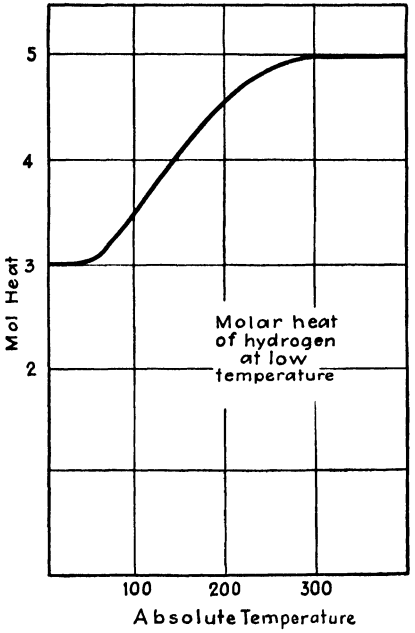


FIG. 100.—Molar heat of hydrogen at low temperatures.

the molecules have lost their rotation. At these temperatures nothing but translation remains to the molecule. The molar heat drops from 5 cal. to 3! Hydrogen acts as a monatomic gas.

Here, as with the decreasing temperature the molecular collisions become weaker, another set of quantum "tracks" have become effective and the rotational degrees of freedom are lost. A strange picture this at low temperature of the collisions knocking the molecules here and there but never being able to rotate them! And even at normal temperatures the axial spin of diatomic molecules does not play a role. Now at low temperature these gentle impacts cannot even make our dumbbell

"tumble." This remarkable phenomenon reminds us of the vanishing of specific heat in solids at low temperatures.

To obtain quantitatively exact agreement with the experimental results the new quantum mechanics must be used. The expression for the kinetic energy is

$$\text{K.E.} = \frac{\hbar^2}{2I} \cdot l(l+1) \qquad (36')$$

(Substantially the same results were obtained in the Bohr theory by using half quantum numbers.) Also must be borne in mind the separation of a symmetrical molecule into para and ortho states to which we shall presently refer.

Heavier Molecules.—Heavier molecules have greater moments of inertia and smaller frequencies of rotation and the quantum states are closer together. In no case other than hydrogen are conditions appropriate for observing a decrease in specific heat due to this quantization of molecular rotation. Next to hydrogen in frequency are compounds like hydrochloric acid where the light hydrogen atom rotates around the massive chlorine. The energies of the rotational states in this case are given in Table 47.

TABLE 47.—ENERGY STATES (ROTATIONAL) OF HCl

l'	0	1	2	3	4	5
Energy	0	0.125	0.50	1.125	2.00	3 125
Energy difference		.125	.375	.625	.875	1.125
Energy (N.Q.M.)	*0*	*0.25*	*0.75*	*1.50*	*2.50*	*3.75*

Because the energies of the states increase as the square of n, the energy *differences* between successive states increase at a constant rate as shown in the table. Hydrochloric acid condenses before very low temperatures are reached and hence the decrease in specific heat cannot be demonstrated in this case. However, the existence of these rotational states is beautifully demonstrated in the absorption spectrum which we shall presently discuss.

Vibratory Motion of Molecules.—A bob oscillating on a spring is an instance of simple vibration. Its frequency is equal to $\frac{1}{2\pi}\sqrt{\frac{k}{m}}$ where k is the elastic constant of the spring, the restoring force for unit stretch. The energy of the vibrator alternates

between kinetic and potential; it is proportional to the square of the amplitude of vibration. Now in the atomic vibrator all amplitudes are not possible. The motion is restricted by the quantum theory to those amplitudes in which the energy is equal to $h\nu$ (first state) or $2h\nu$ (second state) or $3h\nu$, $4h\nu$, etc.[1]

Example.—In hydrochloric acid the atoms are bound 1.3 angstroms apart. If the atoms be separated slightly from this equilibrium position, an attracting force enters whose value is 1700 atomic dynes per angstrom of separation. Hence the frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{1700}{1}} = 8.7 \text{ vibrations per subsecond}$$

The energies ($n_v h\nu$) of the various quantum states are then 0, 35, 70, etc., as given in Table 48.

According to the new quantum mechanics the energy in vibrational states is given by half quantum numbers: Energy = $\frac{1}{2}h\nu$; $\frac{3}{2}h\nu$, etc.

TABLE 48.—VIBRATIONAL STATES OF HCl

n_v	Action	Amplitude	Energy	*Energy N.Q.M.*
0	0	0	0	*17.5*
1	4	0.15	35	*52.5*
2	8	0.21	70	*87.5*
3	12	0.26	105	*122.5*
4	16	0.30	140	*157.5*

This vibrational motion of the HCl molecule is not excited at normal temperatures. The chance that 35 atomic ergs of energy will be available in the normal molecular chaos (where

[1] *Proof:* Let A be the amplitude. The maximum velocity is $v_{max} = 2\pi\nu A$; the weighted average (obtained by calculus) is $\bar{v} = \frac{\pi^2}{2}\nu A$.

The energy $= \frac{1}{2}mv^2_{max} = 2\pi^2 m\nu^2 A^2$
The action as the oscillation goes to and fro a distance $4A$ is
$m\bar{v} \cdot 4A = 2\pi^2 m\nu A^2 = n_v h$

Hence

$$A = \sqrt{\frac{nh}{2\pi^2 m\nu}}$$

So the permitted amplitudes are in the ratios 1: $\sqrt{2}$; $\sqrt{3}$; $\sqrt{4}$; etc.
Energy $= 2\pi^2 m\nu^2 A^2 = n_v h\nu$

the average energy is 4 atomic ergs) is quite remote. Therefore the molecule is rigid, it has only five degrees of freedom and has a molar heat of 5 cal. So with most of the diatomic molecules. Molecules like O_2, N_2, NO, etc., with heavier atoms have slower vibratory motion than this, closer energy levels, but even in these cases the vibration is excited in only a very small proportion of the molecules at ordinary temperature. As the temperature is raised, more of the molecules are set into vibration and the molar heat increases to seven. Iodine (I_2) is one of the heaviest of diatomic molecules. The frequency of vibration is here 0.7 vibration per subsecond, the energy steps 2.6 atomic ergs apart, and even at room temperature vibration plays its role in thermal equilibrium. The molar heat of iodine is 7 cal.[1]

It cannot be expected that this molecular vibration will be exactly simple harmonic. The force cannot be strictly proportional to the displacement. In compression the possible displacement quickly reaches a limit; in extension the restoring force at first increases as in Hooke's law and then as the interval between them is made still larger the mutual attraction between the atoms decreases. The nature of this force between the hydrogen and chlorine atoms can be best illustrated by plotting the potential energy of the molecule as a function of the interval (Fig. 101).

Were the force strictly proportional to the displacement as in an ideal oscillator, the potential would vary as the square of the displacement and the potential-energy curve would be the parabola (shown dotted). The curve shows the variation from this relation. The *slope* of the potential-energy curve gives the force: very strongly repulsive under large compressions, attractive under extension, but falling off at large intervals. Without vibration the atomic spacing would be represented by the point of lowest potential energy. Other quantum states of increasing amplitude are represented at energy intervals of $h\nu$.

It is from band spectra or the Raman effect that we get the data for such energy curves, but today we can, with the aid of the new quantum mechanics, go far toward computing them. This energy minimum is, of course, what the chemist calls a "chemical

[1] Each degree of vibrational freedom absorbs κT of heat and increases the molar heat by 2. This is because it has both potential and kinetic energy (p. 63).

bond." The exact determination of such curves as that shown in Fig. 101 would seem to be the first problem of mathematical chemistry. We have today the necessary theoretical and experimental technique for solving this problem and it is probable that a period of rapid advance is in immediate prospect for theoretical chemistry.

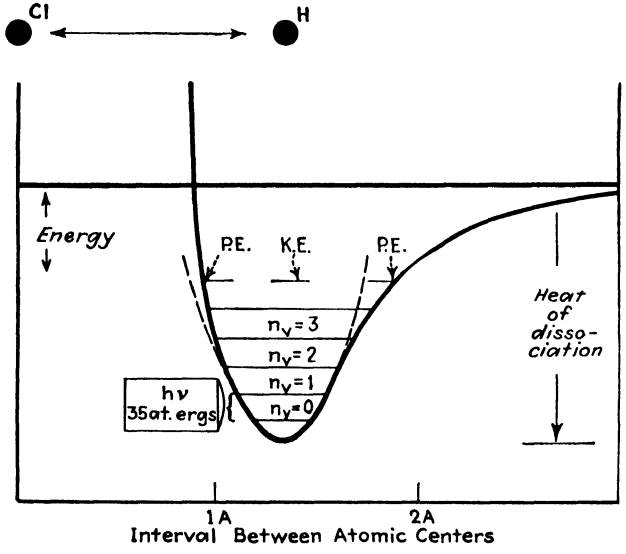
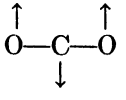


FIG. 101.—Potential energy as function of atomic interval in HCl.

Vibration in Polyatomic Molecules.—In more complicated molecules slower modes of vibration occur. It is always easier to bend a long molecule transversely than it is to stretch it—transverse vibrations have small frequencies. In carbon dioxide, for instance, the transverse vibration



has a frequency of 2 per subsecond. The energy required to excite the first state of this vibration is only 8 atomic ergs. Many carbon dioxide molecules vibrate in this way even at ordinary temperatures. At higher temperatures, longitudinal vibrations in this chain are also set up. Two types of longitudinal motions occur. In one, the two oxygen molecules move

to the right as the carbon moves to the left; the frequency is 10 per subsecond.

$$\begin{array}{c} \rightarrow \ \leftarrow \ \rightarrow \\ \mathrm{O{-}C{-}O} \end{array}$$

In the other, the carbon is at rest and the two oxygens pulsate back and forth, toward it and away from it, with a frequency of 7 per subsecond.

$$\begin{array}{c} \rightarrow \quad \leftarrow \\ \mathrm{O{-}C{-}O} \end{array}$$

These longitudinal vibrations are excited only at high temperatures.

The transverse mode of vibration can be in either of two planes. Hence when fully excited the specific heat of carbon dioxide is 3 (owing to translation) + 2 (owing to rotation) + 8 (owing to vibration). The effect of the vibration is evident in the rise of the molar heat from a value 5 at ordinary temperature to 12 cal. at 2000°C.

In the longer chain compounds many modes of vibration occur and the molar heat increases to large values.

The Molecular Scene.—Do not the quantized motions of nature seem very near to us as we contemplate the molecular world about us? The air molecules are tumbling hither and yon, but their rotations are not entirely disorderly; each molecule is rotating with exactly one, two, three, or more units of angular action. They are also *space quantized* with definite orientations in space. (Or at least we shall always find them so whenever fields are applied which are competent to distinguish between different directions in space. How they are oriented when we are not observing them is a matter of indifference to us.)

One per cent of the atmosphere is argon; for this there is no rotation. An O_2 or N_2 molecule may rotate about a direction perpendicular to the axis through the two atomic nuclei, but not about this axis, for this would be spin of the very atoms themselves and would require a hundred times as much energy for its excitation. Each molecule is rigid, with no vibration. But among others in the air are a few carbon dioxide molecules. These molecules are less rigid, transversely. Most of them perhaps are vibrationless, but a few are vibrating, all with the same amplitude, in the first state of transverse vibration; the second state could hardly be excited at normal temperature.

Few physical subjects seem at first more prosaic than specific heats. Yet the exact determination of the specific heats of gases have revealed to us the molecule. Let us picture the scene at other temperatures. As the temperature is lowered, molecules condense into the liquid and solid forms. But hydrogen may be carried as a gas to quite low temperatures; it then has only translatory motion—it acts like a monatomic molecule, molar heat 3. Then at ordinary temperature the rotation is excited; it is a rigid diatomic molecule, molar heat 5. As the temperature is raised up to white heat, the molecule vibrates, a nonrigid molecule, molar heat 7. At still higher temperatures, 3000,

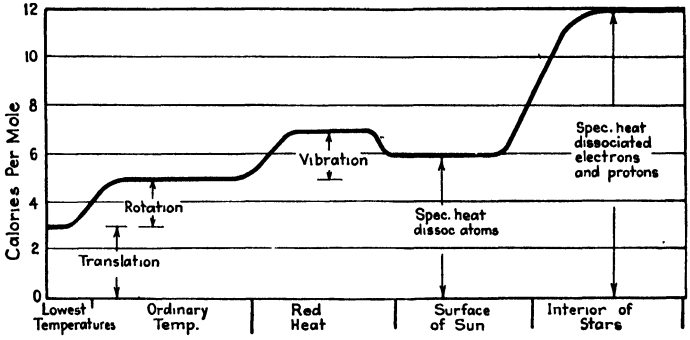


FIG. 102.—Specific heat of hydrogen (theoretical).

4000, 5000°, the molecule is dissociated, into two monatomic rigid, nonrotating atoms, the two with a combined molar heat 6. Then at very much higher temperatures, the electron within the atom may be displaced from the first state to the second; a change from $1S$ to $2P$ changes the rotation or from $1S$ to $2S$ changes the vibration of the electron. And finally at still higher temperatures the atoms are ionized, two electrons and two protons now with molar heat 12, out of the original diatomic molecule. But for us at 300° above absolute zero, thanks to the quantum "tracks," the molecule is a rigid dumbbell with five degrees of freedom.

A Superselection Rule for Molecule Rotation.—It is almost impossible for a hydrogen molecule to change from an even to an odd rotational state! At a molecular collision a molecule in the fourth state (see Table 46) can change to the sixth or second but not to the fifth or third or first. Perhaps this is the strangest fact we have met in all this quantized world of the

molecule. This rule is different from the selection rules of optics which forbade certain transitions for the free atom as it radiated light. The forbidden transitions now under discussion are (almost) impossible even when one molecule makes a collision with another.[1]

The rule holds only for symmetrical molecules like H_2, O_2, etc. It does not apply to hydrochloric acid. The result is that hydrogen may for many purposes be considered a mixture of two different gases—even-turning and odd-turning molecules. These two species of hydrogen molecule are called parahydrogen and orthohydrogen.

The existence of these two states of hydrogen was first demonstrated spectroscopically (compare Fig. 107). It is also shown by the specific heat. Very seldom does a molecule go from the first to the 0th state. Perhaps one collision in a million million million results in such a change. If for many months the temperature of hydrogen gas is kept very low, almost all the molecules will eventually (despite the rule) lose their rotation. The forbidden transfer from the first to the 0th state is expedited by the use of charcoal as a catalyzer. If after bringing the molecules to rest in this manner the temperature is raised, the molecules will be in the 0th, second, fourth, sixth states; the odd states will be missing. The specific heat of this gas is different from normal hydrogen. Only after several months does the normal proportion of odd states reappear.

Molecular Spectra.—As with the atom, so with the molecule: our most specific knowledge about it comes from the spectrum. The subject of molecular spectra is larger and more involved than that of atomic spectra. Here a few pages must suffice to present the simplest facts. Typical spectrograms are reproduced in the "Encyclopaedia Britannica" (Band Spectrum) to which the reader is referred.

The spectrum of hydrogen shows, in addition to the four visible Balmer lines, a great number of other lines. This many-lined spectrum is due not to the H atom but to the H_2 molecule. Usually in such molecular spectra the lines are arranged in bands, the lines being sometimes so close together as to be inseparable even by instruments of the highest resolving power.

[1] The forbidden transitions would *never* occur if H_2 were completely symmetrical. Actually the two protons are slightly different because of a difference in protonic spin. In O_2 the symmetry is probably perfect.

Molecular spectra are due (1) to molecular rotation, or (2) to a combination of rotation and vibration, or (3) to a combination of rotation and vibration and electron jump in the atom. The simple rotational spectra are in the far infra-red, the rotational-vibrational spectra are in the near infra-red, and the rotational-vibrational-electronic spectra are usually in the visible or ultra-violet.

Pure Rotation Spectra.—The hydrochloric acid molecule consists of a positively charged (H^+) and a negatively charged (Cl^-) part. The rotating molecule can radiate heat as it changes from one state of rotation to another. The selection principle for angular motion is (as we know) that the angular quantum number l' can change only by ± 1.

Refer now to Table 47. The hydrochloric acid molecule can change from the l'th to the $(l' - 1)$th state emitting radiation. The following table gives the energy differences (from Table 47) and the frequencies which, by the relation $\Delta W = h\nu$, should be emitted.

TABLE 49

Transition	Energy difference, atomic ergs	ν computed	Observed lines[1]	
			ν	λ, millimeter
$1 \rightarrow 0$	0.125	0.03		
			(0.06)	(0.48)
$2 \rightarrow 1$	0.375	0.09		
			0.12	0.24
$3 \rightarrow 2$	0.625	0.15		
			0.18	0.16
$4 \rightarrow 3$	0.875	0.21		
			0.24	0.12
$5 \rightarrow 4$	1.125	0 27		

[1] These values are approximate. There is a slight variation from this equal spacing due to a change in the moment of inertia as the molecule stretches under centrifugal force.

These are very much smaller frequencies than have been involved in atomic spectra. In the far infra-red starting with a wave length of half a millimeter (though this first extremely long line has not actually been observed), the physicist has found the absorption spectrum of HCl, a series of almost equally spaced lines. The observed lines are listed in the last columns of the table. The frequency intervals between lines are 0.06 per

subsecond as in the lines computed from the theory, *but the actual frequencies fall midway between the theoretical values.*

This is another instance in which Bohr's theory agrees almost—but not quite—with experiment. The theory will agree with the experimental results if half quantum numbers ($\frac{1}{2}$, $\frac{3}{2}$, etc.) are substituted for integral numbers for molecular rotation [Eq. (22″)]. This is artificial. The truth appears only in the new quantum mechanics according to which the energies are proportional to $l'(l' + 1)$ instead of l^2 (compare page 233). The true values of the energies of the hydrochloride rotational states are 0, 0.25, 0.75, etc., as given in the last row of Table 47.

Rotation-vibration Spectra.—In addition to these lines in the far infra-red, another band of absorption lines occurs in

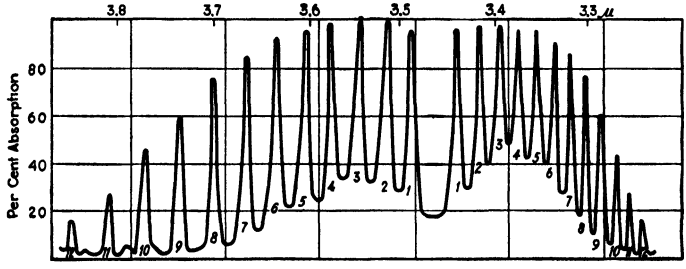


FIG. 103.—Absorption spectrum of HCl. Corresponding to $\Delta n_v = 1$ and $\Delta l' = +1$ (to left) and $\Delta l' = -1$ (to right).

HCl in the nearer infra-red, with its center at 34,600 angstroms. This wave length corresponds to a frequency of 8.7 per subsecond. The lines within the band are separated by 0.06 vibration per subsecond. This band is shown in Fig. 103. This figure represents the percentage of absorption as measured with a bolometer when infra-red radiation passes through hydrochloric acid gas.

This is the rotation-vibration spectrum. Normally the HCl molecule is not vibrating. It takes 34.5 atomic ergs to excite the first vibrational state. This vibration can be produced by light of suitable frequency. Along with the vibration always comes a change in rotation, from the 0th state to the first, second to the first, or fourth to the fifth, etc. A molecule which happens to be rotating in the first state may have its rotation increased to the second requiring half an atomic erg; or the rotation may be decreased to zero saving the photon a quarter of an atomic erg. The light energies absorbed would be, respec-

tively, 35 atomic ergs and 34.25 atomic ergs. The corresponding absorbed frequencies may be computed from the Planck formula. Transitions between other rotational states can be computed as in the table.

TABLE 50

Initial state		Final state		Energy difference, atomic ergs	Absorbed frequency
n_v	l'	n_v	l'		
0	3	1	2	33.75	8.52
0	2	1	1	34.00	8.58
0	1	1	0	34.25	8.64
0	0	1	1	34.75	8.76
0	1	1	2	35.00	8.82
0	2	1	3	35.25	8.88
0	1	2	0	68.75	17.09
0	0	2	1	69.25	17.31

Selection Principles.—In a simple harmonic oscillator the vibrational quantum number n_v can change only by ± 1 or 0. $\Delta n_v = 0$ gives the far infra-red spectrum considered earlier in the chapter. $\Delta n_v = -1$ gives emission lines. In the absorption lines represented in Fig. 104 $\Delta n_v = +1$.

Actually, as has been remarked, the forces binding the molecules together do not obey Hooke's law—the motion is not simple harmonic. The classical theory would allow overtones besides the fundamental frequency; correspondingly the quantum theory allows n_v to change by more than one (page 185). Δn_v can be ± 2 or even larger. This gives harmonics of the fundamental band. A second HCl band is found with its center at 17,300 angstroms ($\nu = 17$ per subsecond).

Angular motion must change by $\Delta l' = \pm 1$. The absence in Fig. 104 of a central line which should correspond to a pure vibrational change ($\Delta W = 34.50$) shows that the rotation always changes during light emission.

Rotation-vibration-electronic Bands.—In the preceding the molecules have rotated, the atoms have been set into vibration, but the electrons within the atom have not been disturbed. At the expense of much greater quantities of energy, one of the electrons in the molecule can be displaced. If this electron then

returns, energy will be radiated. This of itself would give a line, analogous to the lines which are observed for the free atom (Chap. XIV).

But accompanying this electron jump the molecule may well change its state of vibration by one or more steps. If the vibration decreases, more energy, higher frequencies will be radiated; if the vibration increases, the radiated frequency is decreased. Instead then of a single line there will be a number of nearly equally spaced lines corresponding to electron excitation and vibration.

But also there will be changes in rotation of the molecule. These involve less energy than the vibratory changes—very much less than the electron displacement. In the place of each

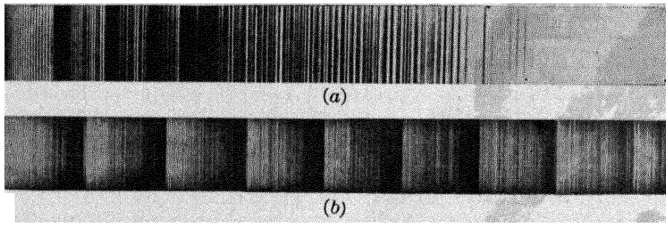


FIG. 104.—Band spectra. (*Mecke.*) (*a*) Cyanogen; showing band heads at 3884, 3872, 3862, 3855, and 3850 angstroms. All are due to $\Delta n_{vib} = 0$. ($0 \rightarrow 0$, $1 \rightarrow 1$ etc). (*b*) Iodine spectrum.

single one of the electron-vibration lines, a number of very closely spaced lines will appear, usually too close to be resolved except on instruments of very high resolving power. These lines become closer and closer; they come to a head. Sometimes this band head is toward the red, sometimes toward the violet.

The band spectrum corresponding to any particular electronic transition is divided into groups according as the change in vibration number is 2, 1, 0, −1, etc. The case is further complicated by the fact that the binding force between the excited atoms is different from that in the unexcited state and that the vibration frequencies differ.

Figure 104 shows the λ3884 group of cyanogen. This corresponds to an electron jump (from a molecular $2S$ to $1S$ state) and no change in n_v. A group at 3590 angstroms corresponds to $\Delta n_v = -1$; a group at 4216 angstroms to $\Delta n_v' = +1$; and at 4606 angstroms to $\Delta n_v' = +2$. The five bands seen in the group in Fig. 104 correspond to transitions between different pairs of

similar vibration levels as $0 \rightarrow 0$, or $1 \rightarrow 1$. Under this high magnification the lines within the bands stand out, each line corresponding to a different rotary transition (compare "Encyclopaedia Britannica," Band Spectra, particularly Fig. 2 showing more of the cyanogen band system).

The cyanogen (CN) spectrum is found when the carbon arc is operated in air. The reader should observe for himself the nitrogen bands (in the discharge in air) or observe the "Swan spectrum" which gives the light-blue color to the inner cone of the Bunsen burner. This latter spectrum is due to a pair of carbon atoms in some unidentified molecule. The strongest bands have heads 5165 angstroms (green), 4737 angstroms (blue), and 5635 angstroms (yellow) and correspond respectively to an electron jump of vibration number 58, or this electron jump plus or minus 5 due to increased or decreased vibration. The rotational lines are too close to be resolved except with a large grating.

All these band spectra confirm definitely the theory of specific heats. Molecular rotation and vibration are quantized as truly as are the motions of the electrons in the atoms.

Electron States in the Molecule.—These molecular spectra show that the electrons in the molecule have states which can be classified by very much the same scheme as that which has been used for atomic spectra. A diatomic molecule differs from an atom in that the valence electrons go about a double nucleus and a double kernel. There is a general tendency for atoms to combine so as to leave eight electrons in the outer shell. This notably stable structure, similar to that of the noble gases, gives the molecule its stability. In ammonia and methane the hydrogen protons may be supposed attracted close into the kernels of the nitrogen or the carbon, respectively; about this composite kernel are eight electrons in the outer shell. From these molecules we should expect electron energy states and electron transitions closely resembling those found in neon. Compounds such as BO, CO^+, CN, and N_2^+ are seen to have one valence electron more than sufficient to form the octet; their electronic levels are doublets; the separation of these doublet bands is comparable with that of the sodium doublet; the external structure of sodium atom is similar to that of these molecules.

Raman Effect.—In 1929 it was discovered that some of the light scattered by a transparent medium (solid, liquid, or gas) differed in frequency from the incident light. The effect had been predicted by theory; it was discovered experimentally by the

Indian Raman. The quantum of light in this case effects a transfer of the molecule in the medium from one electron-vibration-rotation state to another, and the light photon either loses or gains frequency thereby. Whatever the incident wave length, light of unchanged frequency is always scattered by the medium and along with the unchanged line appear fainter satellites with

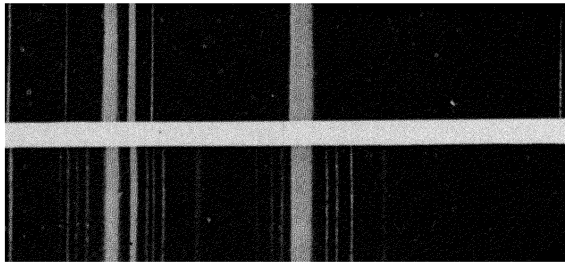


FIG. 105.—Primary and scattered spectra. Mercury violet lines scattered by carbon tetrachloride. (*Raman.*)

characteristic separation. The spacing of these Raman lines gives the energy states of the molecule.

The upper spectrogram in Fig. 105 shows the violet portion of the mercury spectrum; it contains two very strong lines, broad in these photographs because of the great overexposure. The

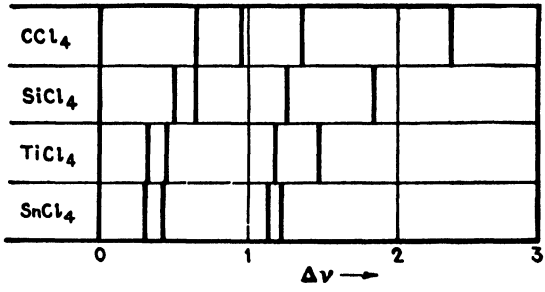


FIG. 106.—Raman effect in the tetrachlorides. This gives the vibration frequencies of the molecule.

lower spectrogram is for the same lines after being scattered from carbon tetrachloride. Four Raman satellites appear with frequency differences of (approximately) 0.6, 0.9, 1.3, and 2.3 vibrations per subsecond (Fig. 106). These correspond to different modes of vibration in the molecule. The carbon tetrachloride molecule is in the form of a tetrahedron, with the carbon

in the center. The third of these Raman lines with frequency 1.35 (period about ¾ subsec.) is due to that simplest mode of vibration in which the chlorine atoms on the corners of the pyramid pulse in and out, the carbon remaining at rest. The atoms are somewhat more than an angstrom apart; in their first quantum state they vibrate with an amplitude of about 0.1 angstrom. The other Raman lines correspond to three other possible modes in which these five atoms can vibrate.

These natural frequencies are all determined in terms of the masses of the atoms and the forces between them. So here the attractive forces between the carbon and the chlorine and the forces between neighboring chlorine atoms are determined. Hence in the Raman effect the chemist gets quantitative insight into the magnitude of valence forces. (Of course, he is primarily interested in valence energies rather than valence forces.)

As illustration we consider the case (mentioned above) in which the four chlorines in carbon tetrachloride pulse in and out together. Each chlorine atom in equilibrium is bound by the attractive-repulsive forces of the carbon and of the three neighboring chlorines. The elastic constant k, the restoring force per unit (angstrom) displacement, is 2600 atomic dynes per angstrom. (Of this, 1200 units are due to the carbon, 1400 to the neighboring chlorines.) Hence the period:

$$T = 2\pi\sqrt{m/k} = 2\pi\sqrt{35/2600} = 0.73 \text{ subsec.}$$

We have observed the line corresponding to this particularly simple kind of vibration ($\nu = 1.35$) in Fig. 106.

The Raman effect offers a powerful means for analysis of interatomic forces in molecules. It has the great advantage that it can be observed in liquids or solids as well as in gases. Papers have been appearing in the physical and chemical journals at the rate of more than a hundred a year since the discovery of the effect. Hundreds of molecules have been studied and the forces determined between different atomic groups and for different types of valence binding. To the chemist band spectra are of even more interest than are atomic spectra. Band spectra speak to him of the distances and forces between atoms in the molecule.

Rotational Spectrum of Gases.—Peculiarly interesting Raman spectra are shown in Fig. 107. In the lower spectrogram the scattering substance was nitrogen gas. The original line is shown, very much overexposed and broadened, in the center of the picture. The lines extending out from this

correspond to transitions from one rotational state to another. The heavier of the recurring lines represent changes of rotational state from 0 to 2, 4 to 2, and so on in orthonitrogen. The fainter lines represent changes between odd states in paranitrogen.

Here again we find operative the selection principle for symmetrical molecules (page 291). Even to even and odd to odd. In the case of oxygen, where the two atoms (without spin) are exactly alike, only states with odd values of l exist (para-oxygen).

Although this phenomenon received its immediate explanation from the new quantum mechanics and did not, like other phenomena which we have described, pass through the intermediate stage in which it received an

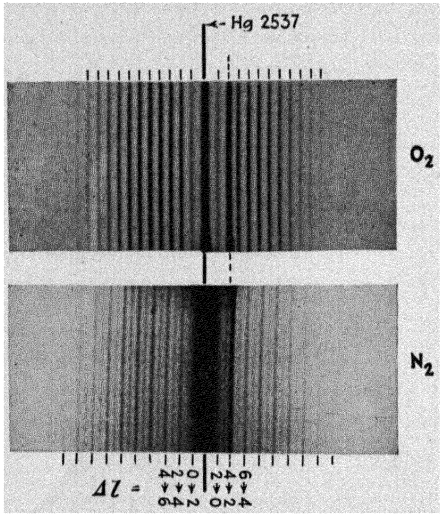


FIG. 107.—Raman effect in oxygen and nitrogen. (*Rasetti.*) Nitrogen shows the (strong) lines of paranitrogen interspersed with (fainter) lines of orthonitrogen. In oxygen (without nuclear spin) only the para form exists.

approximate explanation by the Bohr theory, it will be of interest to us to attempt an explanation in terms of Bohr's planetary model. The selection principle follows directly from the correspondence principle. The analysis of the rotation of a molecule consisting of two exactly similar atoms would show not the fundamental but the first overtone, because the configuration is repeated twice in every revolution. Hence by the correspondence principle only double quantum jumps will be allowed (page 186). Even to even, or odd to odd. If the two atoms are very nearly but not exactly alike, there will be an extremely weak fundamental frequency; by correspondence there will be an extremely small probability of a single quantum jump.

Heisenberg, using the new quantum mechanics, derived this selection principle and showed that it remained inviolate even in collision processes. The following consideration will suggest that this selection principle is indeed of very fundamental nature.

If a molecule consists of two exactly similar atoms, without spin, as in O_2, a rotation of 180° returns the atom to the original phase. The quantum conditions will be

$$I\omega \cdot \pi = k'h$$

instead of Eq. (22″) and hence Eq. (22″) becomes

$$I\omega = 2k'\hbar = k\hbar \ (k = 2, 4, 6, \text{etc.}) \qquad (22''')$$

(We are now using $k = l + 1$ instead of l, just as we did in our orbital representation of hydrogen, $k' = 1, 2, 3$, etc.). It is evident that the integers k in Eq. (22″) can have only even values. States such as

$$I\omega = \text{odd multiple of } \hbar$$

do not exist. This is the case with oxygen. As shown in Fig. 107, only even values of k (odd of l) exist.

The same argument will apply to nuclei with spins (as in H_2) if the spins are in the same direction. Such identical atoms can occur only in state of even k.

The exact interpretation of this phenomenon is given by the new mechanics and the new statistics. Alternately the states of rotation correspond to symmetrical and antisymmetrical wave functions and the symmetry type is immutable. The above approximate interpretation by the Bohr theory has been given because of the light it throws upon the meaning of identical atoms. To this we shall refer again (page 375).

Summary.—In this chapter we have supplemented the classical kinetic theory of gases by introducing quantized states of rotation and vibration. The energies of these states are (according to the older quantum theory)

$$\text{Energy}_{\text{rot}} = \frac{\hbar}{2I} \cdot l'^2$$

$$\text{Energy}_{\text{vib}} = n_{\text{vib}} h\nu$$

The new mechanics modifies these relations.

In modern physics the kinetic theory has suffered much greater changes than these—the very significance of the subject seems to have changed. It will be necessary, however, to postpone these considerations to Chap. XXVIII. Let us turn now to a very different field: the nucleus of the atom.

CHAPTER XXIV

THE EXPLOSIONS OF THE NUCLEUS

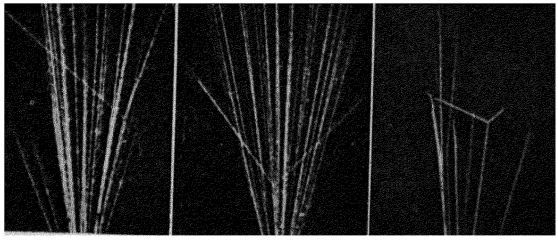
Projectiles: alpha, beta, gamma rays and how they are measured. Heredity among the elements.

Much of what is known of the nucleus is due to studies of radioactivity. Shortly after Becquerel and the Curies discovered radioactivity, Rutherford (1899) identified the alpha and beta ray; the gamma ray was discovered the following year. The identification of the alpha ray as the nucleus of helium and the proof of the spontaneous transmutation of elements followed in the next decade—at the time almost unbelievable discoveries. These alpha rays were the most energetic, the beta rays the swiftest particles known. Their properties were extensively studied. Throughout the years of this century the indefatigable Rutherford has been delving into this most deep-seated center of mystery, the nucleus. The story of the nucleus is a story apart; many of the results are gathered into a book by Lord Rutherford and his coworkers.[1] It is a fascinating story of which we can give but a brief summary.

Alpha Rays.—There is an even chance that any given uranium atom will explode in the next 5 billion years. When it explodes, it hurls an alpha particle through space with a speed one-twentieth that of light. Four million electron-volts of energy. The alpha particle is a helium nucleus; it is doubly charged. This alpha particle from uranium goes 2½ cm. through the air and is stopped. The track of this ray can be seen in the Wilson cloud chamber (Fig. 108). The particle ionizes the air molecules through which it passes but is itself undeflected by its collisions except occasionally when by chance it hits into the very nucleus of an atom. When such a direct hit occurs, we find a break in the alpha track and sometimes it happens that the atom nucleus is smashed.

[1] RUTHERFORD, CHADWICK, and ELLIS, "Radiations from Radioactive Substances."

These rays will go through an aluminum leaf 0.01 mm. thick. In the leaf it goes through 40,000 layers of aluminum atoms. It was experiments of this kind which led Rutherford and Bohr



(*a*) (*b*) (*c*)

FIG. 108.—Cloud chamber tracks of alpha particles. Showing collisions with nuclei of (*a*) hydrogen, (*b*) helium, (*c*) oxygen. Observe the conservation of momentum. (Proton track is to left in *a*; O track to right in *c*.) (*Blackett.*)

to their concept of the concentrated nucleus (the planetary atom rather than the "plum pudding" type). Occasionally an alpha particle is deviated in its path as it approaches too close to some atomic nucleus. But not often. The nucleus is too small.

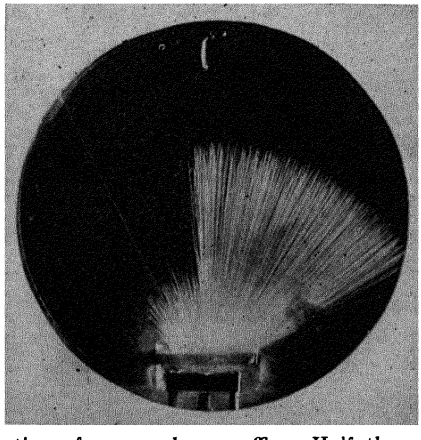


FIG. 109.—Absorption of α rays by paraffin. Half the rays have passed through paraffin film; the range has been reduced and a proton has been ejected from the hydrocarbon. (*Meitner.*)

Scattering experiments lead to the best estimates of the size of the nucleus. The nuclear radius in copper is about 10^{-4} angstrom, in silver 2×10^{-4} angstrom, in gold 3×10^{-4} angstrom (see Table 4).

These rays from uranium are among the slowest alpha particles which have been measured.[1] The energy of the nuclear explosion is closely connected with the life of the nucleus. The law is known as the Geiger-Nuttall relation:

$$\log \text{life} = C_1 \log \text{range} + C_2$$

The fastest alpha particles are expelled from thorium C′. This atom has a transient existence of 10^{-11} sec. (!); the alpha projectiles in this case have three times the penetration of those ejected from uranium.

Measurement of Radioactive Rays. 1. *Cloud Chamber.*—Alpha rays, beta rays, gamma rays, all produce ionization, produce luminescence in fluorescing substances, and blacken the photographic plate. The alpha rays are the most quickly absorbed and produce each of these effects most intensely. They are the rays easiest to measure.

C. T. R. Wilson devised a method for photographing the tracks of alpha rays directly. A piston periodically expands the air in a glass-covered cylinder. This air is normally saturated with water vapor; in consequence of the expansive cooling the air becomes momentarily supersaturated, but unless suitable nuclei are present the water droplets cannot condense. If a substance is projecting alpha rays into the cylinder, the alpha particles in their career through the gas leave behind a trail of ions. These ions act as condensation centers and along each alpha track a threadlike cloud appears. Protons and electrons (beta rays) also leave tracks in the Wilson expansion chamber—finer than alpha-ray tracks and, in the case of electrons, of irregular density, like a string of beads.

The same method is also used to photograph the ions produced by gamma rays and x-rays. In these cases it is the secondary rays produced by the primary beam which produce the tracks.

2. *Scintillations and Geiger Counter.*—Two other methods have been devised to detect the individual alpha particle. The oldest is that of noting the scintillations produced when the high-speed

[1] The rays mentioned are those from the parent uranium. The recently purified element uranium is a mixture of the isotopes UI and UII—the alpha rays from UII are more energetic. Speeds of alpha particles range from 4½ per cent of the velocity of light (from UI) to 7 per cent (from ThC′); the corresponding ranges in air are 2.4 to 8.1 cm.—but there seem to be a few exceptionally long-range particles.

particle strikes on a zinc sulphide screen. With a magnifying glass the individual burst of light may be observed. This was the first discovered method by which the physicist could observe the action of the individual atom, the break-up of the individual nucleus. By observing scintillations, the number of disintegrating atoms of radium can be counted; this leads directly to a value of Avogadro's constant (Table 17).

The observation of individual scintillations is extremely tedious. The individual alpha particles can also be recorded electrically by the "Geiger counter." Just behind a small hole in a plate a fine-pointed wire is placed. The wire is charged until almost ready to discharge; whenever an alpha particle

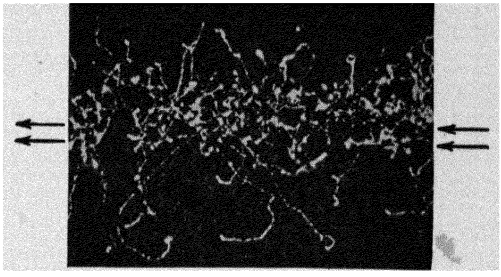


FIG. 110.—X-rays through air. Showing cloud tracks produced by liberated electrons. (*Wilson.*)

enters the hole, it produces in its train a large number of ions and the discharge of the counter occurs. Other forms of Geiger counters have been devised. They have been extensively used not only for alpha rays but to detect individual high-speed electrons and protons.

Ionization Chamber and Electroscope.—The standard method of measuring radioactivity is by measuring the rate of leak produced in an electroscope. The sample is placed in the ionization chamber; the alpha, beta, or gamma rays ionize the air and slowly discharge the electroscope. This gives a measure of the radioactivity.

The greatest ionization is produced by the quickly absorbed alpha rays. Alpha rays usually produce about a hundred times as much ionization as beta rays and these may produce a hundred times as much as gamma rays.

Filters are used to separate these different types of rays. From a thin layer of radioactive material which emits rays of

all three types, the ionization will be almost entirely due to alpha rays when no filter is used. If the sample is covered by aluminum foil 0.1 mm. thick or by a sheet of ordinary paper, the alpha rays will be completely absorbed without appreciable absorption of other rays. A millimeter of lead cuts out the beta rays and leaves the gamma rays alone. As a rough rule, beta rays are one hundred times as penetrating as alpha; gamma rays are from ten to one hundred times as penetrating as beta rays.

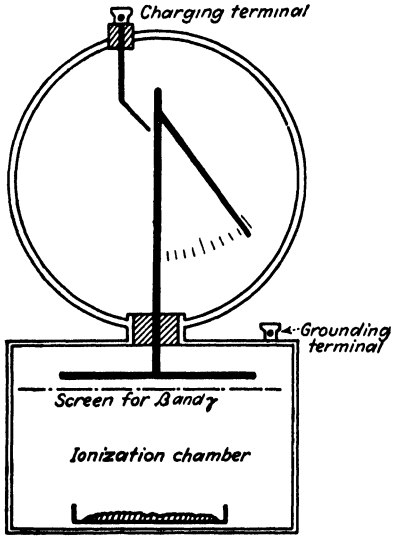


FIG. 111.—Electroscope and ionization chamber.

Beta Rays.—The average life of uranium is 5 billion years. Giving off an alpha particle, it changes to element 90 (uranium X_1). But uranium X_1 is not satisfied with itself; it has a half life of but 2¼ days. Poof! It is a mild explosion. An electron is emitted, its energy less than 100,000 volts. (Insufficient to ionize its own *K* shell!) Its penetrating power is slightly more than that of an alpha particle.

Then in a minute: Bang! Another electron is emitted, and with it a photon. This time the electron has more energy—about a million *e*-volts. It may penetrate nearly a millimeter of aluminum. The uranium atom, having relieved itself of an alpha particle and two electrons, is now (except for mass) itself again (UII an isotope of uranium, mass 234) and remains so for 2 million years (mean life).

These electrons which are emitted are the beta (β) rays; the photon (electromagnetic radiation) is the gamma (γ) ray. Unlike alpha rays, beta-ray emission is far from homogeneous. The ray can be deflected by a strong magnetic field and its velocity so determined ("beta-ray spectrograph"). When the electrons of different speeds are filtered out one from the other magnetically in this fashion, the beta rays which have come from the nucleus are found to give a *continuous* "velocity spectrum." Usually distinct velocity groups will also be found ("beta-ray lines") but these are due to secondary electrons expelled from the

x-ray levels by the photoelectric action of gamma rays. The primary beta rays which come from the nucleus appear to have no well-defined single velocity.

The beta rays do not have the definite range of the alpha particle—they are more easily scattered, their path through a gas is a very tortuous affair. It was once supposed that the intensity of the beam passing through a layer of matter followed the negative compound-interest law. This is not true; a definite absorption coefficient cannot be ascribed even to a homogeneous beam of beta rays. The intensity does, however, gradually drop off as more and more matter is traversed.

The fastest beta rays are emitted from radium C′ and thorium C′. They have a velocity 95 per cent that of light.

Gamma Rays.—Often accompanying the emission of beta rays, sometimes with alpha rays, short-waved electromagnetic radiation occurs. These are the gamma rays. When homogeneous, gamma rays are absorbed by the compound-interest law. These rays usually penetrate through several centimeters of aluminum; yet some are comparatively soft (Fig. 33).

Gamma rays (photons) appear to be emitted as a consequence of a nuclear readjustment following the emission of alpha or beta rays. The wave lengths have been measured. Most of the values found lie between 10 and 100 X units (*i.e.*, 0.01 and 0.1 angstrom, see page 272). The shorter gamma rays have a half range of more than 1 cm. of lead. Gamma-ray frequencies as distinct and well defined as x-ray frequencies are found; this indicates that well-defined energy levels exist for the alpha and beta particles within the nucleus.

Radioactive Transformations.—When radioactivity was first discovered, a veil of mystery cloaked the phenomena. The radiation emitted by radium is such as to keep the radium salt always two or three degrees above the temperature of its surroundings. A gram of radium with its decay products produces 2 cal. of heat per minute—this hour after hour, day after day, year in and year out, without apparent weakening. This seemed like getting energy from nothing, producing heat without a change of state.

In 1912 Soddy published his theory of radioactive transformation. It had become evident that radium gave birth to radon and this in turn to radium A and this to radium B and so on but what these different manifestations of radium meant was

not so clear. No evident decrease in the radium could be observed. The chemist Soddy working with Rutherford first established that each of these substances was a distinct element and for the first time showed that chemical elements could transform one into the other. It was difficult to separate radium from barium; evidently it was an alkaline earth. Radon was a noble gas, like helium and argon. Radium A belonged to the sulphur group, radium B resembled carbon, silicon, and lead, in fact was chemically identical with lead. These substances fitted into the periodic table with numbers 88, 86, 84, 82 and were certainly elements. Each of these elements was derived from the preceding element by the emission of an alpha particle. If the radium did not appear to decrease in amount, it was because its life was so long.

Soddy's Rule.—*When an alpha ray is emitted, the element is metamorphosed into another element which is* 2 *smaller in atomic number.* This agreed with the view (which in 1912 was just beginning to find expression) that the atomic number depended upon the nuclear charge. The loss of the alpha particle reduces by 2 the charge on the nucleus. It reduces the weight of the element by 4.

Radium B (82) emits a beta ray; it is transformed into radium C, and radium C is identical in every chemical reaction with bismuth (83). Soddy's rule continues: *When a beta ray is emitted, the element changes to one of* 1 *higher atomic number.* The loss of the electron increases by 1 the charge on the nucleus. The mass of the element is practically unchanged.

By the discovery of transmutation of elements, the law of conservation of energy was saved. Whenever one of these high-speed particles is emitted, nuclear energy is lost; atoms of high nuclear energy are destroyed. Lead and helium form the ashes of radioactive elements of the past. The law of conservation of energy was saved but a long-treasured tradition of the immutability of the chemical element was destroyed. The atom was no longer the "uncuttable."

The Radium Family Tree.—Radium traces its ancestry back for billions of years. Its ancestors belong to the fourth transition group of the periodic table. Its great, great, great grandfather was uranium, heaviest of all elements. Uranium (92) resembles tungsten[1] and hence is placed in the sixth group of the condensed periodic table.

[1] For instance, it can replace tungsten in tungsten steel.

And Uranium lived 5 billion years and, giving up an alpha particle, begat UX_1, isotope of Thorium (70). And UX_1 lived 25 days and, giving out a beta ray, begat UX_2 (91). And UX_2 lived but a minute and, losing a beta ray, begat UII (92). UII was the exact image of his great grandfather Uranium I. And UII lived 2 million years and (losing an alpha particle) begat Ionium (90). And Ionium lived 70 thousand years and (losing an alpha particle) begat Radium (88).

Law of Radioactive Decay.—In this family chronology we have used the word "life" very loosely. The question of atomic transformation is entirely one of chance; the number of atoms breaking down per second is proportional to the number present. In other words this is the compound-interest law. The "life" of the atom as used above (and the period given in Table 51) means the "half-life" or the probable life or the time required for half of the atoms to change.

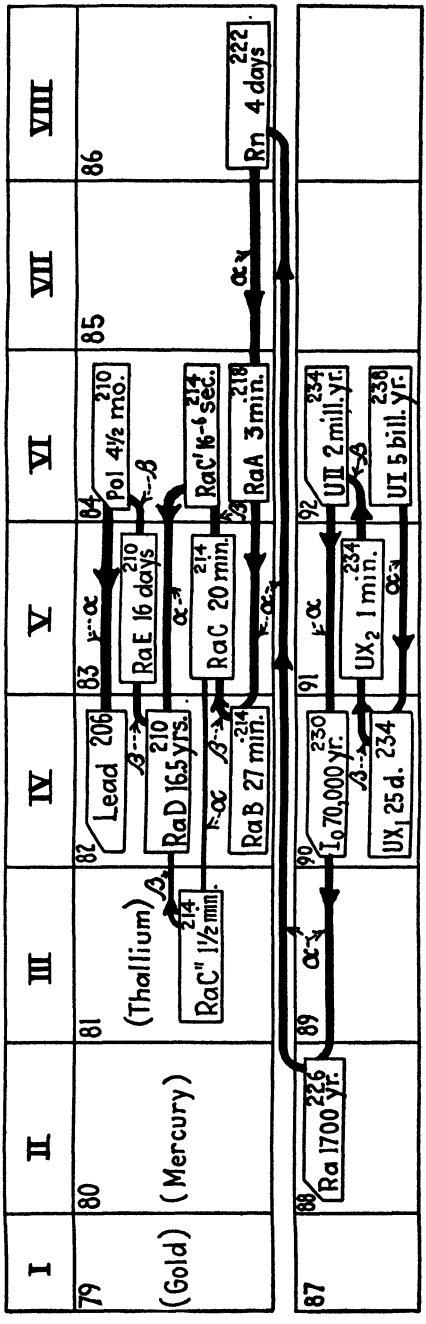


TABLE 51.—Radioactive transformations. Radium sequence.

Figure 112 shows the compound-interest curve of decay of UX_1. An interesting experiment is to separate chemically UX_1 and UX_2 from uranium and observe the decay of this segregated UX_1 and UX_2 and to observe the rebirth of more of these elements from uranium. At the start, just after the separation, the uranium emits only alpha rays, the UX_1 and UX_2 only beta rays. If we follow the course of this beta-ray activity for several months, we find that it gradually decreases, following the decay curve of the figure. After 24.5 days the activity has fallen to half, showing that half of the UX_1 and UX_2 have changed to UII.

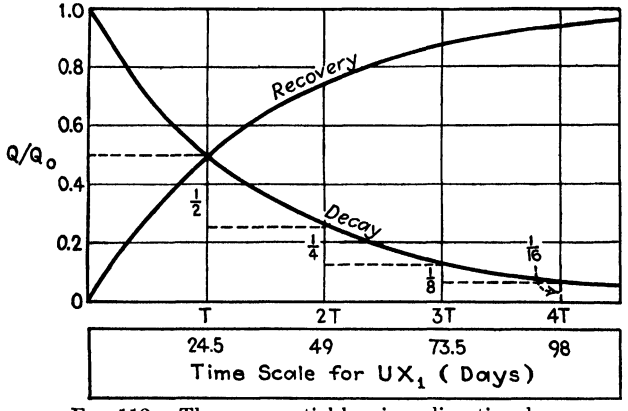


FIG. 112.—The exponential law in radioactive decay.

In the same time, if we follow the beta-ray activity of the uranium, we find that starting from zero it has built up to a value which now, after 24.5 days, exactly equals that of the other sample. New UX_1 and UX_2 atoms have been born. The combined beta activity of the two samples together remains constant—equal to the beta activity of the original material before separation. As time continues, the decay and recovery curves continue their course. In another 24.5 days the activity of the UX_1 and UX_2 sample decreases to a quarter, in another like period to an eighth, and so on, following the compound-interest curve. The beta activity of the uranium increases nearer and nearer to its steady value.

If instead of following the beta-ray activity of UX_1 we should watch the alpha-ray activity of uranium itself, we might hope to find this following a similar decay curve but this experiment would require time—the half life is 4.5 billion years. In one

year uranium decreases only by 1 part in 6,500,000,000! A gram molecule of uranium (238 gm.) containing 6.06×10^{24} atoms should lose about 10^{15} atoms per year or 30 million per second.[1] Such a minute annual loss of weight is much too small to be detected by direct weighing.

This suggests one method by which the half-life of an element can be measured: by measuring the rate of decomposition per second. This, of course, is done by counting the alpha or beta particles emitted.

Radioactive Equilibrium.—Another method of estimating the half-life is by measuring the relative masses of different radioactive elements in equilibrium one with the other. After a long period of time an element reaches an equilibrium with its decay products, such that the relative amounts of these different products do not change. Such an equilibrium is reached for UX_1 and UX_2 after several months when the recovery curve (in Fig. 112) has reached practical saturation. When equilibrium is reached, the number of UX_1 atoms formed per second equals the number lost per second; these latter are transformed into UX_2 and the number of UX_2 atoms formed per second likewise equals the number lost. In other words, just as many alpha particles are emitted by the uranium as beta particles by UX_1 as beta particles by UX_2. For this condition to obtain, the slow decay rate of the parent uranium must be compensated for by the larger amount of this element present. The law is: In the equilibrium state the number of atoms of any element present is proportional to its half-life.

$$\frac{N_U}{T_U} = \frac{N_{UX_1}}{T_{UX_1}} = \frac{N_{UX_2}}{T_{UX_2}} \tag{37}$$

and so on through the rest of the sequence.

The relative lives of uranium and radium are ascertained by determining the ratio of the two elements in very old minerals. The ratio is 1 : 3 million, or 1 gm. of radium in 3 tons of uranium. The life of uranium is 3 million times that of radium.

Only a few of the radioactive elements are present in such quantity that they have been actually separated and weighed. The amounts which are handled and detected are often inconceivably small. In 1 gm. of uranium there is present 5×10^{-16} gm. of UX_2 (a milligram in 2 million million tons!) and yet is it

[1] There are 31 million seconds in a year.

(in virtue of its radioactivity) as easy to detect as uranium itself. There are 2 quadrillion times less of it present. It is exactly 2 quadrillion times as radioactive.

Radium.—Radium is especially important because it has a life so long as to be fairly permanent and yet so short as to ensure strong activity. Its half-life is 1600 years. It loses 1 per cent of its mass in 23 years. It is refined from old uranium ores like pitchblende; it costs about $60,000 per gram. Like calcium, strontium, and barium, it is seldom used free; usually it is in the form of the chloride or bromide salt. A gram of radium together with its decay products evolves 2.3 calories of heat per minute or 2.5 billion calories during its total life.

The Descendants of Radium.—Radium has eight linear descendants, each radioactive; and then ultimately lead. Emitting an alpha particle, radium forms the noble gas radon (radium emanation), which has a half-life of 4 days. One-eighth of a cubic millimeter of radon is formed from a gram of radium per day. (At the same time an equal volume of helium appears. This latter from this single transformation. In all, five alpha particles are emitted in the successive transformations of a radium atom.) This radioactive gas is used extensively in medical practice. It may easily be condensed by cooling with liquid air and held in minute glass tubes. The radon though small in amount is emitting alpha rays exactly as profusely as the radium itself because of the reciprocity law [Eq. (37)]. But in a few days it is gone. These old radon tubes still containing radium D, E, and F afford a convenient source for radioactive experiments.

The gas radon decomposes (alpha ray) where it chances to be and produces on the walls of the vessel the so-called active deposit. This active deposit is first radium A which in the course of a few minutes changes to radium B, C, C′, and then to radium D. RaD has a half-life of 25 years and is relatively inactive. The successive transformations of this deposit can be easily demonstrated. A negatively charged wire in radon quickly becomes coated with radium A. We may follow the alpha-ray activity. We find that at first this alpha activity diminishes rapidly as the radium A disintegrates; its half-life is 3 min. (Radium B emits beta rays.) Then presently the longer lived radium C appears and more alpha rays. Most of the alpha emission comes not from radium C itself but from its short-lived product,

RaC′. The half-life of radium C is 20 min.; gradually the alpha rays decrease in intensity as radium C and radium C′ are converted into the relatively inactive radium D.

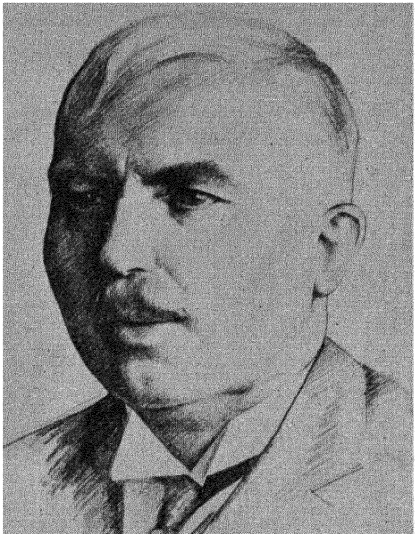
Or we can follow the beta rays. These rays come from radium B and C. From zero for the fresh deposit, the emission increases as radium B is born and then, as first radium B and then radium C are transformed, it drops off to practically nothing.

At radium C the line of descent branches. Usually a radium C atom emits a beta ray followed a millionth of a second later by a most energetic alpha ray. One dissociation out of two thousand reverses the order—first an alpha, then a beta ray. But in either case we get radium D.

Slowly radium D transforms (beta ray) into radium E, which transforms (beta ray) into radium F (or polonium, named by Mme Curie for her native land). Polonium with a half-life of 4½ months, emits an alpha ray, and gives lead.

Thorium and Actinium Families.—It would but be repeating this same story to trace the transformations of thorium and actinium. Thorium is element 90, weight 232, often found with the rare earths. Its life is three times as long as that of uranium. Among its descendants are radiothorium (an isotope of radium), thoron (an emanation like radon), an active deposit, and ultimately lead (weight 208).

Actinium (89, weight 226) is a short-lived element (life 20 years) which is supposed to be descended (as a cousin of radium) from uranium. Its ancestry has not been entirely worked out. It also has an emanation and an active deposit and ultimately gives lead (weight 207).



LORD RUTHERFORD

Rutherford belongs to the British Empire. Born in New Zealand, educated at Cambridge, became professor in McGill University in 1898. *His fundamental experiments in radioactivity were started while he was in Canada. In* 1907 *he went to the University of Manchester, in* 1919 *to the Cavendish Laboratory at Cambridge. Received the Nobel Prize in* 1908. *Was Ernest Rutherford until* 1914, *then Sir Ernest, and after* 1930 *Lord Rutherford.*

His method: get the facts, let the theories take care of themselves—and they always have.

Lord Rutherford succeeds Clerk Maxwell, Lord Rayleigh, and Sir J. J. Thomson as director of the Cavendish laboratory—a proud succession of scientists!

CHAPTER XXV

NUCLEAR PHYSICS

New particles: positron, neutron, deuton. Nuclear structure and nuclear energy. Atom smashing.

Investigating the scattering of alpha rays by matter, Rutherford was led to the conclusion that the atomic nucleus has a radius usually less than 1/10,000 angstrom. This is about the radius attributed to an electron; the radius of the proton is a thousand times smaller. The radius of the atom itself is usually about 1 angstrom. Only one part in a million of the atomic volume is occupied by this central "sun" which, attracting the electron "planets," ultimately determines the properties of the atom. The radius of the K orbit in uranium is about 0.01 angstrom. In size the nucleus stands to this smallest of K orbits about as our own sun does to the orbit of its nearest planet (Mercury). Some one has remarked that the nucleus and the surrounding electrons "fill" the space occupied by the atom in about the same way that so many flies might occupy the space in the dome of a cathedral.

Until recently most of our knowledge of nuclear structure has been derived from radioactivity. Before 1919, radioactivity furnished the only direct evidence that one element could be transformed into another. In that year Rutherford showed that many of the light elements could be shattered by alpha-ray bombardment. In the same year Aston made his first measurements with the mass spectrograph; in the years which followed, this instrument played an important part in the development of nuclear physics. In 1932 came the discovery of three new elementary particles: the neutron, the deuton, and the positron, and the same year saw the first transmutation of elements without the use of radioactive rays. Almost at once nuclear physics became the focus of scientific interest.

The Structure of the Nucleus.—Until recently the physicist had two kinds of prime particles: electrons and protons; these were the building stones from which he fashioned his nucleus.

The nucleus of hydrogen ($_1H^1$) is a single proton;[1] the nucleus of helium ($_2He^4$) was supposed to consist of four protons and two electrons. (This is the alpha particle.) Since the electronic mass is comparatively insignificant, the atomic weight (M) gave the number of protons in the nucleus; the atomic number gave the net charge. The third element, lithium, consists of two isotopes. The nucleus of $_3Li^6$ was composed (according to this theory) of six protons and three electrons, the nucleus of $_3Li^7$ of seven protons and four electrons. And so on. In uranium ($_{92}U^{238}$) the nucleus was pictured as containing 238 protons and 146 electrons. The reader is probably familiar with this description of the nucleus.

The discovery of three new elementary particles, together with considerations of a theoretical nature, has led to a rather different view of nuclear structure. (1) The positron (or positive electron) is a particle resembling the negative electron in mass but with positive charge. (2) The neutron has approximately the mass of a proton but is not charged. (3) The deuton has the charge of a proton but has approximately double its mass; it is presumably a proton-neutron combination. Out of protons and neutrons, combining when possible as deutons and alpha particles, we attempt to fashion our nuclei. Negative electrons (or *negatrons* as we may henceforth call them) and positrons are left out of the picture.

The hydrogen nucleus ($_1H^1$) is a proton. The deuton ($_1H^2$) we shall suppose to consist of a proton and a neutron.

$$_1H^1 + {}_0n^1 = {}_1H^2 \qquad \text{(I)}$$

The alpha particle (or helium nucleus) consists of two deutons

$$2\,{}_1H^2 = {}_2He^4$$

or of two protons and two neutrons.

The number of protons always equals the atomic number; the number of neutrons is given by the difference between mass number and atomic number. Isotopes differ only in the number of neutrons; $_3Li^6$ has three protons and three neutrons; $_3Li^7$ has three protons and four neutrons.

[1] It being now necessary to distinguish between isotopes, it is customary to write the mass number as an exponent after the atomic symbol. It is also convenient to express the atomic number as a prefix.

Figure 113 gives the nuclear structure of the lighter atoms; it shows a very interesting progression in the formation of the elements.

Negatrons and Positrons in the Nucleus?—One is tempted to think of the neutron as simply a proton embedded in a negatron. Or perhaps of a proton as a neutron embedded in a positron. (But we could as well consider it as two positrons, one negatron and a neutron, or as three positrons, two negatrons and a neutron—and so on.) The theoretical physicist, however, tells us that no meaning can be given to such views; nor can any meaning be given to an electron, positive or negative, as existing in any nucleus. When an electron charge enters a nucleus, it loses its identity

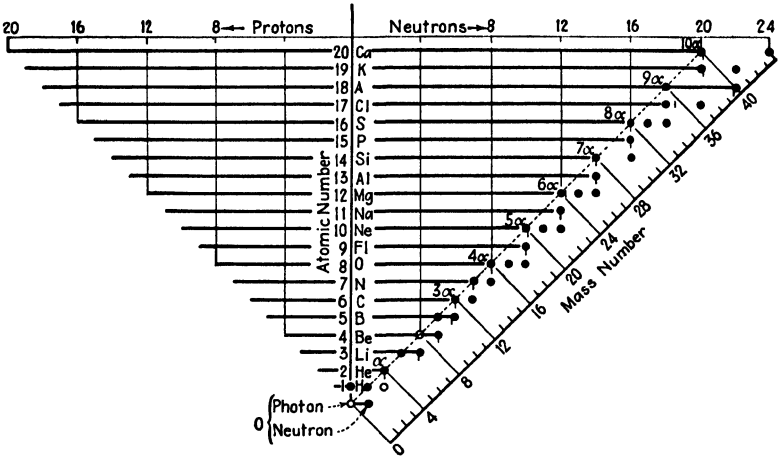


FIG. 113.—Nuclear structure in lighter elements.

just as does a photon lose its identity when light is absorbed by an atom. The theoretical physicist shows (from the Uncertainty Principle, Chap. XXVIII) that, for a particle as light as an electron, the very sign of the charge becomes indistinguishable in the nucleus. A more elementary argument, but one which hardly goes to the heart of the matter, is this: Certainly an electron cannot preserve the identity with which we are familiar within a nucleus which is itself little larger than the free electron (page 136). Moreover, since their charges cancel, the number of positrons and negative electrons in even the simplest nucleus could never be counted. We shall, therefore, build our nuclear structure out of heavier (and therefore smaller) particles: protons, neutrons, deutons, and alpha particles.

Heat of Combination of the Helium Nucleus.—The forces and energies which are involved in this binding of protons and neutrons into nuclei are enormous in comparison with those which bind the planetary electrons about the nucleus or which hold

atoms together in molecules. These nuclear energies are vastly greater than the few hundred atomic ergs which measure the ionizing potential of the valence electrons; they are very large even in comparison with the ionizing energy of the K electrons of heavy elements. The energies here are counted in hundreds of millions of atomic ergs, in millions of e-volts.

This building up of nuclei out of a common element is practically Prout's hypothesis of a century ago. Prout reasoned that atomic weights should be whole numbers. Many of them are indeed nearly so. When an atomic weight differs greatly from an integer (as, for example, Cl = 35.46), the element is always found to be a mixture of isotopes. As a matter of fact, however, the weights of the individual atoms are not exact multiples of the hydrogen weight. The atomic weight of hydrogen is approximately 1.008; of helium 4.002. If four hydrogen atoms combine (as we suppose to be possible) into a helium atom, there is a loss of weight of 0.030 protol. This loss of energy has been called the *packing effect;* it gives a measure of the energy of the nuclear reaction.

We found in the theory of relativity that mass was an aspect of energy. A body, when moving, has increased mass; a body with potential energy has increased mass. The energy in ergs equals c^2 times the mass in grams.[1] Under what conditions four hydrogen atoms coalesce to form helium we do not know; once started, this must be the most energetic of reactions. As the protons and electrons combine into the new nucleus, energy must be radiated of enormously short wave length, an enormously large energy quantum. The protons lose potential energy (mass). This is the cause of the packing effect. The loss in mass gives a measure of the energy of this atom-building reaction. When 4.032 gm. of hydrogen unite in this fashion to form 4.002 gm. of helium and 30 mg. of light, this radiant energy amounts to 2.7×10^9 kilojoules.

Nearly 3 billion kilojoules, more than a half billion large calories! Suppose a catalyst is discovered which permits the

[1] In "einsteins," $c = 1$ and energy equals mass. In atomic units $c = 300{,}000$. This gives 9×10^{10} atomic ergs = 1 protol. In c.g.s. units: 9×10^{20} ergs = 1 gm. A ten-thousandth protol, which is the mass unit in which the packing effect is usually expressed, is equivalent to 94,000 e-volts. It will be well for the reader to translate the packing energies which are given in this chapter into millions of e-volts; he may take a packing unit as approximately equivalent to 100,000 e-volts.

association of hydrogen into helium. Suppose the experiment is performed in a copper vessel (specific heat 0.1). How heavy a vessel must be used? Half a billion large calories will raise 5 million kilograms (5000 tons) a thousand degrees centigrade—up to the melting point of copper. This 4 gm. gives out as much heat as a hundred tons of coal. A few grams of hydrogen would furnish the fuel for a lifetime if we but knew the secret of synthesizing helium. The energy released in the synthesis of a single helium nucleus (alpha particle) is 2.7×10^9 atomic ergs; this is forty-five millionths of an erg in a single atom.

We may write the equations for the coalescence of protons and two electrons into the helium nucleus as

$$4_1H^1 + 2e^- = {}_2He^4 \qquad \text{(II')}$$

Heat of reaction = 0.030 protol

It would be somewhat more in keeping with the current views to consider this as a synthesis of two protons and two neutrons (or as the synthesis of two deutons) but, since this reaction, unlike others to be described, is purely hypothetical, we need not stress the point.

Packing Fractions and Atomic Stability.—The average change in mass of each proton or neutron in any nucleus due to this packing is called the packing fraction.[1] Oxygen is taken as a standard. According to Aston's measurements with his latest mass spectrograph, the atomic weight of hydrogen is 1.00778 and the packing fraction (in ten-thousandths of a mass unit) is 77.8. Aston's weight for helium is 4.00216 and the corresponding packing fraction 5.4. (Here 0.00216 must be divided by 4 to give the mass decrement per proton.)

Similarly in other atoms the energy of nuclear binding is found from the exact atomic weight determinations of Aston and of Bainbridge. These are given in Table 52. It is seen that in most cases these numbers differ slightly from the exact integral values; these differences give a measure of the binding energies of the different nuclei (in terms of oxygen).

High values of the packing fraction indicate looseness of packing, instability, high potential energies. It is noteworthy that

[1] This interpretation is not exact since the neutron and proton differ slightly in mass. More exactly defined: the packing fraction is the fractional part of the atomic weight divided by the mass number. As a matter of fact the packing fraction is not so important in the new "nuclear chemistry" as the total energy of the nuclear reactions.

among the lighter elements those with lowest packing fraction are He, C, and O. These elements have masses divisible by 4; it seems probable that the protons and neutrons enter these nuclei grouped into alpha particles. In forming the alpha particle the protons and neutrons give up much energy and consequently (by Boltzmann's law, page 72) the alpha particle is a very stable configuration. The heavier nuclei are probably composed mostly of alpha particles.

TABLE 52.—PACKING FRACTIONS OF LIGHTER ELEMENTS FROM DATA OF ASTON AND OF BAINBRIDGE

	Atomic weight	Packing fractions	Possible nuclear structure	Change from preceding element (with energy decrements)
H^1	1.00778	77.8	Proton	
*H^2	2.0136	67.5	Deuton = p + neutron	n − 10
*H^3	.....	.....	$d + n$	n }
He^4	4.0022	5.4	$\alpha = 2d$	d } −248
Li^6	6.0145	24.2	$\alpha + p + n$	d − 12
Li^7	7.0146	20.9	$\alpha + p + 2n$	n − 66
*Be^8?	.....	.....	$\alpha + 2p + 2n$	p }
Be^9	9.0155	17.2	$\alpha + 2p + 3n$	n } −146
B^{10}	10.0135	13.5	$\alpha + 3p + 3n$	p − 98
B^{11}	11.0110	10.0	$\alpha + 3p + 4n$	n − 92
C^{12}	12.0036	3.0	3α	p −152
*C^{13}	13.004	3.0	$3\alpha + n$	n − 63
N^{14}	14.008	5.7	$3\alpha + p$	p − 74
*N^{15}	15.007?	4.7	$3\alpha + p + n$	n − 77
O^{16}	16.000	0.0	4α	p −137
*O^{17}	17.0029	1.7	$4\alpha + n$	n − 38
*O^{18}	18.0065	3.6	$4\alpha + 2n$	n − 28
F^{19}	19.000	0.0	$4\alpha + p + 2n$	p − 69
Ne^{20}	19.9967	−0.2	5α	p −111
*Ne^{21}	.....	.....	$5\alpha + n$	n }
Ne^{22}	21.9947	−0.3	$5\alpha + 2n$	n } −154

*Scarce isotopes. Existence of Be^8 is not definitely established. Estimated abundance of H^2: H^1 is 1:30,000; of O^{18}: O^{17}: O^{16} is 5:1:3000.

Energies given in ten-thousandths of a mass unit. Mass of neutron has been taken as 1.0067 protols.

Figure 114 shows the packing fractions for the elements. The value drops, becomes negative, has a minimum for elements in the neighborhood of iron in the periodic table, and then gradually

rises. For the lighter elements the curve splits into two branches; the lower contains the elements composed of alpha particles alone. From the curve it is seen that the building up of the lighter elements is an exothermic process (giving out heat). The lighter atoms tend to associate into heavier ones. With the heavier elements the case is different. Here the tendency is not for association but for dissociation of the element into lighter elements. The most stable of atoms would seem to be those near iron.

It is generally supposed that the heat of the stars is largely due to these processes of disintegration of heavier nuclei or aggregation of lighter ones. It may well be that these trans-

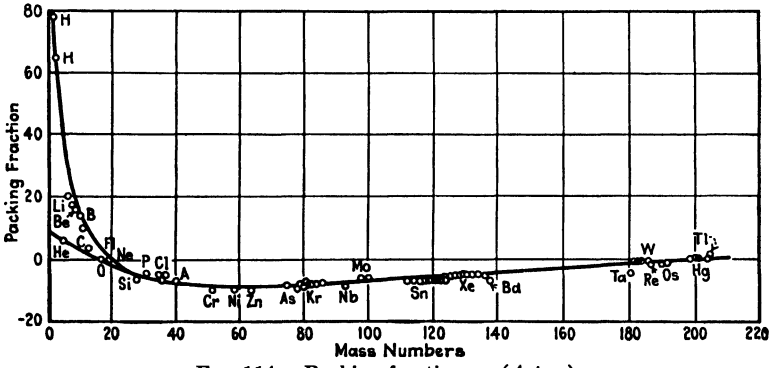


FIG. 114.—Packing fractions. (*Aston.*)

formations can take place at the enormous temperatures and pressures which exist within the stars. Among a few of the heaviest elements, spontaneous disintegration is observed under terrestrial conditions. This radioactive disintegration was described in the preceding chapter.

Radioactivity has been detected in potassium and rubidium. In each case a negatron (beta ray) is released from the nucleus. This must raise the atomic number by unity, giving, respectively, calcium and strontium nuclei. Recently it has been reported that samarium and beryllium are radioactive. In each of these cases a very easily absorbed alpha ray is emitted. With these four exceptions, spontaneous dissociation of the nucleus occurs as far as we know only in the heaviest elements. None the less, atomic stability seems to play a role in determining the abundance of elements. The 30 lightest elements are responsible for all

but 1 part in 500 of the earth's crust. Oxygen with its nucleus of four alpha particles makes up about half of the earth's crust. Even-numbered elements are far more commonly found than odd.

Artificial Transmutation by Alpha Particles.—When high-speed alpha particles are projected into nitrogen, some of the collisions result in the ejection of protons from the nucleus. The range of the protons is several times that of the alpha particles; this enables the physicist to detect them in spite of the fact that only about one disruptive collision occurs for 100,000 alpha particles.

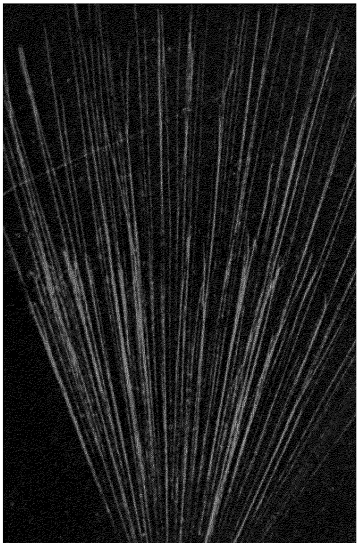


FIG. 115.—Transmutation of nitrogen. Proton is seen ejected toward left and a short track, presumably O^{17} is projected forward. No track is formed corresponding to the alpha particle after collision. Also note the alpha particles of different ranges. (*Blackett and Dee.*)

This method of breaking the nucleus was discovered by Rutherford in 1919. He observed similar disruption for all of the elements between boron and potassium except carbon and oxygen. (Notice that carbon and oxygen lie on the lower branch in Aston's curve, Fig. 114, indicating great stability.) The effect is usually more pronounced and the range of the ejected proton greater for the elements of even number.

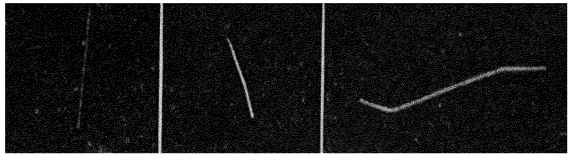
The actual process occurring in these experiments is something more than the simple removal of a proton. The alpha particle combines with the nucleus and simultaneously there is the ejection of the proton. This results in a net increase by 3 in the mass number of the nucleus and an increase of its charge by 1. Nitrogen, for instance, is transformed into the isotope of oxygen of mass 17.

$$_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1 \qquad \text{(III)}$$

Recently beryllium and lithium have been added to the elements which can be dissociated by alpha-particle bombardment.

But these reactions are of a very different kind and led to the detection of a new kind of elementary particle, the neutron.

The Discovery of the Neutron.—Mme. Curie-Joliot (daughter of the discoverers of radium) and M. Joliot discovered that, when beryllium was bombarded with the alpha rays from polonium, a very penetrating radiation resulted. It required 5 or 6 cm. of lead to reduce this radiation to half-value. When the radiation was passed through a substance containing hydrogen atoms (as paraffin), very long-range protons were ejected. It was supposed by the Joliots that these rays from beryllium were gamma rays, and that the hydrogen nuclei (protons) were ejected by the Compton effect (Chap. XXVI). The difficulty with this interpretation



(*a*) (*b*) (*c*)

FIG. 116.—Neutron collisions: (*a*) with hydrogen; (*b*) with carbon; (*c*) a transmuting collision with oxygen. (*Feather.*)

was that, for photons to have sufficient momentum (as discussed in the next chapter) to project protons with the observed range, they would have to have extremely short wave lengths, much shorter than any gamma rays which had hitherto been observed.

In the Cavendish Laboratory Chadwick repeated these experiments. He criticized this explanation of the effect. When the alpha particle strikes the beryllium atom, it presumably unites with it and forms carbon.

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{13}$$

The energy of the alpha particle from polonium is known (9 million *e*-volts). From values of the packing fractions of beryllium and carbon (Table 52) the amount of available energy can be computed (just as we have done for the helium synthesis). Chadwick pointed out that gamma-ray photons with this energy could not project protons with the high speeds which had been observed. Their momenta would be too small. Something more massive than a photon was required. Chadwick suggested that this was a new kind of ejected particle—the neutron. This view is generally accepted.

The neutron is an uncharged particle of (approximately) unit atomic weight. The atomic weight of beryllium is approximately 9. When it is bombarded with alpha rays, the reaction is

$$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1 \qquad \text{(IV)}$$

A similar reaction was observed with boron and with lithium. With boron the reaction is

$$_5B^{11} + {}_2He^4 \rightarrow {}_7N^{14} + {}_0n^1 \qquad \text{(V)}$$

H.R. = −0.0016; estimated from velocities of particles

Being of nuclear dimensions and uncharged, the neutron passes through matter with little resistance. In air only one ionizing collision is made in several meters. Penetrating matter freely, the neutron cannot be held—presumably what free neutrons the earth may possess are concentrated near the center of this (to them) porous planet. The neutron may be considered as the chemical element of atomic number zero, with zero nuclear charge and no orbital electrons—without chemical affinity, like the noble gases to an exaggerated degree. According to our best estimate [obtained from the energy relations in Eq. (V)] the atomic weight of the neutron is 1.0067; there is still some disagreement about the exact value.

The Discovery of the Positron.—The neutron was discovered early in 1932. On August 2 of that same year C. D. Anderson at the California Institute of Technology, using a Wilson expansion chamber, obtained the remarkable photograph reproduced in Fig. 117. He was investigating cosmic rays (Chap. XXVI). The expansion chamber which he used was of large diameter and was set in the field of an extremely powerful electromagnet. The secondary emission produced by cosmic rays was supposed to consist of very high-speed electrons and protons and photons, possibly of neutrons and alpha particles. Across the center of Anderson's expansion chamber ran a lead plate 6 mm. thick. He was studying the properties of these rays in terms of their penetrating power and their curvature in the magnetic field; and on the second of August Anderson got the photograph which we have reproduced.

The track shown in this picture has all of the properties of a beta-ray track except that it curves in the wrong direction. It must have been due to a *positively* charged particle, but to a particle very much smaller in mass than a proton. It has been called the positive electron or the positron.

The crux of the argument here is the behavior of the particle as it passes through the lead plate. The very fact of its passing through 6 mm. of lead is significant, for this is no mean feat; no alpha particle or beta particle from radioactive disintegration could begin to do this. A gamma ray or a neutron might, but by its curvature this particle shows that it is charged. The curvature is greater in the upper part of the photograph, corresponding to a loss of energy in traversing the lead plate. Hence the direction of motion of the particle was evidently upward, not downward; the ray was evidently deflected to the left, not to the right, and the charge was positive. But its mass must be much

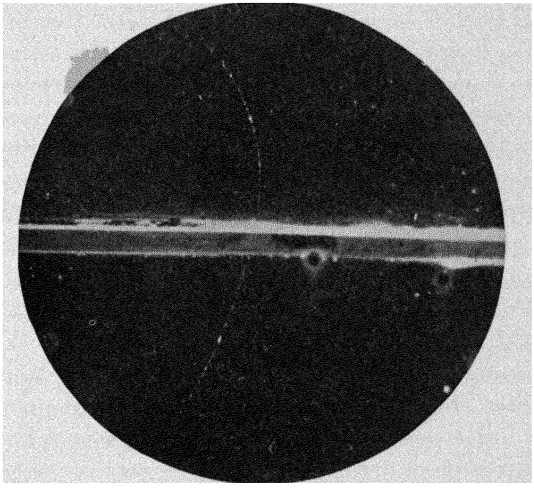


FIG. 117.—Cloud track of a positron. (*Anderson.*)

smaller than that of a proton. It would be only a comparatively slow-moving proton which could be deflected in the magnetic field as much as this ray; it would be only a proton with extremely high velocity which could pass through the lead plate. So by eliminating all other possibilities Anderson was forced to conclude that this was a positively charged particle of mass certainly not much greater than that of the electron. It seemed a justifiable hypothesis to suppose that it has the same mass as the electron. (This has been confirmed by measuring its deflection in an electric field.) The "positive electron" which registered its story in this photograph was probably released from the bottom of the chamber by the impact of cosmic rays; it had an original energy of

some 63 million *e*-volts, lost 40 million *e*-volts in passing through lead, and emerged with a residual energy of 23 million *e*-volts.

The discovery has been confirmed in the Cavendish Laboratory. In fact these positrons can be obtained at will by bombarding a lead plate with the neutrons from beryllium. They can also be obtained as a result of induced radioactivity (page 322).

Discovery of the Deuton.—No atomic weight ratio has been more carefully studied by the chemists than that between hydrogen and oxygen. With this, Aston's determination of the $H^1:O^{16}$ ratio agreed well. This was quite satisfactory until the heavier isotopes of oxygen were discovered; then it had to be explained. It was suspected that hydrogen also had a heavier isotope.

Urey, Brickwedde, and Murphy noticed a very faint satellite in the Balmer lines of hydrogen, displaced from the main lines of the series like the lines of ionized helium but not quite so far. Perhaps it was a "ghost." So they liquefied the hydrogen and subjected it to fractional distillation—and the satellite was stronger. Thus H^2 was discovered. Shortly thereafter G. N. Lewis showed that separation of the isotopes could be effected with surprising efficiency by electrolysis. Almost pure H^2 can be obtained. Bainbridge has measured it in the mass spectrograph and gives its mass as 2.0135 protols.

In the sense of having identical chemical properties, H^2 is not exactly isotopic with H^1. The possibility of electrolytic separation was mentioned. The two hydrogens have markedly different boiling points and freezing points. "Heavy water" made from the new isotope has been found to be lethal to aquatic life. Its freezing point is 4°C. The chemical difference is not unexpected, since the difference in mass gives H^1 and H^2 very different vibration frequencies and hence different energy states. The name deuterium was given to the new isotope or element. Its nucleus is called the deuton;[1] presumably it consists of a proton and a neutron; probably it plays a very important role, like that of the alpha particle, in nuclear synthesis.

The H^3 Isotope.—With the discovery of deuterium an intensive search began for another, heavier hydrogen isotope. From the converging results of three investigations it appears that such an isotope of mass 3 does indeed

[1] It is also called the *diplon* (and the element *diplogen*). There seems to be a very real objection to "deuton" in that in speech it can be confused with neutron. It is however generally used in this country.

exist in exceedingly small quantities. (1) Rutherford has reported that when deutons are bombarded with deutons such atoms are produced: $H^2 + H^2 = H^3 + H^1$. (2) The mass spectrograph has indicated the probable presence of H^3 in normal hydrogen to the extent of about one part in a billion. (3) It appears that a positive-ray discharge operated for several days in deuterium effects a transmutation into the H^3 isotope in sufficient quantity to be detected by the mass spectrograph. (If confirmed, this is the most efficient case of transmutation so far achieved.)

TABLE 53.—MASSES OF ELEMENTARY PARTICLES

Corpuscle	Mass, protols	Charge	Spin
Negative electron	0.00054	$-e$	$\frac{1}{2}\hbar$
Positron	0.00054	$+e$?	$\frac{1}{2}\hbar$?
Photon	No rest mass	0	0 or $\hbar$
Proton	1.0073	$+e$	$\frac{1}{2}\hbar$
Neutron	1.0067	0	$\frac{1}{2}\hbar$
Deuton	2.0130	$+e$	$\hbar$
Alpha particle	4.0011	$+2e$	0

Proton Guns.—New projects, new tools. As the physicist faces the future investigation of nuclear structure, he is seeking for sources of particles of greater and greater speeds. In cosmic rays he has found particles with speeds such as he can never hope to rival by artificial means; but he demands a source of high voltage and a supply of high-speed particles which is more directly under his control. He has set himself to devising gigantic super-voltage machines.

In Switzerland, voltages of several million volts have been drawn from the clouds, recalling the famous experiment of Benjamin Franklin. At the Massachusetts Institute of Technology a huge "static" machine, of simplified construction, has been erected which gives a steady potential difference of over 10 million volts. In this giant machine the observers perforce locate themselves and most of their experimental apparatus within the huge terminal knobs of the machine as being the only place in the neighborhood free from the electric field. The high-speed ions will originate in a huge discharge tube which is to be placed between the terminals. Comparatively large currents are expected; possibly as much as 10 milliamp. will be

obtained—a thousand kilowatts to be employed in a giant vacuum tube for smashing atoms!

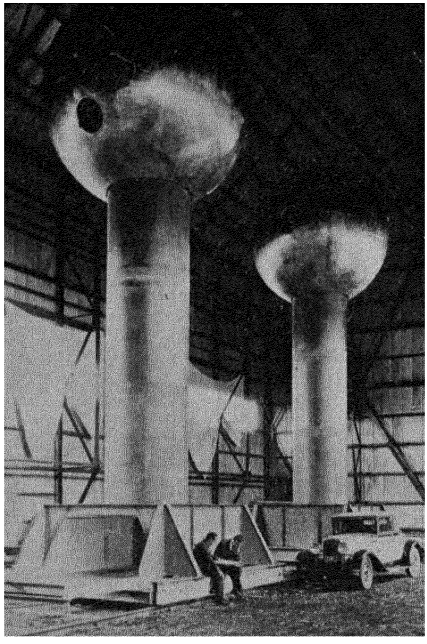


FIG. 118.—The Van de Graaf generator.

In California, Lawrence and Livingston devised a most ingenious method for the excitation of high-speed particles. It is a sling shot for protons. Protons are released between the pole pieces of a huge magnet. (The pole pieces are more than 2 ft. in diameter.) In this field a proton with constant speed would travel round and round in a circular path. But at each half revolution Lawrence adds a little to its energy, and so as it goes around it goes ever faster, in ever-enlarging circles until ultimately it is thrown from the periphery of the pole pieces.

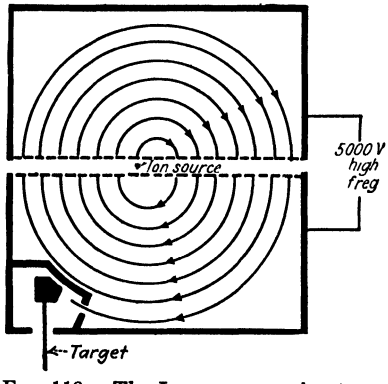


FIG. 119.—The Lawrence accelerator—the accelerating chamber (schematic).

Without employing more than 5000 volts, Lawrence has in this manner obtained 1.5 million volt protons. This involved 150 revolutions of each proton before it was released. With these protons he has succeeded in disrupting many of the lighter atoms. None of the energy in this "magnetic sling shot" comes from the magnetic field. The only function of the field is to supply the centripetal force to hold the proton in its circular path, to bring the proton back time after time for the increment of energy which it receives from the exactly timed alternations of the electric field.

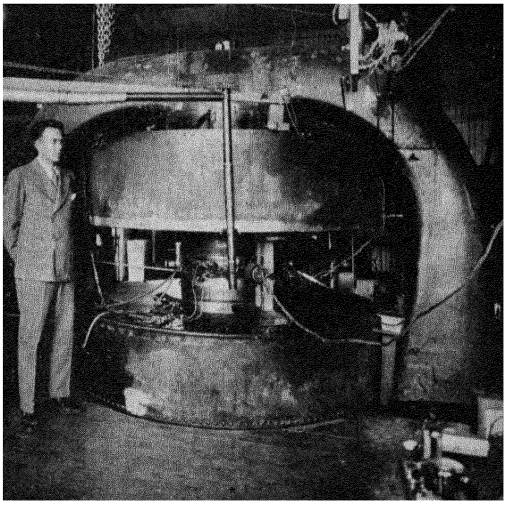


FIG. 120.—The Lawrence accelerator, showing electromagnet.

But the first of the proton guns to be brought into action was rather simpler; it used an arrangement of thermionic tubes to give potentials of several hundred thousand volts. It was devised by Cockroft and Walton in the Cavendish Laboratory. It was with this that atoms were first transmuted by proton bombardment.

Transmutation by Protons.—The year 1932 was a remarkable year in physics. It has been remarked that in this year the neutron and the positron and the deuton were discovered.

This same year saw a great development in the problem of nuclear disintegration. Rutherford had shown that all atomic nuclei lighter than potassium except H, He, Li, Be, C, and O

could be transmuted by alpha-ray bombardment. Now these modern alchemists began to use other kinds of projectiles—the proton, cosmic rays, the neutron, and the deuton. Cockroft and Walton succeeded in effecting a series of very interesting nuclear transformations by bombardment with high-speed protons. The first element tested was lithium.

Protons with a speed corresponding to several hundred thousand volts were hurled into lithium. The proton seems to have been added to the nucleus of lithium ($_3Li^7$) and the latter then broke up into two alpha particles. The nucleus was perhaps



FIG. 121.—Transmutation: Gold (the sun) dissolved by quicksilver (the green wolf). From an old alchemic emblem.

($_4Be^8$) momentarily; it then exploded into two alpha particles ($_2He^4$), each fragment with a kinetic energy of nearly 9 million *e*-volts!

$$_3Li^7 + {}_1H^1 \rightarrow 2\,{}_2He^4 \qquad \text{(VI)}$$
H.R. = 0.0180 protol

This experiment is unique in three respects. (1) For the first time the nucleus was altered by man-made electrical energy. (The transmutation mentioned on page 322 was effected by alpha particles from a radioactive element.) (2) For the first time protons were added to and alpha particles dispelled from the nucleus by bombardment. (3) For the first time the energy of the nucleus was tapped. The projected alpha particle had up to one hundred times the kinetic energy of the impinging proton.

The voltage required is remarkably low. (Disruption has been found to occur with potentials as low as 30 kv.) However, there

seems to be no immediate prospect of tapping nuclear energies for practical purposes in this way, for in these experiments, even under most advantageous conditions, not more than one proton in a hundred million made such a disruptive collision.

Similar reactions, with the addition of a proton and the release of an alpha particle, were affected for boron, fluorine, and beryl-

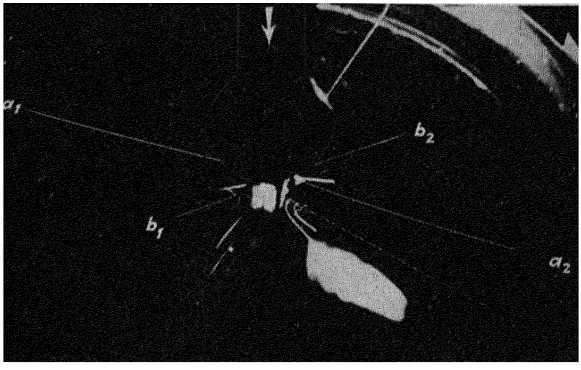


FIG. 122.—Transmutation: lithium into helium by proton and deuton bombardment. (*Dee and Walton.*) Protons and deutons projected through tube from above. Notice the pairs of tracks opposite except for slight forward motion imparted by the projectile. The longer pair a_1, a_2 has a range of 13 cm. (11.5 million e-volts) and is caused by the deuton bombardment.

$$Li^6 + H^2 \rightarrow 2He^4 + 22 \text{ million } e\text{-volts}$$

The shorter pair b_1 b_2 with range of 8.4 cm. (8.6 million *e*-volts) is presumably due to proton bombardment.

$$Li^7 + H^1 \rightarrow 2He^4 + 16.9 \text{ million } e\text{-volts}$$

lium. Deutons have also been used as projectiles. The probable reaction when deutons are hurled against lithium is

$$_3Li^6 + {}_1H^2 \rightarrow 2{}_2He^4 \qquad \text{(VII)}$$

Energy Relations in Nuclear Reactions.—When the masses of all the reacting nuclei are accurately known, the heat of reaction in a transmutation can be computed. Unless gamma radiation is given off, this liberated energy must appear as kinetic energy of the fragments of the exploded nucleus. In cases where the energies of these fragments have been found (by direct measurement of the range in air) the energy relation has been confirmed. (Incidentally this furnishes a confirmation of the relativity concept of mass and energy.)

For example, in reaction (VI) the masses of the constituents are: $_3Li^7 = 7.0146$, $_1H^1 = 1.0078$, and the mass of the resultant:

$_2He^4 = 8.0044$. The difference is 0.0018 protol or 16.8 million *e*-volts. Cockroft and Walton found the ranges of the two alpha particles in this case to be 8.4 cm. (Fig. 122), corresponding to an energy of 8.6 million *e*-volts for each of the resultant fragments—a very satisfactory agreement.

Mass of the Neutron.—The energy relations in Eq. (V) have been used to determine the mass of the neutron. Here the mass of the neutron is evidently equal to $B^{11} + He^4 - N^{14}$ plus the difference in kinetic energy of the primary alpha particle and the secondary proton. From Aston's values we have

$$B(11.0110) + He(4.0022) - N(14.0081) = 1.0051$$

Chadwick estimates that the kinetic energy of the alpha particle exceeds that of the neutron by 0.0016 protol. Hence the mass of the neutron becomes 1.0067 protols.

Induced Radioactivity.—It is difficult to keep pace with the discoveries in nuclear physics. As this book goes to press, word comes of the discovery of artificial radioactivity. We have seen that when boron is bombarded with alpha particles it is transformed into nitrogen with the release of a neutron. Positrons are also emitted under the bombardment and it is now found that this positron emission persists for a considerable time after the bombardment has stopped. The nitrogen formed is evidently an unstable element; it has a half life of 14 min. and changes into carbon. The reaction is

$$_5B^{10} + {}_2He^4 \rightarrow {}_7N^{13} + {}_0n^1 \rightarrow {}_6C^{13} + e^+ \qquad \text{(VIII)}$$

This discovery, made by the Joliots, has been confirmed in other laboratories (Cambridge, California). Other elements (magnesium and aluminum) have been shown to give similar radioactive products when bombarded with alpha rays. Radioactivity can also be induced by bombardment with protons or deutons or neutrons. Using neutrons, Fermi (in Rome) has excited radioactivity in many heavy elements—phosphorus, iron, silver, arsenic, uranium etc. For the neutron and electron this is the opposite process to that described above. Here the neutron is added to the nucleus, possibly a proton emitted, a radioactive isotope results, and after several seconds or several minutes or several hours this emits a beta ray (negatron) and transmutes into the element of next higher atomic number.

In all the instances previously cited, the proof of artificial transmutation has been found only in the rays emitted; in no case was it possible to detect the new element chemically. This the Joliots were able to do in the case of radioactive nitrogen. Immediately after the alpha-ray bombardment of boron, the activated material was subjected to a reaction which changed the nitrogen to ammonia; then this ammonia was removed. The induced radioactivity went with it. This furnishes the final test of transmutation.

So the famous problem of the alchemists has been solved. Rather different technique from stewing and brewing and magic incantations—these newer alchemists use proton guns and mathematical equations. True, we have not as yet exorcised the baseness from the grosser metals to make gold. But all of the lighter elements, except helium, have proved vulnerable. In many instances the heavy elements can be built up by neutron bombardment; there has been less success when using protons or deutons or alpha particles. We cannot manufacture gold but we have synthesized new species of atoms.

These experiments throw much light on the general constitution of the nucleus. It is composed of protons and neutrons, probably often associated into alpha particle or deuton groups. Something, but not much, is known of the energy levels within the nucleus; something, but not much, is known of the laws of physics which rule in the nucleus. In this ten-thousandth part of an angstrom do the protons and neutrons which make up the nucleus have their own energy levels? What kind of physical law reigns in this nuclear world? These are problems for the future. All we can say is that the physics of the nucleus is probably greatly different from any physics of which we know.

CHAPTER XXVI

LIGHT WAVES AND PHOTONS

Scattered x-rays have longer wave lengths—light as a corpuscle and light as a wave. Cosmic rays—are they shortest of light rays or fastest of material particles?

Collisions of Particles.—When a moving billiard ball hits a stationary one squarely, the first one stops, the second carries on. When, as in this case, the masses are equal, the momentum is merely transferred from one ball to the other. When a heavy object hits a lighter one, it continues forward after the collision. When a light object strikes a much heavier one, the latter moves forward slowly, the former, if the collision is perfectly elastic, rebounds with slightly diminished velocity. The relative change in its speed (Δv) depends on the ratio of the mass of this lighter ball (m) to that of the heavier one (M):

$$\frac{\Delta v}{v} = 2\frac{m}{M}$$

Illustrations.—(1) Suppose a boy jumps on to a stationary boat and then, equally hard, jumps back again. Suppose the mass of the boat is ten times that of the boy. Because of the velocity which his jumps have given to the boat, his return velocity will be reduced by 20 per cent. (2) When high-speed positive ions of potassium strike mercury molecules, those making direct hits rebound with a loss of two-fifths of their original speed. (Mercury is five times as heavy as potassium.) (3) When an electron makes an elastic collision with mercury (page 215), it does not retain quite all of its energy. The loss is very small; however, since the mercury atom is nearly four hundred thousand times as heavy as the electron. (4) When a neutron strikes a nitrogen atom squarely, it must rebound with six-sevenths of its original momentum.

In terms of momentum instead of velocity we may say: the impinging ball suffers a decrease in momentum (Δp) given by

$$\frac{\Delta p}{p} = 2\frac{m}{M} \qquad (38)^1$$

Proof.—This relation follows from the laws of conservation of momentum

$$mv_b = -mv_a + MV \qquad (a)$$

and of energy

$$\tfrac{1}{2}mv_b^2 = \tfrac{1}{2}mv_a^2 + \tfrac{1}{2}MV^2 \qquad (b)$$

Here v_b represents the velocity of the impinging ball before collision and $-v_a$ its velocity after collision. V is the speed given the larger ball. These equations may be written:

$$m(v_b + v_a) = MV \qquad (c)$$

$$\tfrac{1}{2}m(v_b^2 - v_a^2) = \tfrac{1}{2}MV^2 \qquad (d)$$

Dividing Eq. (*d*) by Eq. (*c*):

$$\Delta v = v_b - v_a = V \qquad (e)$$

Now since $v_b + v_a$ is nearly equal to $2v$, Eq. (*c*) gives approximately $V = m/M \cdot 2v$. Hence Eq. (*e*) gives

$$\frac{\Delta v}{v} = 2\frac{m}{M}$$

Or, in terms of momentum instead of velocity,

$$\frac{\Delta p}{p} = 2\frac{m}{M}$$

This relation holds for a direct hit. In an oblique hit the change (in magnitude) of the momentum is less, approaching zero for very glancing collisions.

Refraction of Waves.—Radio waves are best picked up when the receiving set is tuned, *i.e.*, when the natural frequency (ν_0) of the set equals the frequency (ν) of the waves. There is always a feed-back from the set into the ether. This is such as to decrease the wave length of the incident wave when $\nu < \nu_0$ and to increase it when $\nu > \nu_0$. Each of the atoms in a solid or liquid or gas acts as such a combined receiving-sending set. There are billions of billions of such reacting atoms in the material body. If the atom is attuned to the radiation, there

[1] Δp refers to the change in *magnitude* of the momentum. This is here assumed to be small. Of course, the actual change in the vector value of

is complete absorption in the medium. But in any case each atom must influence the wave length of the light. The change is only a few hundredths of 1 per cent for gases; in the solid or liquid, a thousand times denser, the effect is very considerable. The wave length of visible light is decreased 33 per cent in water, 50 or 60 per cent in glass. Usually the frequency of visible light is less than the natural frequencies of the electrons in the atoms; hence the wave lengths of light are shortened when light goes through a transparent medium. The index of refraction is usually greater than unity.[1]

Waves vs. Particles.—While Huygens was contending that light was a wave motion, Sir Isaac Newton was upholding the corpuscular theory. Where was the evidence for a wave structure? asked Newton. This was in 1700. Such was Newton's authority that he carried the day.

A century or so later Young discovered the phenomenon of interference. This was the evidence that Newton had asked for. Fresnel expanded the theory. Light is unquestionably a wave motion.

So things rested for another hundred years. Then Planck showed that light was emitted in quanta. He kept the Huygens-Young-Fresnel wave model—but these waves are emitted in bursts, in wave trains of energy $h\nu$. Einstein supported the new theory but was more radical than Planck. He considered light energy as localized in space, as a light particle transmitted from one atom here to another atom there. Light is emitted as a quantum by one atom; a quantum is later absorbed by another. This is all we really know of its history. Is not the intervening wave stage rather superfluous? Why not consider light as localized in space (*i.e.*, as a particle) at all times, as it surely is localized in space at the time of emission and of absorption?

Suppose that an atom somewhere in space radiates one single quantum of light. By the wave theory this light travels outward in all directions. After 1 sec. the energy is spread very thinly over the surface of a sphere 187,000 miles in radius. Now this quantum may be absorbed. How can all this light energy be gathered up into a single atom? This was an awkward question. Einstein considered light to be the emission of corpuscles (photons). These space-localized quanta were not, however, generally accepted until 1923.

[1] "Encyclopaedia Britannica," Vol. 14, p. 79.

The Compton Effect.—In 1923 A. H. Compton measured the recoil of an electron when struck by the individual photon.

"The Compton effect is the change in quality of a beam of x-rays when it is scattered. Imagine that a piece of paper when held between the eyes and a green light always appears green, but that when the paper is moved to a position at right angles with the light its color changes to yellow, and when turned to the opposite side from the light its color becomes red. Such a change in color would correspond to the increase in wave length which x-rays undergo when they are scattered, a small change when scattered at a small angle but a larger difference for the rays scattered at a large angle."[1]

When x-rays pass through matter, they may be either absorbed or scattered. It had generally been supposed that the scattered x-rays had the same frequency as the primary beam. Compton showed that this was not the case. The wave length of the scattered x-rays was lengthened by an amount depending upon the angle of scattering.[2]

The wave length of the K_α line of molybdenum is 0.708 angstrom. When this ray passes through a piece of graphite, it is partly scattered in every direction. Small-angle scattering shows no appreciable change in wave length. Rays at other angles have modified wave lengths as shown below:

TABLE 54.—COMPTON EFFECT: K_α LINE OF MOLYBDENUM SCATTERED FROM GRAPHITE

Scattering angle, degrees	Wave length, angstroms	$\Delta\lambda$
0	0.708	0.000
45	0.715	0.007
90	0.732	0.024
135	0.749	0.041
180	0.756	0.048

Scattering of Photons.—Compton saw in these results convincing evidence for the existence of photons. From the corpuscular point of view, scattering is the result of photons being reflected at various angles from the electrons which they strike in the medium. It is a matter of chance how these photons strike; if the collision with the electron is a glancing one, there will be only

[1] Compton, "Encyclopaedia Britannica."

[2] An unshifted line is also found. This is due to reflection of photons not from the electron as an individual but from the atom as a whole.

a slight momentum change; a more direct collision gives a larger change. In the photon this change in momentum is symbolized by a change in frequency.

Let us consider the wave-length shortening only for those x-rays which are deflected directly backward. For such directly reflected ray a wave length change of about $\frac{1}{20}$ angstrom is always found, irrespective of wave length. In this particular case of the K_α line of molybdenum the change in wave length is 6.8 per cent. A photon has energy $h\nu$, momentum $h\nu/c$, mass $h\nu/c^2$ [Eq. (3), page 18] or, in terms of wave length, hc/λ, h/λ, and $h/\lambda c$. The photons of this K_α line of molybdenum have 1,680,000 atomic ergs of energy; 5.6 atomic units of momentum, and 1.87×10^{-5} protol of mass. So the mass of this x-ray photon is about 3.4 per cent of that of the electron (5.45×10^{-4} protol).

When a photon strikes an electron, the electron gives before it[1] and the photon must rebound with a loss of momentum which for the direct collision is given by

$$\frac{\Delta p}{p} = \frac{2m}{M} \tag{38}$$

In ordinary bodies at low speeds momentum (p) changes because of a change in speed. A photon can move only with the single speed c; the momentum of a photon changes through a change in its mass or energy! Hence Eq. (38′) can be written

$$\frac{\Delta\frac{h\nu}{c}}{h\nu/c} = \frac{\Delta\nu}{\nu} = \frac{2\frac{h\nu}{c^2}}{M} \text{ or } \frac{2h\nu}{c^2M} \tag{39}$$

Inserting the values we find that the relative change in frequency for the K_α line of molybdenum is 6.8 per cent. This is in agreement with the experimental result for a direct-hitting photon.

It is not difficult to compute the effect expected for oblique collisions; the result of this computation is in exact agreement with Compton's experiment. This Compton experiment shows then that a beam of x-rays consists of a shower of particles. These strike the more loosely bound electrons in matter, sometimes striking on one side, sometimes on another, and are scattered with a loss of momentum. These particles of light differ

[1] The Compton effect is usually measured in light elements (silicon, carbon, aluminum, etc.) where the outer electrons are for present purposes practically free.

from other material particles chiefly in this: their momentum changes by a change in mass, not by a change in speed. The change in mass (and energy) is, of course, accompanied by the change in frequency. $\Delta W = \Delta h\nu$.[1]

Recoil Electrons.—Such a result required confirmation. It received this when Compton actually photographed the paths of electrons recoiling after collisions of photons. The Wilson cloud chamber revealed as small "fish tracks" the paths of these electrons propelled slowly, obliquely forward, by the collision of an x-ray photon.[2] In some cases the reflected photon would betray its direction by producing a second ion, a second fish track, in some other part of the tube. And in each case the x-ray photon went in one direction, the recoil electron in another, the exact angles quite in accord with the theory.

Could such experiments as these have been performed a few years earlier, before interference of x-rays was discovered, it would have been a serious blow to the wave theory. The intervening years, however, had securely established x-rays as being electromagnetic wave motion, like light. If x-rays acted as corpuscles, this must be interpreted as only one aspect of these rays, and one which must somehow be consistent with the other aspect of x-rays as a wave motion. How can a thing be at once a particle localized in space and a wave spread through space? This was a difficult dilemma. But it is a dilemma which must be resolved. X-rays must be recognized as being at the same time waves and particles.

X-ray Spectra from Gratings.—The best evidence for the wave nature of x-rays was obtained about this same time and Compton's name is likewise associated with this. Hitherto crystals had been used as space gratings to obtain diffraction of x-rays. In 1925 Compton showed that excellent results could be obtained from ordinary ruled diffraction gratings if the x-ray impinged upon the grating with a grazing angle of less than a half degree. The effective grating interval, the projected interval between the

[1] An interesting correspondence with the classical theory is this: The Compton shift is just that which would be obtained by the Doppler principle if the scattered radiation were emitted as a wave from the recoiling electron. This, however, leaves unexplained the random directions of these electrons.

[2] Several such tracks appear in Fig. 1*g*—not very clearly because of the reduction in size of the cut. The longer electron tracks which are conspicuous are not due to such elastic collisions but to the photoelectric effect.

rulings seen from the direction of the oncoming beam is, under these conditions, very small.

When a crystal grating was used, it was necessary to know Avogadro's number in order to compute the grating space. Compton knew the grating space of his machine-ruled gratings. He was able, computing backward, to estimate Avogadro's number, the charge on the electron, and other atomic constants. Compton's value of e is 4.804×10^{-10} e.s.u.

Refraction of X-rays.—The early investigators attempted to refract x-rays but they failed. With the more delicate technique of recent years, this refraction has been observed. It is always very small. In entering a material medium, x-ray refraction is always away from the normal! The index of refraction is less than unity and the wave length is increased in the medium! This is a consequence of the fact that x-ray frequencies are higher than the vibration frequencies of most or perhaps all of the electrons in the medium (page 335).

Siegbahn was the first to observe the refraction of x-rays. He used a prism (of metal, glass, etc.) with very obtuse refracting angle. X-rays entered and left the crystal at a very small grazing angle. The ray was bent slightly *toward* the refracting edge. The index of refraction could be found from the observed deviation.

When even smaller grazing angles were used, total reflection was observed. This total reflection for x-rays occurs when the ray *enters* the prism! In glass the critical angle for x-rays of 1 angstrom length is 10 min. The corresponding index of refraction is 0.999997.

Wave Velocity and Group (Energy) Velocity.—An index of refraction less than 1! A wave velocity greater than c! This perhaps sounds very strange. It is rather important to consider exactly what is meant by wave velocity.

A wave velocity always measures the rate of propagation of a certain configuration. It does not necessarily measure the rate of flow of any material thing. It is in general quite possible for wave *energy* to flow either faster or slower than the wave *form*.

An example is furnished by water waves. If a stone is thrown into water, a group of circular waves is sent out. Any individual wave in the group can be followed as it moves outward. The velocity of propagation of the water wave is just twice as great as the velocity of the group. The individual wave moves through

the wave group. Appearing to originate from within the circular wave group, it moves outward, at first increasing in amplitude, then as it passes beyond the main group it becomes smaller and eventually the wave becomes indistinguishable in the quiet water far beyond the wave group. The wave *form* has one velocity; the *cnergy* of the waves as represented by the wave *group* has another. Such a distinction between wave speed and group speed must always be made whenever waves of different wave lengths travel with different speeds. This is the case with water waves where the wave velocity is proportional to the square root of the wave length. This is the case for visible light traveling in a dispersive medium where the longer wave lengths travel faster than the shorter. The shorter components of blue light drag behind the longer (red) components. The wave form is constantly changing. The group velocity is different from the wave velocity.

Wave velocities may have any value. Matter, energy, wave groups, photons—these things cannot move faster than c.

The two aspects of light wave and particle are suggested by the photographs reproduced in the frontispiece. The upper pictures show characteristic interference patterns in diffracted light. Where the wave is, there we find the blackening on the photographic negative. (Figures a, b and c are positives, the white representing the presence of light.)

But when one looks at the negative more closely, the smooth continuity of the process disappears. The silver bromide emulsion is in the form of small triangular crystals. The blackening has occurred in the emulsion crystal by crystal. There tend to be more of these black developed grains where the light wave is strongest—but it is a matter of chance. If the light were so weak that in the whole plate only a single crystal developed, where would that crystal be?

We are tempted to think that this granular structure of the developed photographic negative is direct evidence for the corpuscular nature of light. Indeed it was formerly supposed that each photon which was absorbed in an emulsion grain activated it, so that on development this grain turned black. Here was apparently direct evidence for photons. In fact the case is not quite so simple. We do not get one blackened grain for each photon absorbed. Nevertheless it is certainly true for

the individual atom in the grain, if not for the silver grain as a whole, that the activation occurs photon by photon. The wave tells us only where the photons are most apt to be. This granular structure of the developed film certainly symbolizes beautifully, even if it does not prove, that in the process of absorption it is the randomly distributed photons, not the waves as such, which are absorbed.

Cosmic Radiation.—Photons become larger and the quantized nature of electromagnetic radiation becomes more pronounced as the frequency is increased. We now turn to a form of radiation the exact nature of which is not yet understood. Until recently it was supposed to be an electromagnetic wave of extraordinarily short wave length; more recent work seems to show that it is composed of material particles with energies very much greater than the fastest beta rays.

In each cubic centimeter of normal air some 10 ions are formed per second. Of these, 5 are due to radioactive emanation in the atmosphere, 2 to radium in the soil, 3 to a penetrating radiation which is known as "cosmic rays." A few centimeters of lead will screen out all of these ionizing agents except the last. Observations have been made on mountains and from balloons. Observers have ascended over eleven miles into the stratosphere and self-recording instruments have been sent even higher. It is found that this penetrating radiation increases very rapidly at higher altitudes. At an elevation of 10 miles, 300 ions are produced per second. The radiation appears to enter our atmosphere from outer space. Observations have been made at great depths in mountain lakes. The most penetrating component of the radiation was still to be detected at a depth of 250 meters. This is equivalent to a penetration of some 15 meters of lead!

Millikan has supposed the primary source of this radiation to be an electromagnetic wave. The hardness (*i.e.*, penetration) of electromagnetic rays depends on their wave length. We have noted this for x-rays and gamma rays. The definite relation is known and, the electromagnetic nature of the rays being assumed, this gives the means of measuring the wave length and frequency and hence the mass-energy of the individual cosmic ray photon. Millikan, Compton, and others have made most careful observations of the penetration. Figure 123 shows their observations of the strength of cosmic rays after passing through

the atmosphere and then through successive distances of water.

From the figure it appears that in the high-altitude measurements the negative compound-interest law is followed, at least approximately. This is shown by the approximate parallelism of the intensity curves drawn to successively different scales. But this relation soon breaks down. In passing through the atmosphere (which is equivalent to 10 meters of water) the radiation is reduced 100 fold; in 10 meters more the reduction is

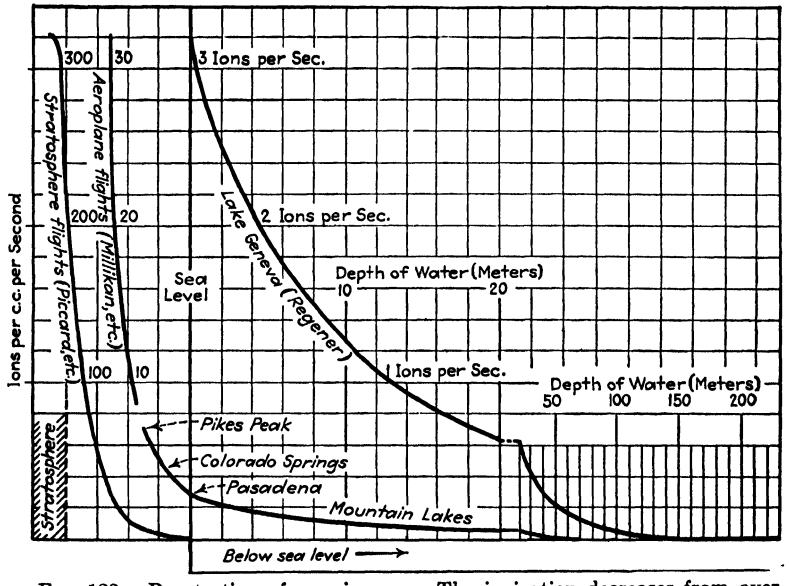


FIG. 123.—Penetration of cosmic rays The ionization decreases from over 300 ions per cubic centimeter per second at high altitudes to 10 ions per cubic centimeter per hour for deep lake measurements.

only 2 or 3 fold; in another 10 meters it is still less. This is not the compound-interest law. It was evident to Millikan that the radiation was not homogeneous. He proceeded to make a careful analysis of the curve.

Millikan found three chief components. The softest, very largely absorbed even at high altitudes, is halved by about 1 meter of water, another by 3 meters, another by 7 meters. Even the softest of these components is five times as hard as the hardest gamma ray. Regener, working at still greater depths,

found still another component which is halved by 35 meters of water. The corresponding values of the absorption coefficient (the negative "interest rate" in the compound-interest curve) are 0.80, 0.20, 0.10, and 0.020.

Origin of Cosmic Rays.—What is this cosmic radiation? Whence can come waves or particles of such transcendent energies? Observations were made on mountain peaks and in deep lakes, on land and sea, at the Equator and near the magnetic poles, in Northern Hemisphere and Southern. The rays are found at all longitudes and latitudes; they are some 15 per cent stronger near the magnetic poles than at the Equator. They have been measured night and day, winter and summer; they have been measured coming from east and from west and from north and from south. They do not come from the sun or the stars, or from the milky way; apparently they come to us in about equal numbers from all directions in empty space. If they are electrons or protons, they must have energies of some 10 billion volts. Slower charged particles could not reach the earth near the Equator; they would be turned around in their paths by the magnetic field of the earth long before they reached our atmosphere (see page 121).

If the primary rays are, as Millikan contends, electromagnetic waves, they must have wave lengths far shorter than gamma rays. From the absorption coefficients (given above) he computed the wave lengths (less than a milliangstrom) and the energy of their quanta. The softest component (coefficient 0.8) appears to have an energy of some 3×10^9 atomic ergs (30 million *e*-volts). This is equivalent to 0.03 protol of mass. Millikan attributes this to the synthesis of hydrogen into helium in interstellar space.

However, the trend of scientific opinion is toward a different view of these rays. A recent world survey of cosmic radiation organized by Compton has shown definitely a falling off in the rays in equational regions, the decrease of some 15 per cent occurring rather suddenly at magnetic latitudes of about 30°. This supports the view that the rays are charged particles (probably positrons or protons). If they are indeed material particles, they must be moving with a speed differing by less than a foot per second from the limiting velocity!

There are astronomers who hold that these particles are the dust left from some early stage in universe building.

Superspeed Ions.—Physicists are only beginning to understand exactly what these rays do. The Geiger counter is being used to detect the individual cosmic photon or cosmic charge. Most of the evidence obtained in this way seems to support the view that the rays are charged particles. But the most striking evidence is obtained by the Wilson cloud chamber.

The straight cloud tracks produced by cosmic rays can occasionally be observed in the Wilson apparatus. Anderson,

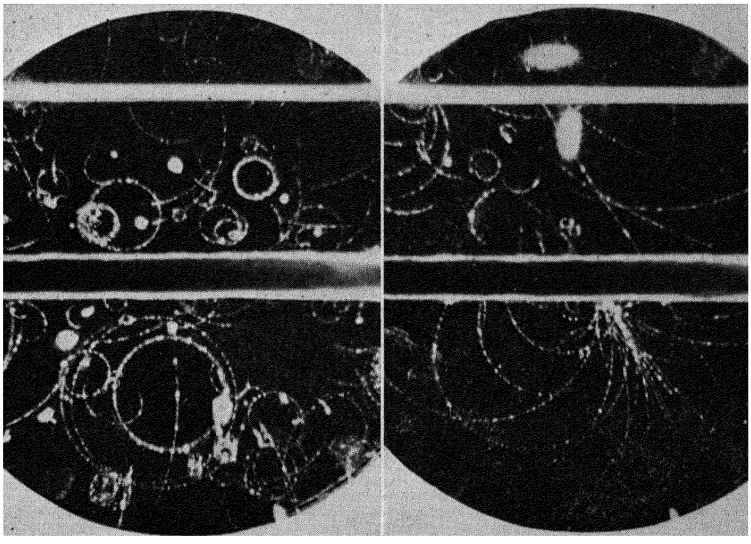


FIG. 124.—Positrons and negatrons excited by cosmic rays. (*Anderson.*) Occasionally, in "bursts," large numbers of electrons are released simultaneously; the mechanism is not well understood. The curvature of the cloud tracks is produced by a strong magnetic field. One very fast particle is illustrated which passes through the lead plate and shows no curvature in the field.

working together with Millikan, devised a powerful magnet by which these tracks could be bent. Some tracks were curved to the left, some to the right (Fig. 124). Negatrons and positrons! Some electrons (with less than a million *e*-volts of energy) were curled into small circular paths; some were bent less; for some the curvature was too small to measure with certainty. The fastest particles had velocities of several billion *e*-volts. At such speeds the mass of the electron is practically as great as that of the proton—each mass has increased enormously.

This experiment shows that much of the effect of these cosmic rays is due to charged particles of enormous energies. Some of

these electrons and protons must be secondary products; projected from space, a billion-volt electron would be turned by the earth's magnetic field so that it could not reach the earth at the Equator. The primary ray which enters our atmosphere may be the hundred-million- or billion-volt photon of Millikan or, as most physicists are coming to believe, the ten-billion-volt positron or proton of Compton. At all events passing through the atmosphere this primary ray creates secondary high-speed ions. And the ions in turn must produce short-waved radiation. Together the primary ray and the secondary ions and photons bombard us and produce the effects of the cosmic ray. Whence this energy?

Electromagnetic Energy into Charged Matter.—We have told how Anderson in his cosmic-ray experiments discovered the positron. So new is this discovery that as yet the role played in the general scheme of things by this new corpuscle has not been determined with any degree of certainty. From the present evidence it appears that the positron is created out of electromagnetic radiation!

Possibly (according to current views) a small part of the primary cosmic rays is electromagnetic; in addition secondary gamma rays are excited. When these rays, primary or secondary, pass through matter, an impinging photon may (according to this theory) separate itself into a positron and a negatron. The simultaneous production of opposite charges from the uncharged photon does not violate the law of conservation of charge. The rest mass of the two opposite electrons (0.00055 protol or about 500,000 *e*-volts each) comes from the energy of the parent photon. This corresponds to a wave length of about a hundredth angstrom and this is probably the threshold value for the production of these rays.

Positrons have been produced from the short gamma rays of ThC′. They also are emitted in induced radioactivity (page 332). But the positron has a very transitory existence. In this universe, teeming with negatrons, it is not long before it finds a mate, and positron and negatron unite to produce a gamma ray.

This is a strange page of physics which we have just begun to read. The total cosmic-ray energy which we receive is about

one-fifth as great as that received as starlight. We, situated in our favored position close to our sun, receive most of our energy as sunlight. But, by and large, in the great distances of interstellar space, it is energy radiated from stars which is rushing, as waves or as particles, through space. And if, as we are prone to believe, cosmic rays fill all space not only in our own galaxy but also in the vast spaces between the galaxies, they must be, from the cosmic viewpoint, the most important form of radiation. Yet until comparatively recently the radiation was not suspected.

As one commentator has remarked, cosmic rays are "unique for the minuteness of the phenomena, the delicacy of the observations, the adventurous excursions of the observers, the subtlety of the analysis, and the grandeur of the inferences." At the moment, with cosmic rays and neutrons and positrons thrust upon us, we feel somewhat confused—very much as our fathers did when they first heard of x-rays and Becquerel rays.

CHAPTER XXVII

THE NEW MECHANICS

A new theory—in three different languages. Energy has a period and momentum has a wave length. Why speeds of particles must be different—particularly in a crowd. Refraction of matter waves; total reflection and atoms. Experimental proof of matter waves.

The experiments of Compton, demonstrating the corpuscular nature of light, are surprising enough. Yet they can be balanced by other equally startling experiments which have demonstrated that electrons, protons, atoms, molecules—things which we have been want to consider as corpuscular—are waves. But before turning to these experiments it will be well to describe the revolution which has recently been waging in the views of theoretical physicists.

This theory of Bohr's was a proud achievement of science. Bohr discovered for us the energy levels in the atom which so exactly elucidate atomic spectra. But today the exactly defined planetary orbits which enter into his theory are taken *cum grano salis*. No one today believes implicitly in these orbits any more than Bohr and his fellows believed implicitly in the classical theory. Not implicitly. Yet there is a close correspondence between Bohr's theory and our latest views, just as Bohr found a correspondence between classical physics and his quantized physics. We now know that it is impossible to make in terms of the mechanics of daily experience a concrete model of the atom, a model faithful in each detail. The protons and electrons are not that kind of things. Of objective models Bohr's model is probably as good as we can hope for.

Defects of the Bohr Theory.—Many have been the successes of this Bohr model; we have found it unsatisfactory in the following respects:

1. It explained emission and absorption of light on the quantum theory; it left reflection and refraction and interference of light to be explained by the classical wave theory. It was sometimes alleged that the physicist believed that light was a wave motion on Monday, Wednesday, and Friday, and a shower of particles on Tuesday, Thursday, and Saturday.

2. There was only a rough correspondence between orbital frequency of the electron and the frequency of the radiated energy in the hydrogen atom (page 185).

3. Analysis of the helium atom led to wrong values for energy levels (page 195).

4. In considering the angular momentum of the orbital motion of the electron we first considered it as proportional to k (page 186), then were forced to consider it as equal to l (page 202), then in some equations (pages 233, 286) we used a cross between k and l.

And so forth. In a critical analysis this list of discrepancies could be greatly extended.

Chance and the Propagation of Electron.—We can think of a very simple ideal experiment which will illustrate directly the fundamental nature of the difficulties which face the physicist. Let us consider the motion of an electron as it passes through the slit system represented in Fig. 125. In the plate A is a narrow slit, in B are two parallel slits; C represents a detecting screen, where by scintillations or in some other manner the arrival of electrons is indicated.

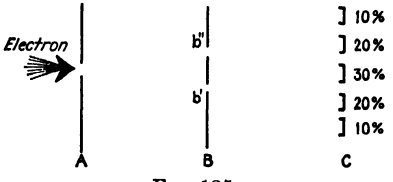


FIG. 125.

Ordinarily, in the absence of a field, an electron may be considered to travel in a straight line. *But not exactly so.* Suppose the slits are very narrow and but a few angstroms apart. Electrons are passing through A and occasionally one will also pass through B. When it does so, it will be detected on C. Now it appears to be an established fact that this electron reaches C sometimes at one place, sometimes at another—it is a matter of chance. There are more favored regions and less favored regions, in parallel strips. The percentages given in the figure are intended to represent these regions of probability (although the precise numerical values which are given have no significance; the values would depend on the speed of the electron and the spacing of the slits). Where the particle goes is a matter of chance.

Although this experiment cannot be performed exactly as described, this is the significance, reduced to simplest terms, of the experiment of Davisson and Germer which will be mentioned presently.

The two parallel slits in *B* have given this particular chance distribution. How does the electron "know" that both slits are there? Must we consider it as having passed through *both* of the slits in *B*? Perhaps. And yet we know that, had we moved the screen up very close to *B*, to detect the electron just as it passed through *B* we should have detected it with certainty passing through either the one slit or the other—certainly not at both. But then, this would have been a different experiment; had we done this, we should not have had the phenomenon described, of the strips of chance. We cannot do both experiments with the same electron; when we are measuring the diffraction, the passage through the slit is not an "observable." Under these circumstances does it have a pragmatic meaning to speak of *which* slit the electron went through?

Instead of an electron, a gas molecule or a photon would have served as well in this experiment. Indeed with photons the experiment can be readily performed and is very familiar. When (as in Young's interference experiment) we get a diffraction pattern from two parallel slits, does each photon pass through both slits?

The Matrix Mechanics.—It was to give a more self-consistent basis to quantum theory and to resolve these obvious difficulties that Heisenberg and Schroedinger and Dirac in the years 1925, 1926, and 1927 proposed their three respective forms of New Quantum Mechanics. These three systems, although on the surface appearing radically different and although they were developed by independent lines of reasoning, are in fact all equivalent. This convergence of these separate methods of attack accounts for the strong confidence which the physicist has in his new mechanics. The three systems are not, however, all equally easy to present. Take, for instance, the matrix mechanics of Heisenberg.

Heisenberg approached his theory by insisting that the physicist should deal only with "observables" in forming his models. One speaks of an electron being now here, now there, in its orbital motion in the atom, while, as a matter of fact, what one actually observes are the frequencies of the light which the atom radiates. No one could possibly perceive the electron in its rotation in its steady state; the only time the atom becomes visible to the outer world is when it changes its state. What does the radius of the atom mean? A meter means the distance

between two scratches on a standard bar. A foot or a centimeter or a millimeter each means the length of a certain bar. But what kind of a bar is it which is half an angstrom in length? Would not Einstein ask us to define our terms? Heisenberg suggested that we should describe the atom in terms of frequencies and energies rather than in centimeters and seconds.

In the Heisenberg theory, as it came to be developed, the energies of state or the frequencies of spectrum lines or other observables are listed in tabular form and these tables of numbers (or matrices as the mathematician calls them) are considered as the fundamental quantities to take the place of distance and momentum, etc. in physical formulas. Action equals momentum times distance—we might consider p and q as simple quantities

TABLE 55.—MATRIX REPRESENTING MOMENTUM IN SIMPLE HARMONIC MOTION

$$\begin{Vmatrix} 0 & \alpha & 0 & 0 & 0 \ldots \\ \alpha & 0 & \sqrt{2}\alpha & 0 & 0 \ldots \\ 0 & \sqrt{2}\alpha & 0 & \sqrt{3}\alpha & 0 \ldots \\ 0 & 0 & \sqrt{3}\alpha & 0 & 2\alpha \ldots \\ 0 & 0 & 0 & 2\alpha & 0 \ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{Vmatrix} \qquad (\alpha = \sqrt{\tfrac{1}{2}m\hbar\nu})$$

And infinitely many rows and columns

and deal with them, or perhaps as vectors with three components and deal with them. But what if we consider each quantity as a whole table of components? (And a table with an infinite number of rows and columns at that!) How shall we add and subtract and multiply and divide two tables together?

Heisenberg and his followers proceeded to develop this algebra of matrices. The result was a physics apparently in exact accord with experiment. But we cannot here attempt to present it.

The Operational Mechanics.—The most elegant form of the new mechanics is the symbolic form of Dirac. With cold logic, paucity of words, absence of analogy, with nothing superfluous, he develops the doctrine:

"We denote each state by a symbol ψ. . . . We now introduce another set of symbols ϕ_1, ϕ_2, etc., also denoting states. . . . We suppose that any ψ and ϕ have a product, in general complex. This product must always be written $\phi\psi$; that is, the ϕ must be on the left-hand side and the ψ on the right. . . . We now denote each observable by a symbol. . . . Any symbol α denoting an observable can be multiplied into any symbol ψ denoting a state giving a product which must be written $\alpha\psi$. . . . The observable is represented by a diagonal matrix whose diagonal elements are its eigenvalues. . . . We are led to the following general formula for the quantum Poisson Bracket $[\xi, \eta]$

$$\xi\eta - \eta\xi = \sqrt{-1}\, h[\xi, \eta] \cdot \cdots"$$

But this symbolic development does not lend itself to simple presentation! The frigid beauty of this theory must be reserved for the advanced student.

Wave Mechanics.—Let us turn then to the third interpretation of the New Mechanics. We now deal with waves. No longer are the electrons in the atom particles following their orbits, completely governed by the laws of Newton; instead, the motion of these particles (if particles they be) are ruled by the patterns of their standing waves.[1]

De Broglie first suggested the wave theory of matter; its development is largely due to Schroedinger. De Broglie's first theory came shortly before Heisenberg proposed the matrix mechanics and so it was the forerunner of this recent revolution in physical thought. Schroedinger's amplification of De Broglie's idea came in 1926.

De Broglie was thinking in terms of relativity. The fundamental hypothesis of the quantum theory was Planck's equation

$$\text{Energy} = h\nu$$

De Broglie observed that the same law which one observer would write as

$$W = h\nu \tag{40'}$$

another moving observer would write as

$$\text{Momentum} = \frac{h}{\lambda}$$

[1] A little consideration of the standing waves as found in a string with their nodes and antinodes, and in elastic plates with their nodal lines, and especially in elastic solids with their nodal surfaces will be useful for the appreciation of the wave mechanics.

To each body, with a certain energy W, De Broglie ascribed a Planck frequency ν. This was revolutionary—for of course Planck had applied his relation only to electromagnetic radiation. It followed then as a consequence that a body with momentum mv must have a wave length λ.

$$\lambda = \frac{h}{mv} \tag{41'}$$

And this is wave mechanics.

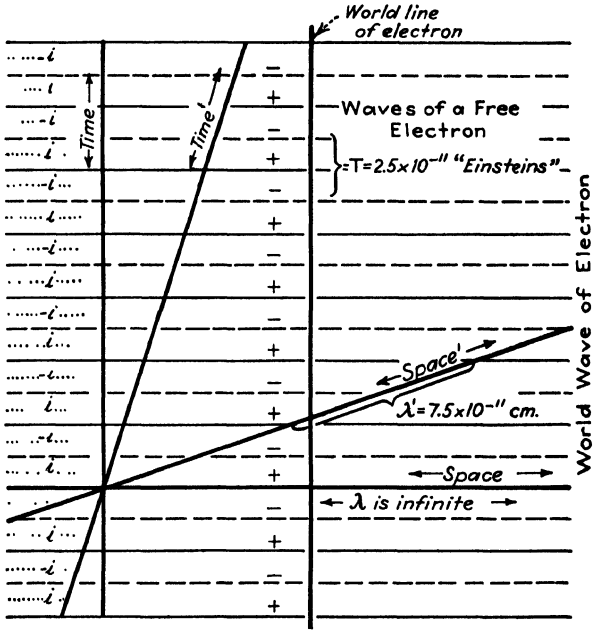


FIG. 126.—Electron as a wave and a particle. In two dimensions. As seen by stationary and moving observer (velocity $\frac{1}{3}$ c). To the stationary observer all points are alike in phase; u is infinite. The greater the velocity the shorter the wave length. The wave has an imaginary as well as a real part as is indicated at the left of the figure. (To avoid complicating the figure no correction is made for the relativity foreshortening.)

If the fundamental relation between momentum and energy is understood, this consequence follows naturally. The three components of momentum are the space components of a four-vector (page 19); its time component is mass (*i.e.*, energy). Now for the wave the wave length λ is the *distance* between points in the same phase and the period ($T = 1/\nu$) is the *time* elapsing

between recurrences of the same phase. Planck's equation may be written as

$$\text{Energy} = \frac{h}{T} \tag{40}$$

Quite clearly the analogous relation (in space instead of time) is

$$\text{Momentum} = \frac{h}{\lambda} \tag{41}$$

Wave Velocity and Particle Velocity.—It will usually be necessary to distinguish the velocity of this wave from that (v) of the particle.

The wave velocity will be represented by u. The fundamental relation in wave motion is

$$u = \frac{\lambda}{T}$$

Hence from Eqs. (40) and (41) the velocity of the De Broglie wave is

$$u = \frac{\text{energy}}{\text{momentum}} \tag{42}$$

A remarkable relation now follows. The relation between energy and mass will be recalled: Energy = mc^2. Hence for the wave velocity

$$u = \frac{c^2}{v} \text{ or } \frac{u}{c} = \frac{c}{v} \tag{43}$$

For light the velocity of the photons (v) and the velocity of the light wave (u) each equals c. For other particles v is always less than c; the velocity u of the corresponding waves is always greater than c. The wave velocity is as many times greater than the velocity of light as the particle speed is smaller. The wave of a resting particle is propagated with infinite speed.

This difference between the speed of the particle and the speed of the wave should not be confusing. In fact, in the last chapter it was shown that the energy of the wave system (the wave group) could travel at a different speed from the waves themselves. This is exactly the situation here; v, in fact, is just the velocity of the wave group as found by ordinary mechanics.

Light Waves and Photons.—In light, waves of all frequencies travel with the same speed (in a vacuum) and the group velocity is identical with the velocity of the waves themselves! Photons

and waves each have a velocity (v and u, respectively) of 187,000 miles per second. Not so in a denser optical medium.

Newton upheld the corpuscular theory of light, Huygens and later Young upheld the wave theory. Newton explained refraction of light by a speeding up of the light particles as they entered the denser medium. The photons (as we now call them) were attracted toward the medium as they approached it and (assumed Newton) the corpuscular speed v was increased in it. Δv represents the added velocity in the figure. Huygens explained refraction by the slowing down and consequent bending of the light waves as they entered the medium. This illustrates the two aspects of light. In the medium, u is less than c, v greater than c. Again in these two complementary theories we find the relation $u/c = c/v$.

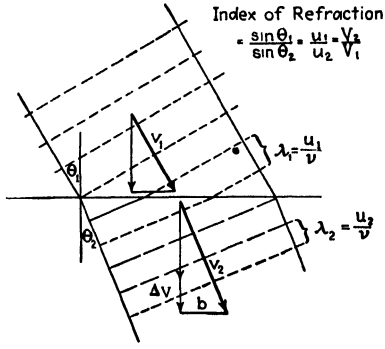


FIG. 127.

In the light of relativity we should (in applying the argument today) substitute the momentum (p_1 and p_2) for the velocity (v_1 and v_2). As it enters the medium the photon increases its momentum and the wave length is shortened in accordance with Eq. (41). (The energy of an electromagnetic wave depends on the dielectric constant of the medium.)

Waves of Chance.—Not only light but all other things appear in this dual role of particle and wave. An electron, entering a metal, attracted by the surface field, can be treated just like the photon in Fig. 127 as either wave or particle. The velocity of the particle increases; its wave length decreases. Each thing has its particle aspect with its speed v and its momentum and its energy, and each thing has its wave aspect with its wave velocity u and its wave length λ and its frequency ν.

TABLE 56

Particle		Wave
v.....	$v/c = c/u$	u
mv.....	$mv = h/\lambda$	λ
W.....	$W = h/T$ (or $h\nu$)	T (or ν)

These waves are called De Broglie waves or matter waves —but what are they? We are familiar with waves of molecules (for instance, ocean waves) and with the alternating tendency for a charge to move (radio waves) and with waves of sentiment; what are these waves of De Broglie?

Perhaps it will be well not to ask too much about these waves at present. This much can be said: where the waves are densest there these particles—photons, electrons, atoms, whatever they are—are most likely to be. None can say where a particle *will be* but it is *most apt* to be found where the De Broglie waves are most intense. Are these waves pure inventions of the mind of the physicist to help him to guess where the particles, ultimately lawless, are apt to be? The particle obeys no sharp law of motion; as rigorous laws for the electron or atom the laws of motion of Newton go into the discard; these waves tell us where the particle is apt to be. The De Broglie waves are waves of chance and the laws of chance are the ultimate laws of physics.

Matter Wave of a Molecule.—As an example consider a single hydrogen atom moving in a cubic box. Let us at first consider the atomic *particle*, since this is its aspect with which we are all most familiar. Suppose this hydrogen particle has a speed of exactly 1 km. per second—300,000 times less than the velocity of light. This molecule travels, who knows where, in that cubic box.

The corresponding wave has a velocity of 9×10^{10} km. per second (300,000 times faster than light). While the particle moves 1 mm. (in a millionth of a second), the wave travels 9×10^{4} km.—back and forth across the box many millions of times. This atom has a mass energy (W) of c^2 atomic ergs and (as a wave) it has a frequency of 22 billion vibrations per subsecond (W/h). The wave length of this matter wave is 4 angstroms (from either h/mv or u/ν). Back and forth that matter wave travels, 300,000 times faster than light, forming by the interference of direct and reflected waves a system of standing waves in the box. And where is the particle? Who knows? But somewhere amongst those standing waves. With a slight refraction due to gravity neglected, the waves are equally dense at all parts of the box; the particle is to be found as often in one position as another. This is the method of wave mechanics.

Quantized Translation.—Out of this we may draw one strange conclusion. Suppose our box is extraordinarily small, a few

angstroms on an edge. Then clearly there would be only a certain few directions in which these 4-angstrom waves could move in the box to form the stationary wave. If the box had a 2-angstrom edge, the half wave length would just cover it—the atom could move in three directions (parallel to an edge) and in no other. If the box were smaller than this, no such wave length could exist—the particle could not move with this speed! A rather impractical example. But, says this wave theory, in any containing vessel the velocities of the particles can have only certain quantized values. Discrete states in translation![1]

The effect is important, however, only when the box is very small or, equivalently, when the number of molecules in the vessel is very large. It becomes significant for hydrogen when the average distance between molecules is but a few angstroms.

The New Statistics.—Along with the new mechanics has come a New Statistics. The M-B law (page 73) states: The numbers of molecules in different states of kinetic energy or potential energy depend upon the quantity

$$\frac{1}{e^{W/\kappa T}} \qquad (8''')$$

This M-B relation is no longer regarded as true, although the corrections are usually extremely small except at high pressures and low temperatures. The New Statistics takes two forms: (1) the Bose-Einstein statistics, applicable to photons and to certain atoms and molecules (depending on the nuclear spins); (2) the Fermi-Dirac statistics, applicable to electrons and protons and in general whenever the Pauli exclusion principle is applicable. The probable distribution of individuals among the states in the two different statistical doctrines are given by

$$\frac{1}{e^{W/\kappa T} - \epsilon} \qquad \text{(B-E)}(8'''')$$

$$\frac{1}{e^{W/\kappa T} + \epsilon} \qquad \text{(F-D)}(8''''')$$

The B-E statistics applies to the "evaporation" of photons from a black body. Here ϵ equals 1; compare Eq. (16). For gases ϵ is usually very small; the M-B law is usually valid within the limits of experimentation. The most serious discrepancy is in the case of electrons in metals.

Electrons in Metals.—It has been generally supposed (page 146) that electrons move in a metal like the molecules of a gas, with Maxwell distribution of velocity, with energy $\frac{3}{2}\kappa T$, with mean velocity of 100 km. per second. Actually this must be far from the case.

[1] Of course, in a certain sense this motion (with reflexion from the walls of the box) is periodic.

Electrons moving 100 km. per second have only 0.055 unit of momentum.[1] The wave length is 70 angstroms.[2] This wave length of the electron is many times longer than the average distance between electrons in the metal!

Pauli's principle (page 278), translated to the wave mechanics, is that no two electron waves can have exactly the same length and direction. The wave of each electron must be different in length or direction. But the number of distinct standing waves of length longer than 70 angstroms which can exist in a cubic centimeter can be computed (page 154—it is only a bit more difficult than to compute the number of long standing waves which can exist on a string of given length). The number of distinct waves 70 angstroms long or longer in the cube is only 10^{18}. There are about 10^{21} free electrons in a cubic centimeter of a metal; no two electrons can be alike; and hence only one in a thousand can possibly have a speed as low as this value (100 km. per second). Without any regard to equipartition of energy or to temperature, merely because of the necessity of having

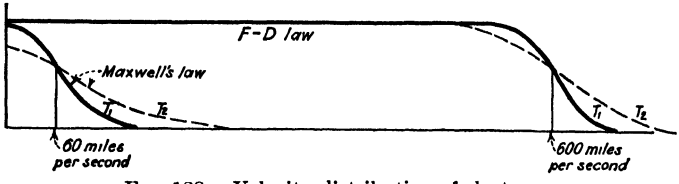


FIG. 128.—Velocity distribution of electrons.

every electron velocity (*i.e.*, every electron wave) different, the electron waves must extend down to ten times shorter lengths, the velocities must extend upward to 1000 km. per second. The electrons indeed must move with these speeds even at absolute zero.

It perhaps seems strange, this law which prevents different electrons from having exactly the same motion. In reality it is the same case as with the electrons in the atom. Only two electrons (with opposite spins) can be in the K state of the atom; similarly only two electrons, spinning oppositely, can be at rest in the metal. Both cases are examples of Pauli's exclusion principle.

This gives us a very different view of the solid state, of energy and temperature from that we have hitherto held. Absolute zero is not the temperature of zero motion. It is only the temperature of the least possible motion.

The Fermi-Dirac statistics applies and ϵ has a large value in this case of electrons in a metal. The distribution of velocities is entirely different from the Maxwell law. The speeds are almost independent of temperature. It is for this reason that the electrons do not contribute to the specific heat of a metal (page 89).

This theory of metals is due to Sommerfeld. It has been very successful in dealing with many of the most puzzling problems of electron conduction.

[1] $100 \times \frac{1}{1840}$. [2] $\frac{4}{0.055}$.

The Wave in a Force Field—Schroedinger's Wave Equation.—De Broglie dealt primarily with waves of constant velocity. Schroedinger concluded that there must be an increase in wave velocity at points in space where the potential is high. Whenever the wave velocity changes there is refraction. Schroedinger studied refraction of waves in the atom.

Consider the effect of gravity upon that same hydrogen atom in the box which was considered on page 356. We are now thinking of a very tall container, indefinitely tall. Suppose the atom has unit speed at the earth's surface. Here its total energy (W) is kinetic. Its energy ($\frac{1}{2}mv^2$) is $\frac{1}{2}$ atomic erg. Whenever it is at a higher elevation (where its potential energy is V), its speed (v) will be reduced. For its kinetic energy is $W - V$ and its momentum is given by $\sqrt{2m(W - V)}$.

The speed of the wave (u) in this case increases with altitude. Its wave length is [by Eq. (43)] given by

$$\lambda = \frac{h}{\sqrt{2m(W - V)}} \qquad (44)$$

The wave length increases and becomes infinite at that altitude where $W = V$.

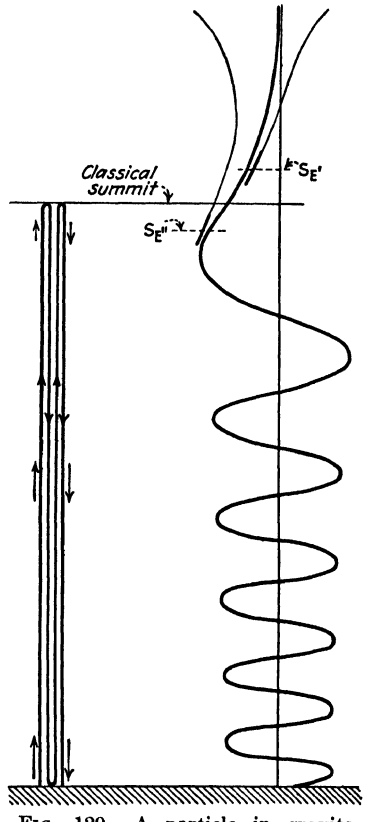


FIG. 129.—A particle in gravitational field, according to the old (ray) and the new (wave) mechanics. (Note the non-convergence for non-characteristic values of the energy.)

Although not a very practical application, this brings out the general method of the wave mechanics. Figure 129 illustrates this case of the molecule in the gravitational force field, or of a bouncing ball. Contrasted with the ordinary mechanics, in which the ball goes upward more and more slowly to a definite summit (which depends on the energy) and returns, we now have a wave of increasing wave length. There are nodes where the

ball (or molecule) is never to be found. At what, in the old mechanics, would be the summit of its orbit the wave curve is momentarily straight; above that its curvature is reversed, and unless at this point its slope is exactly right the amplitude will become infinite. Hence, since the curvature depends on the energy, only certain energies are possible. These are the "characteristic values" of the energy. It happens that these are the values which make the action a multiple of h—hence the older quantum mechanics theory.

It is to be understood that for an ordinary ball the momentum will be large, the action will be a very great multiple of h, the waves will be very short, their amplitude will fall off to zero very quickly at the classical summit, and for all practical purposes the ball follows the usual mechanics. And the value of g is too small to make this case of importance with atoms and molecules. It is in the stronger fields within the atom that the new mechanics finds its most important application.

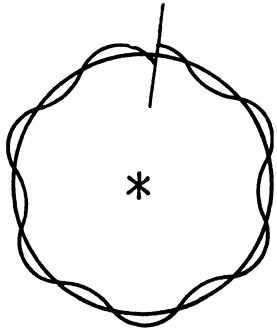


FIG. 130.

Equation (44) is substantially *Schroedinger's wave equation.* It shows how the wave length changes at different points of space. By its means the matter wave for the electron in any atom can be found.

Simple Derivation of the Quantum States of Hydrogen.—De Broglie was able to treat the circular orbits of hydrogen in a very simple manner. He imagined the wave as traveling around the orbit, refracted somehow into this circular path. The wave length here must evidently fit an exact number of times into this orbit.

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

But $\lambda = h/mv$ and hence

$$nh = 2\pi mvr$$

Exactly Bohr's quantum condition (page 179)!

Schroedinger Wave Theory.—This derivation of De Broglie roughly corresponds to Bohr's earliest theory in which the discussion was confined to circular orbits. Schroedinger attacked

the larger problem of how waves would travel in space about the nucleus.

The wave speed increases (with the rise in potential) at points distant from the nucleus. The potential energy of the electron

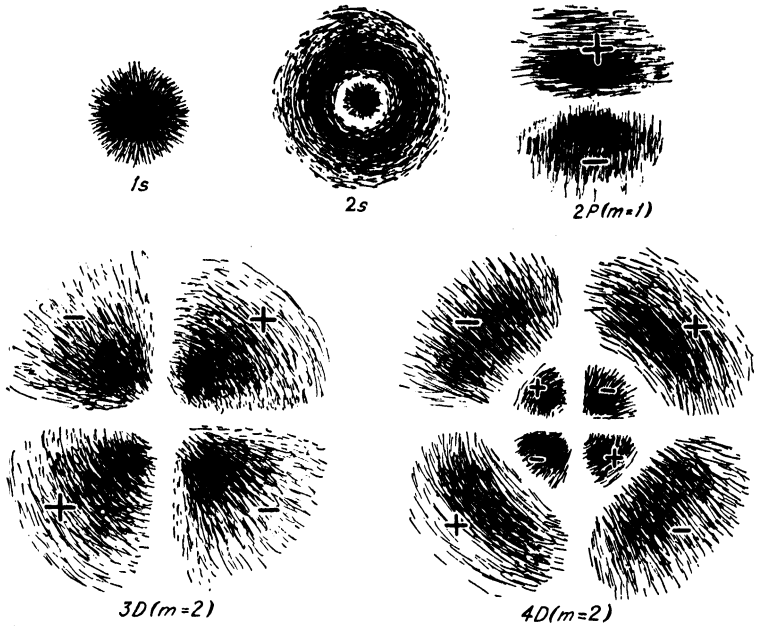


FIG. 131.—Wave patterns for states of hydrogen atom. Diagrams give only the *real* part of the wave, in the equatorial plane. (The *imaginary* part is similar but twisted so that the nodes fill in the antinodes. 90° for the *P* states, 45° for the *D* states.) Meaning of the wave: the "intensity," obtained by squaring both parts, gives the chance of finding an electron which is known to be in a certain state of energy in a certain (state of) position.

at a distance r from the nucleus is e^2/r; the wave-length equation here becomes

$$\lambda = \frac{h}{\sqrt{2m\left(W - \frac{e^2}{r}\right)}}$$

The velocity of a matter wave rises toward infinity (and ultimately becomes imaginary) as it travels farther and farther from the nucleus. A wave directed radially outward is totally reflected backward, other waves are refracted around the nucleus, in any case standing waves are set up.

Number of Nodal Surfaces Depends on Total Principal Quantum Number.—Schroedinger analyzed the possible types of standing waves which could obtain. The simplest are the *S* states in which the wave form is purely radial—the hydrogen atom like some jelly pulsing out its waves of chance radially from its center. In the normal atom (the 1*S* state) this electron wave is a single loop.

In the 2*S* state there is a nodal surface located about two angstroms from the center. In this state there are two loops of the wave. In the 3*S* state there are three loops (there are two nodal surfaces, one about 2 angstroms, one about 7 angstroms out). In addition to these there is always of course a nodal surface at infinity. With this surface at infinity, the total number of nodal surfaces equals the principal quantum number.

Angular Nodes Depend on l.—The *P* states differ from these *S* states in having the opposite sides of the atom in opposite phase. There is now a nodal surface through the atomic equator.[1] In the 2*P* state this and the surface at infinity are the only nodal surfaces. Going outward along a radial line from the center we find only a single loop. (The absence of nodal surfaces cutting the radii always means a "circular orbit" of Bohr.) In the 3*P* state there is still this oppositeness of wave displacement in opposite hemispheres but now as we go outward we find two segments. Like the 3*S* state this state has two nodal surfaces; but here only one is a sphere cutting across the radii, the other nodal surface is a plane slicing through the center. 4*P* has two spherical nodes, 5*P* has three spherical nodes, etc. In every case the *total* number of nodal surfaces equals the principal quantum number.

Nodal Surfaces and m.—In the *P* states, the atom was divided by a nodal plane into two hemispheres; in the *D* states there are two nodal planes which divide the atom into several sectors. The exact nature of the symmetry here in these *D* states depends on the *m* number. One nodal surface may pass through the 0-180° and another through the 90-270° circles of longitude, giving four sectors (first plus, next minus, etc.). The sectors are cut like the slices of a melon. (This for $m = \pm 2$.) Or the first nodal surface may go through the equator and the second transverse to this, through the poles. (This for $m = \pm 1$.) Or (for $m = 0$) the two nodal surfaces may cut

[1] We are here describing only the *real* part of the wave. The matter waves are in general *complex*, of the form (as regards the angle of longitude θ) $\sin n\theta + i \cos n\theta$ (where $i = \sqrt{-1}$). The imaginary part disappears when the wave intensity is computed.

through the lines of latitude; applying geographical terms to our atom, we can imagine one surface cutting through the Tropic of Capricorn and another through the Tropic of Cancer, giving altogether a northern polar zone, a central equatorial zone, and a southern polar zone; the wave phases will be plus-minus-plus in these three zones, then an instant later minus-plus-minus. And for the $4D$, $5D$, $6D$ orbits there will be, in addition to these nodes, 1, 2 3 nodal spheres, giving radial as well as rotational standing waves.

Electron spin is more difficult to describe in this concrete fashion. It corresponds to a rather novel kind of polarization in the wave. We shall not undertake to describe it.

Natural Frequencies and Energy Levels.—These standing waves of 1, 2, 3, 4, or more nodes represent the possible energy states of the atom with principal quantum numbers 1, 2, 3, 4, etc. Finding the energy states of the atom is hence reduced to the problem of finding the different possible types of standing waves. The quantum conditions arise naturally. All wave lengths, all frequencies, are not permissible. And those which are permissible give directly (by the quantum relation $W = h\nu$) the energies of the various atomic states.

It must be remembered that the *free* electron has a rapidly pulsating wave.[1] When the electron is bound in the lowest state of hydrogen, its wave pulsates 329 vibrations per sub-second more slowly than for the free electron. (The energy in this state is 1305 atomic ergs less than for the free electron.) For the state $n = 2$, the frequency of the wave is 247 vibrations per subsecond faster than this; when $n = 3$, 293 vibrations per subsecond faster than this. And so, as the energy becomes greater, the wave frequency approaches nearer to that of the free electron. These *differences* in frequency give to the light the frequencies actually found in the spectrum. Radiation seems to be due to the interference (called heterodyning in radio) between the electron when it is in two states at once.

Angular Momentum.—If one wishes to think of the electron as a particle, it must be as a particle whose orbit will never be exactly known. But we know the wave form, and the orbits will in general cut across the nodal surfaces. The electrons are most often to be found in places where the wave intensity is greatest. There is a certain correspondence between this wave picture and Bohr's picture. In the normal ($1S$) state of hydrogen the wave intensity is greatest at a distance of approximately ½ angstrom from the center (corresponding to the definite radius which Bohr

[1] $\nu = mc^2/h$ = 12,400,000 vibrations per subsecond.

found). In the $2P$ state the wave intensity reaches its maximum value about four times as far out. This again is in agreement with Bohr's theory.

However, in the wave mechanics each of the S states presents a state of purely radial motion. The $1S$ orbit is not a circle. The angular momentum is zero. In the P states, which are characterized by a single latitudinal or longitudinal nodal surface, the angular momentum is equal to $\hbar$, not to $2\hbar$, as in the Bohr theory. In the new theory l, not k, gives (in multiples of $\hbar$) the angular momentum. This has been shown to agree with experience and in itself would justify the new theory.

New Mechanics Agrees with Experimental Observation.—The whole atomic theory has been built up on the basis of this Schroedinger wave equation. This wave theory reproduces Bohr's results in so far as those results had been confirmed by experiment; its consequences differ from those of the Bohr theory in just those cases where the older theory was known to be wrong. Fine structure, Zeeman effect, multiplets, rotation spectra, Compton effect, Raman effect, absorption and emission and scattering and reflection and refraction processes—cases where the Bohr theory was usually only applicable in an approximate fashion, if at all—these have all been attacked successfully by the new mechanics. While the old theory found energy levels proportional to $(l + 1)^2$ for molecular rotation (and stumblingly resorted to half numbers), this theory gives the energies as proportional to $l(l + 1)$. The old theory had nothing to say of regular reflection and interference; it left that to the wave theory of light. The new theory was precisely adapted to such problems.

But for us a glimpse of this new physics must suffice. We can picture the inner structure of heavier atoms. The kernel of a heavy atom is an instrument upon which many notes are being played simultaneously. Lowest pitched (least energy) is the electron in the K levels—nodeless,[1] the single loop dropping to zero even very close to the nucleus; the electron pulses out symmetrical S-type spherical waves. Then there are the one noded[1] L waves—L_1 of the $2S$ type, spherical; L_2 and L_3 of the $2P$ type with a longitudinal or latitudinal nodal plane, the wave beating back and forth across the atom. Then the waves of two nodes, M waves of 18 kinds, and then the waves of three nodes (N; 32 kinds). The K electron has the fundamental wave;

[1] Neglecting in the description the nodal surface at infinity.

the other states give harmonic after harmonic, all nicely attuned in energy to their atom. Each feature of Bohr's theory has its counterpart here. Waves instead of orbits.

The Davisson-Germer Experiment.—The experimental physicists have succeeded in directly demonstrating the wave nature of the electron and of the molecule.

Even before the discovery of the New Mechanics, Davisson, working in the famous laboratories of the Bell Telephone Company, had been investigating the scattering of electrons from metals. It had been long known that, when an electron struck an electrode, it might be reflected or might cause the ejection of several secondary electrons (page 146). However, in his studies Davisson paid no attention to the greater part of this reverse current. He measured only the fastest of these electrons which returned from the anode, electrons returning with practically as much energy as those in the primary beam. These he considered to be the result of reflection.

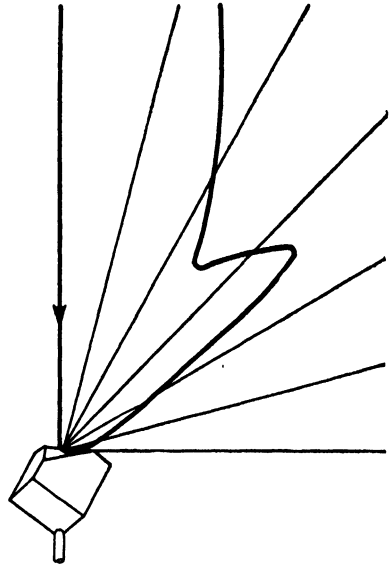


FIG. 132.—Reflection of electrons from a nickel crystal. (*Davisson and Germer.*)

In 1925 Davisson and Germer were studying the angle of scattering from single crystals of nickel. These nickel crystals had been cut so as to show a three-way symmetry (see the corner in Fig. 29). Davisson and Germer found that their electrons, shot directly at this surface, were reflected back at oblique angles and showed the three-way symmetry of the crystal.

The most pronounced reflection occurred in three planes each perpendicular to the crystal face and set at relative angles of 0, 120, 240°. And in each of these planes there were certain definite speeds of the electrons which produced the strongest reflection and for any given speed the reflected beam was strongest in certain definite directions in the plane. The reflection in one such plane is represented in Fig. 132.

In fact the scattering was almost exactly the same as would have been obtained by the constructive interference of x-rays (Laue spots in reflection). Here was concrete evidence for the wave theory of the electron.

The wave length of these matter waves was somewhat shorter than was at first expected. In Fig. 132 is shown the reflected electrons as found at different angles. These particular observations were upon 54-volt electrons. Many of the electrons are seen to be reflected almost directly backward (near 0°) but a sharper maximum occurs at a reflecting angle of 50°. In x-rays this would correspond to a wave length of 1.49 angstroms. Now a 54-volt electron has 5200 atomic ergs of energy. By the Schroedinger formula the wave length of such an electron in *free space* (where $V = 0$) is[1]

$$\lambda = \frac{h}{\sqrt{2m(W - V)}} = \frac{4}{\sqrt{\frac{2}{1840} \times 5200}} = 1.67 \text{ angstrom}$$

This calculated wave length is about 11 per cent too high. The reason for this is the retardation of the wave (acceleration of the electron) as it enters the nickel; these matter waves have an index of refraction of 1.12 in nickel. We have neglected the difference in potential energy of the electron outside and inside the metal. This value of V in the metal would seem to be a matter of some -13 *e*-volts. This does not agree with the work function as given in Table 19. Nor should it. The New Statistics give the electrons very much higher velocities in the metal and must at the same time require much greater potential differences at the surface to prevent their escape.

This experiment of Davisson and Germer is classical. It not only demonstrates the objective reality of the electron wave but demonstrates the validity of the Sommerfeld theory of metals and the New Statistics (page 358).

Diffraction of Electrons.—Higher speed electrons can be made to penetrate thin foils (Lenard rays, page 119). G. P. Thomson (son of "J. J."), Kikuchi (in Japan), and others have observed the diffraction of electrons which have passed through metal foils or thin sheets of celluloid or mica. The metal foils, with their many small crystals, give diffraction-ray patterns not unlike those observed with x-rays (page 238) or, when extremely thin mica is used, a peculiar checkerboard pattern is obtained, in which the mica apparently serves not as a space grating but as a surface grating. Thicker single crystals also give spots like Laue spots.

Thomson and Kikuchi observed these effects at voltages about a hundred fold greater than those used by Davisson and Germer.

[1] It is remembered that this equation is but a different expression for DeBroglie's equation $\lambda = h/mv$.

The wave lengths therefore were about a tenth as great and the diffraction angle is only a few degrees. In comparison with these higher energies of the primary ray, the potential energy

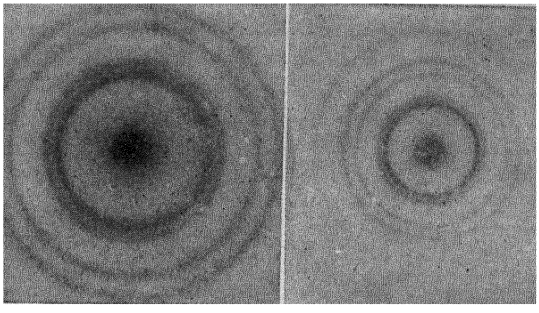


FIG. 133.—Diffraction of 13,500 and 36,500 volt electrons through gold foil. (These patterns were obtained in a student laboratory.) (*Harnwell and Livingood.*)

in the diffracting medium is almost negligible, the index of refraction for the De Broglie waves is practically 1 and the equation $\lambda = h/mv$ is very closely satisfied without correction for the increased speed of the electron in the solid.

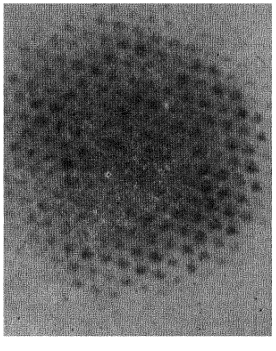


FIG. 134.—Diffraction of electrons through thin mica. (*Kikuchi.*)

Electron waves have been used to explain many physical phenomena. The Compton effect (Chap. XXVI) has been treated as the interference of the x-ray wave with the electron wave. Slow-moving electrons have abnormally long mean free paths. This is explained as due to the diffraction of the long electron waves about the molecules. The atom itself surely cannot be treated as a billiard ball, as was attempted in the earlier days of the kinetic theory (page 55). Collisions between molecules do not take place as they should between rigid spheres; small-angle collisions are most likely, molecules with high speeds (as in canal rays) have extremely long free paths. Atomic collisions must be treated as scattering of atom waves. This is most readily seen when we observe the reflection of atoms from crystal faces.

De Broglie Waves of Molecules.—The atom or molecule, considered now as a mere moving particle, has its wave. Selective reflection of molecules from crystals has been observed. Given the same energy, molecules have much greater momenta than electrons. The wave length of an average hydrogen molecule at room temperature (mass 2, velocity 1.8; $\lambda = h/mv$) is about 1 angstrom.

Stern has observed the deflection of a stream of molecules from a salt crystal. Figure 135 shows his results. Most of the molecular beam is reflected directly (the central peak) but to either

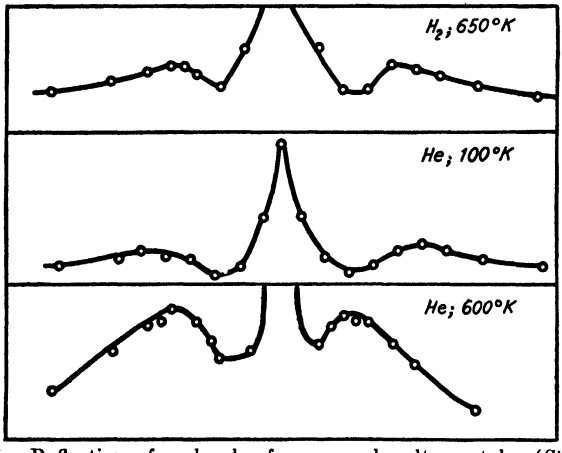


FIG. 135.—Reflection of molecules from a rock salt crystal. (*Stern.*) The peaks (broadened by velocity distribution) at either side of the directly reflected beam determine the wave length of the molecule. $\lambda = h/mv$.

side of this is a diffracted beam. This beam is not sharp because of the Maxwell distribution of velocities (wave lengths) in the beam; but these figures represent clearly the shorter wave length of helium as compared with hydrogen at 600° and show the decreasing wave length as the temperature is raised.

Whenever there is a body with momentum, there is likewise its *alter ego*, the wave with corresponding wave length. A man walking down the street presumably has a wave of length 2×10^{-25} angstrom. Not long enough to seriously discommode him by limiting his freedom of action!

The New Mechanics and the Old.—It is no longer believed that electrons move about the atom in precisely the orbits of Bohr and it is not believed that molecules in a gas go in definite paths from one collision to the next and it is no longer believed

that the electron can be described as simply a particle which repels another with a force equal to e^2/r^2. Much of the picture which has been presented must be considered only as an approximation. Yet in many cases that old picture is very satisfactory.

Just as Bohr found a correspondence between his theory and the older classical theory, so there is a correspondence between the Bohr theory and the theories of Heisenberg and Schroedinger and Dirac. Electron and nucleus still have action and reaction; we still have penetrating and nonpenetrating orbits. These orbits must be less sharply defined than before, and the language of science has become more and more of waves and states and less and less of orbits.

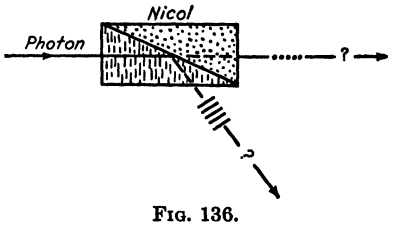


FIG. 136.

The old mechanics may be thought of as a *ray* mechanics. In optics it is often proper to think of light as a ray which goes in straight lines except when reflected or refracted. Only in the finer analysis (as when we look to diffraction) is it essential to remember the light *wave*. So it is with the old mechanics. It is often very satisfactory. But in the final analysis of the motions of electrons, photons, atoms, or any material system it is the waves, the waves of chance, which govern the motion.

Polarization of the Photon.—We may conceive of an experiment, of most fundamental nature, which illustrates admirably the ultimate reign of chance. If a polarized beam of light comes to a Nicol prism, set with its axis parallel to the plane of polarization, all the light, every photon, goes through. If the analyzer is turned through 90°, none of the light goes through. If set at 45°, half the light goes through.

Now let us weaken the light source in this last case until a single photon comes up to the analyzer. Were the analyzer set at 0°, we could be sure that the photon would go through; and if set at 90°, we could be sure that it would not. But if the analyzer is set at 45°, what can we expect? The "wave," to be sure, will be half transmitted, half absorbed, but the photon itself must as a whole either go through or not go through. Our waves tell us that the chances are even. Perhaps it is absorbed, perhaps a next one will be transmitted. Which will happen none can say. Why does one photon act differently from

another? This must always be beyond the scope of physics. Ultimately the behavior of things is based upon the waves of chance.

Dirac has used this illustration as the starting point for his quantum mechanics.

Beyond everything we find an ultimate uncertainty. Not the laws of Newton but the laws of chance are the ultimate rules in this New Mechanics. Newton said: "A free body tends to move in a straight line." The wave theory says: "Approximately so. The waves of chance, if not in too fine a beam, will travel outward as a straight ray with only a slight diffraction at the edge of the shadow." Who can say where the particle is? Where the wave is most intense, there the particle is most likely to be found.

CHAPTER XXVIII

THE NEW PHYSICS

There are more things in heaven and earth, Horatio,
Than are dreamt of in your philosophy.

We should not take too unsophisticated an attitude toward scientific truth. In interpreting nature, the scientist must erect a scaffolding of equations and models and hypotheses, yet much of this is but the instrument of his logic. The only thing that is like an atom is an atom. Studying the atom, we find, within certain limits, that it acts toward other atoms in a way analogous to that of a billiard ball toward other billiard balls. And when this comparison breaks down, we find that by considering the operations between matrices or the interference of waves we are able to calculate results which agree with atomic experiments. So, in our concise scientific formalism, we can summarize the laws of nature—read a majestic unity in all the variegated phenomena of the physical world. But one such formulation of truth does not exclude another—although the two in their externals may present a very different appearance—if both, after the scaffolding is removed, yield the same consequences in "observables." We must not confuse the scaffolding with the atomic structure.

Isomorphism.—I think we had best turn to the mathematician for simplicity. He is able to describe operations and relations with a minimum of scaffolding. He has done this in that branch of mathematics which he calls group theory. As example of a simple "group" of four operations, consider the processes: multiplication (*a*) by 1, or (*b*) by $\sqrt{-1}$, or (*c*) by -1, or (*d*) by $-\sqrt{-1}$. The first operation leaves any quantity unchanged. Multiplying by *b* twice is the same as multiplying by *c*, or by *b* four times is the same as *a*, leaving the quantity unchanged—and so for other interrelations. Another group of operations is (*a*) leaving a body unchanged, (*b*) turning it through 90°, (*c*) turning it through 180°, (*d*) turning it through 270°. This group of four operations resembles the first: applying *b* twice is the same as *c*, four times the same as *a*, and so for all other combinations. The two groups are said to be *isomorphic*.

Another instance of isomorphic groups is given below:

	First representation: Adding	Second representation: Multiplying by	Third representation: Walking
(*a*)	0	1	Not at all
(*b*)	1	2	A block
(*c*)	2	4	Two blocks
(*d*)	3	8	Three blocks
	Etc.	Etc.	Etc.

These are isomorphic groups—for *bb* is the same as *c*, *bbb* as *d*. These are not isomorphic with the first groups which we gave, for *bbb* is not *a* but *e*; indeed the latter are infinite groups. (The mathematician would like to have the reciprocal operations in the group—subtracting and dividing and walking backward—but these are omitted for simplicity.)

Now suppose that an atom is known to us in four states: *A*, *B*, *C*, *D*. Suppose that, operating on it in a certain way, we can change it from *A* to *B*; repeating that we change it to *C*, or operating again to *D* and that four operations change it again to *A*. Then we can evidently associate these states with 1, $\sqrt{-1}$, -1, and $-\sqrt{-1}$. Or, as well, we can think of it as having four rotational positions. Or perhaps it would suit our mood to give to this atom four seasons: spring, summer, fall, and winter. Each of these "theories" is isomorphic with the others; each is only a "representation" of the same *ideal group*. And the mathematician will prove, if you wish, that an infinite number of such representations are possible.

The scientist studies the infinite variety of nature's processes, acquaints himself with nature's group of operations, and then attempts to find a representation, in models or symbols, which is isomorphic therewith. "The only object," says Dirac, "of theoretical physics is to calculate results that can be compared with experiment."

The physicist has devised not one but three "different" representations which seem to be very exact interpretations of nature. Of them, the representation of Dirac would seem to have the greatest elegance because he contents himself with a description of operational groups. He introduces fewer nonessentials. We have a fourth representation in the Bohr

theory. But this is not a perfect representation, is not completely "isomorphic" with the others, not perfectly true. But we may keep it as having a correspondence with the truth. Externally, with its definite particles in definite orbits, it appears quite different from the theories of Heisenberg and of Schroedinger and of Dirac, but it is not, on the surface, more different from these theories than are they from each other. In its essentials the difference is not great; the New Quantum Mechanics puts a certain "fuzziness" into the sharp orbits of Bohr. But when we shoot a rifle at a target, I suspect that we shall continue to make out with the particle theory of matter, despite its shortcomings. The particle theory is not quite so happy in solving the problem of a photon shot at an atom. It is all a matter of degree.

If we look at a half-tone reproduction with a magnifying glass we shall see its true "quantized" structure but we are apt to lose the general outlines of the picture. In a first survey of the basic phenomena of the physical world there is a certain advantage in avoiding the precision of the New Mechanics. This is what we have done. But there is today a new physics which, in its fundamental attitudes, is very different from the old. Some of its methods have been mentioned in the last chapter. We cannot extend this exposition. We wish, however, to suggest in the following sections something of the fundamental nature of the changed point of view.

Mathematical Physics.—One is first impressed with the authority which mathematical physics has assumed in the field of atomic structure. Until recently the theoretical physicist approached the experimentalist with a high degree of humility. As the latter probed into the secrets of the atom the theorist adjusted his theories as best he could to fit the results. Today this is changed. The mathematical physicist applies his laws to collisions of electrons with atoms, to the emission of photons, to chemical reactions of molecules, with a confidence almost like that with which the engineer uses mechanics for the design of a bridge. The foundations of mathematical chemistry seem to be definitely laid.

Periodicity.—In the new physics appears a certain periodicity which was absent from the old. Energy has its frequency, and momentum its wave length. The introduction of this periodicity carries us from the older ray mechanics to the more precise wave

mechanics. This periodicity cannot but alter our elementary concepts of space and time. (Some of the early Greeks, notably Zeno, maintained that time was not a continuous thing, "smoothly flowing," but had a structure. Possibly from the new physics some such concept will emerge again.)

Atomicity.—The new physics found a wave mechanics fully developed in one field—that of light. But here has been introduced the concept of atomicity. Light is emitted and absorbed in quanta just as are electricity and other forms of matter. Photons instead of electrons, protons, and atoms. But these particles all obey the laws of chance, not of Newtonian mechanics.

Physical States.—Quantum theory has given discreteness to physical states and emphasized their importance: states of position, of momentum, and (especially) of energy. In the older mechanics the molecules were very real to us, and they had, rather incidentally, their physical states. The emphasis now seems to be rather reversed. The physical state is now first in the physicist's thought, and the molecule appears to be introduced as a label to distinguish those states which are occupied from those unoccupied. We should (in the older mechanics) have allowed several electrons in the same state (say of energy) but we should certainly not have allowed a single electron to be in two states at once. The case today is reversed. An electron may be (or, as we express it, has a chance of being) in several quantized states at once, but two electrons cannot be in the same state. Our wave patterns are simply devices to show us how particles, definitely prepared to be in a given *energy* state, are distributed (by chance) in the *positional* states. It is quite possible in this New Mechanics for an electron with a definite energy to be (in this probability sense) partly in each of two widely separated atoms, or to consider a photon as partly in each of two entirely different light beams.

This changed concept of physical state is reflected in a changed mathematics in the new physics. A system can be especially "prepared" so that any one chosen physical quantity (energy, position, momentum, angular momentum, etc.) can be expressed as a simple number (so many ergs, centimeters, etc.). But having chosen one quantity exactly in this way the others are not to be expressed as numbers but as matrices of probabilities

Boundary Transitions.—According to the older mechanics a particle in a region completely surrounded by a surface of high

potential could not escape. If the potential energy in the barrier were greater than the total energy of the particle, it could only ascend the barrier a certain distance and return—this regardless of how low the potential just beyond the barrier might be. For the kinetic energy ($\frac{1}{2}mv^2$) could not be negative; imaginary values of the velocity were not allowed.

In the New Mechanics this is changed. The wave of chance extends into these forbidden regions, although quickly decreasing in amplitude (Fig. 129). But in any case, and particularly if the barrier is thin, there is a chance of a passage through the barrier. The particle really belongs (in the sense of the preceding section) to the outside as well as the inside of the boundary. This feature of the new mechanics has had wide applicability. (1) Radioactive disintegration marks the passage of an alpha particle or an electron over one of these "forbidden" potential barriers. (2) When a field is applied to a metal surface sufficiently strong to make the outside very inviting to an electron, an electron can escape, making a surprising jump over the surface potential barrier (page 146). (3) An electron can exchange places between one atom and another; theoretically the exchange can take place at any distance, for in its energy state the electron has the same chance of being in either atom, but practically this interchanging possibility is important only at small separations. Out of this comes the *exchange force* which plays no less a roll than electrostatic forces in chemical binding. With the help of this new force the chemist may at last be said to understand the meaning of "chemical affinity" and from atomic structure he is now able to compute valence forces.

Identity of Similar Particles.—From our new point of view the molecules and atoms and electrons, reduced to counters in our consideration of occupied and unoccupied states, have lost their individuality. Since in the wave mechanics we cannot follow the motion of any single particle, we cannot follow their individual histories, and though we can observe the distribution of molecules we can never tell from moment to moment which molecule is which. Only unlike molecules can be distinguished. Molecules have no more individuality than photons. They have no more individuality than have the dollars in my bank account; they are put in as individuals and taken out as individuals, but in the interim they are only things to balance the books by.

The most striking illustration of this is found in the field of *statistical mechanics.* In tossing two coins there is one chance of a throw of two heads, one of two tails, two chances of a throw of one head and one tail. For this last combination can be obtained in two ways: either the first coin is heads and the second tails, or *vice versa.* Similarly in throwing two balls into two boxes there is one chance that both balls will be in box I, and one chance that both will be in box II, and two chances that there will be one in each. But if for balls and boxes we substitute molecules and quantum states, the chances will be 1:1:1! Because molecules are not "things" in just the sense that balls and coins are. Molecule A in the first state and B in the second are no different from B in the first and A in the second. Indeed, among these molecules there are no A and B. With unlike molecules the case would be different. AB is different from BA, but AA is not different from AA.

It was the recognition of this identity of molecules which led to the Bose-Einstein statistics (page 357). The Maxwell-Boltzmann statistics weights the probabilities of the molecules being both in (I), or both in (II), or divided, as 1:1:2. The Fermi-Dirac statistics, because it does not allow two particles to be in the same state, weights the probabilities as 0:0:1.

The Heisenberg Uncertainty Principle.—There is an essential coarseness in physical methods, a necessary bluntness in our tools. In sampling a charge we cannot take less than one electron; in probing into the atom we cannot change its action by less than h. In making one measurement we spoil our specimen for a second one. It is impossible to measure several physical quantities (as energy, position, momentum) accurately at the same time. It is this necessary inexactness that has forced us to find our ultimate laws in probabilities. It was Heisenberg who first pointed out clearly these limits which are placed upon physical observation.

It is not easy to tell exactly (or even within a hundredth of an angstrom) where a molecule is; and how tell exactly (or even within a hundredth of a subsecond) when it is there; and how tell exactly (or even within 10 meters per second) what its speed is. Now, as matter of fact, we can do each of these things separately with fair precision and there is no logical limit to the precision with which we can, with improved technique, determine either position *or* velocity. But it seems to be a *matter of logic* that we cannot obtain this high precision for both position and velocity on the same particle. Similarly we cannot determine precisely both energy and time. *There must be definite uncertainty in measurement of the product of pq (where p means momentum, q position) or of Wt. This uncertainty (at least as to order of*

magnitude) *is equal to h.* If in canal rays we succeed in measuring the velocity of a H^+ ion to within 0.1 km. per second, we shall surely not be able to determine its position at any instant more closely than some 30 or 40 angstroms. Assuming the wave nature of matter and the impossibility of splitting the primary quanta of physics (the electron, the proton, the photon, the quantum of action), this result follows from pure logic.

This is the *Heisenberg uncertainty principle.* From the wave point of view the reason for this uncertainty is readily seen. Energy means frequency, and to determine the frequency accurately we must count the waves in a considerable train (page 109). But the more extended this train of waves, the less closely defined is the position of the particle in it. Consider a hydrogen atom. Suppose we have a device to count the number of waves in 1 subsec. and find it to be 7+ (*i.e.* between 7 and 8); we then know that the energy ($h\nu$) is between 4×7 and 4×8 and know the time within a subsecond. But if we count waves for 2 subsec., we may get for this same atom 15+ (between 15 and 16). ν is between $7\frac{1}{2}$ and 8. We now know ν and energy twice as closely, but the uncertainty in time is now 2 sec. In each case the error in Wt is of the order of 4.

Another point of view may make the matter clearer. We can never determine anything about any particle without disturbing it. To find either where it is or how it moves, we must catch it, as on a photographic plate, or send against it another particle—atom, electron, photon—and watch the effect of the impact. This alters the very thing which we are measuring. To detect *position* accurately we might use gamma rays,[1] the shorter the better, but these heavy photons in their Compton impacts would hopelessly disturb the *status quo* of momentum. To measure *momentum* accurately it would be well to observe with infra-red radiation, the longer the better. These long waves would produce only slight disturbances in the velocity which we wish to measure. But such rays, bending around the atom, would tell us almost nothing of its position.

Illustrations of the Uncertainty Principle. *a. Linear Velocity of Light.*—We know the velocity of light with greatest accuracy. We know that photons are in the beam but as to just where along

[1] Because the resolution of any optical instrument is greater with shorter wave lengths.

the light beam each photon is we know nothing. For the necessary error of momentum times position is of the order of h.

b. Direction of Ejection of Photon.—When an atom emits light, we know that the velocity of the photon will be exactly radial (transverse momentum exactly zero)—and we know exactly nothing as to the exact direction in which the photon will go. We know exactly the shape and speed of the wave front but nothing at all as to where in the spherical wave—east, west, north, south—the photon will be. Here we have infinite precision in momentum, zero precision in position. Again the necessary error of momentum times position is of the order of h.

c. Most instructive is the case of light converged by a lens. The larger the lens (if it is perfect), the sharper the focus (page 109). With a large lens we can tell with little uncertainty where the photon will strike, but we know little as to the direction in which it has traveled, nothing as to from what part of the lens the photon came. Diaphragm down the lens and the direction of travel becomes more closely defined—but we ruin our focus. Owing to dispersion we know less exactly where the photon will strike. For the necessary error of momentum times position is of the order of h.

Electron Orbits.—As with light so with other particles, either position or momentum can be determined very accurately or, if we prefer, each can be measured fairly accurately but the uncertainty as to *action* will be of the order of h.

We need not now be too chagrined at the failure of our Bohr model. It attempted too much. It attempted to define precisely the orbits of the electrons in the atom and to give precisely their velocity and momentum. Actually we know approximately but not exactly both the position and the momentum of the electron.

It is the energy states of the atom which we know. We do know with greatest precision the exact energy W of these electron states in the atom—perhaps to a ten-thousandth part of an atomic erg—but exactly when the electron enters, when it leaves this state, this we cannot know within 10,000 subsec. For the necessary error of energy times time is of the order of h.

The Uncertainty Principle and Philosophic Thought.—This principle has provoked a large amount of philosophic discussion. This is because of the bearing which it has upon the question of free will.

I do not remember whether, in those rather naive days before 1925, we physicists really thought that, by continued increase of precision, we should ever be able so exactly to corner an electron or a molecule that we should be able to predict exactly what it would do. Certainly we were wont to say: "Cause and effect! Tell me where the molecules are and how they move today and I will predict their where and their how for tomorrow and for all time to come." It was a safe proposition (and quite meaningless) since no one was apt to accept our challenge. We do not say this today. The Heisenberg uncertainty principle has shown definitely the limits which are forever set to human perception.

Standing here upon the bounds of the unknowable the physicist begins to philosophize. The strict rules of causality seem to have dissolved. Too long philosophers have toyed with the idea of man the machine, a creature whose future is "predestined" by the past. "Knowing absolutely the past we can predict absolutely the future." Give me the impossible and I will return to you the more impossible! It should have required no wave mechanics to discredit this point of view.

The uncertainty principle is looked upon by some as giving us back "free will," moral responsibility, a meaning to life, souls, heaven and hell; it is looked upon as redeeming life from the domination of science. Could anything be less realistic! To imagine that any one experiment on an atom, the turn of the galvanometer to right instead of left, could have any connection, direct enough to read by you and me, with man's immortal soul! If we can find no meaning for life in our eating and sleeping and loving and fighting and yearning and attaining, and none in spring and summer and winter, in sun and moon and stars, or in men past and present, good, bad, and indifferent, then there is nothing that galvanometers and square roots and atomic models can do to give meaning to it.

The impact which the new mechanics has made upon philosophic thought has been very great indeed. It has emphasized as never before a lesson which has often recurred in the history of human thought: we must not give objective reality to subjective concepts.

It is a proud epic, this story of science. It is a story of straight seeing, honest thinking, and a vast deal of aspiration; some

success. In everything we have found a great law, in everything a great oneness. We have pushed back the bounds of the unknown. And twice, once far beyond the telescope, once far beyond the microscope, we have stood before the unknowable.

We must stand here and wonder.

TABLE 57.—C.G.S. AND ATOMIC UNITS
(Divide the number of c.g.s. units by ratio to get atomic units)

Name and dimensions		Ratio to c.g.s. units
Proton (p)	Mass	1.650×10^{-24}
Angstrom (A)	Distance	10^{-8}
Subsecond (s)	Time	10^{-13}
A/s, kilometer per second	Velocity	10^{5}
$p \cdot A^2$	Moment of inertia	1.650×10^{-40}
$p \cdot A/s^2$, atomic dyne	Force	1.650×10^{-6}
$p \cdot A^2/s^2$, atomic erg	Energy	1.650×10^{-14}
$p \cdot A^3/$	Action	1.650×10^{-27}
$A/s \cdot \sqrt{pA}$	Charge	1.285×10^{-11}
$1/s \cdot \sqrt{pA}$	Electric potential[1]	1.285×10^{-3}
$A^2/s \cdot \sqrt{pA}$	Magnetic moment	1.285×10^{-19}
$\frac{1}{As}\sqrt{pA}$	Magnetic field	128,500

[1] 1 volt = $1/_{300}$ e.s.u. = 2.6 atomic units of potential.

IMPORTANT PHYSICAL CONSTANTS

C.g.s. units		Atomic units	
2.998×10^{10}	c (velocity of light)	2.998×10^{5}	(3×10^{5})*
6.55×10^{-27}	h(quantum of action)	3.97	(4)*
1.37×10^{-16}	k(Boltzmann's constant)	0.00831	($1/_{120}$)*
4.77×10^{-10}	e(charge on electron)	37.1	(37)*
9.01×10^{-28}	m(mass of electron)	0.000546	($1/_{1830}$)*
9.20×10^{-21}	μ(Bohr magneton)	0.0716	($1/_{14}$)*
109737.4	R(Rydberg constant)	328.963	(329)*
1.591×10^{-12}	Electron-volt	96.4	(96)*

* Approximation closer than 1 per cent.

REFERENCES FOR COLLATERAL READING

This is a list of books some of which should be read collaterally with the text. They vary from the extremely popular to those which may well serve as an introduction to advanced study. Encyclopedia references are included as being universally available. A more formal bibliography will be found in some of the references.

General References

JAUNCEY, G.: "Modern Physics," Van Nostrand.

Physics Staff, University of Pittsburgh: "Atomic Physics," Wiley.

RICHTMYER, F. K.: "Introduction to Modern Physics," McGraw-Hill.

HARNWELL and LIVINGOOD: "Experimental Atomic Physics," McGraw-Hill.

DARROW, K. K.: "Introduction to Contemporary Physics," Van Nostrand.

DARROW, K. K.: Series of articles on "Contemporary Advances in Physics," in *Bell Tech. Jour.*

Chapters I and II

EDDINGTON, A. S.: "Nature of the Physical World," Macmillan. A charming, popular interpretation of physical ideas, especially those relating to relativity.

EINSTEIN, A.: "Relativity," Peter Smith.
A popular presentation. The book sold into the hundred thousands in Germany.

BRIDGMAN, P. W.: "The Logic of Modern Physics," Macmillan.

RICE, J.: "Relativity," Longmans. A good introduction to more advanced study.

"Encyclopaedia Britannica."
Relativity (Jeans).
Space and Time (Einstein).

Chapters III to VI

MEYER, O. E.: "Kinetic Theory of Gases," Longmans.
Written at a time when the simple kinetic theory was exciting. Presents the simpler facts in a thorough manner and with little mathematics.

PERRIN, B.: "Atoms," Van Nostrand.

BRAGG, W. H.: "Concerning the Nature of Things," Harper. Popular.

LOEB, L. B.: "Kinetic Theory of Gases," McGraw-Hill.
Introduction to mathematical theory.

"Encyclopaedia Britannica."
Kinetic Theory of Matter (Jeans).
Brownian Motion (Perrin).
Solid State (Lindemann)

Surface Tension (Thin Films) (Porter).
Motion Picture Films (with sound).
Molecular Theory of Matter, 1 reel, University of Chicago Press.
Oil Films on Water (Langmuir), 5 reels, General Electric Company.

Chapter VII

BROWN, J. CAMPBELL: "History of Chemistry," Blakiston's.
"Encyclopaedia Britannica."
Periodic Law (Main Smith).
Atomic Weights (Richards).
Chemistry, History (Dixon).
Also the lives of chemists.

Chapter VIII

"Encyclopaedia Britannica."
Radiation (Andrade).

Chapters IX to XI

CROWTHER, J. A.: "Electrons, Ions and Ionizing Radiation," Longmans.
MILLIKAN, R. A.: "The Electron," University of Chicago.
KOLLER, L. R.: "The Physics of Electron Tubes," McGraw-Hill.
HOAG, J. B.: "Electron Physics," Van Nostrand.
DARROW, K. K.: "Electrical Phenomena in Gases," Williams & Wilkins.
"Encyclopaedia Britannica."
Electricity, Conduction of, in Gases (Thomson).
Electron (Millikan).

Chapter XII

Read something of the lives of physicists, past and present. The Nobel prize winners are covered by "Encyclopaedia Britannica."
CHASE, C. T.: "A History of Experimental Physics," Van Nostrand.
RICHTMYER, F. K.: "Introduction to Modern Physics," McGraw-Hill.

Chapter XIII

REICHE, F.: "Quantum Theory," Dutton.
RICHTMYER: (see above).

Chapters XIV to XVI

SOMMERFELD, A.: "Atomic Structure and Spectrum Lines," Dutton. Chaps. IV and VI.
ANDRADE, E.: "The Structure of the Atom," Harcourt, Brace. Chap. VIII, The Magneton.
RUARK and UREY: "Atoms, Molecules and Quanta," McGraw-Hill.
GROTRIAN, W.: "Graphische Darstellung der Spektren," Vol. II, Springer. This being a graphical representation of spectra, there will be no language difficulty. Some familiarity with either this or the following references is recommended as giving concrete illustrations of spectroscopy.
PASCHEN-GÖTZE: "Seriengesetze der Linienspektren," Springer.
"International Critical Tables," Vol. V, pp. 392 *ff.* McGraw-Hill.

"Encyclopaedia Britannica."
Spectroscopy (Fowler).
Spectrograms in this reference must be consulted while reading Chap. XIV. The reference also supplements the text by treating of spectroscopic apparatus and methods.

Chapter XVII

FOOTE and MOHLER: "Origin of Spectra," Chemical Catalogue.
SOMMERFELD: (see above).
ANDRADE: (see above).
RUARK and UREY: (see above).
Chap. XIII, Collisions of Second Kind. Chap. XIV.
Original articles might well be read in this field, for instance:
FOOTE and MOHLER: Ionization and Resonance Potentials in Vapors of Magnesium and Thorium, *Phil. Mag.*, Vol. 37, p. 33, 1919.
FOARD: Electron Energy Losses in Mercury Vapor, *Phys. Rev.*, Vol. 35, p. 1185, 1930.
SMYTHE: Ionization of Nitrogen by Electron Impact, *Proc. Roy. Soc.*, Vol. 104, p. 121, 1923.

Chapter XVIII

GERLACH, W.: "Matter, Electricity, Energy," Van Nostrand. Chap. VIII, The Magneton.
"Encyclopaedia Britannica."
Zeeman Effect (Darwin).

Chapters XIX to XXII

ANDRADE: (see above).
SOMMERFELD, A.: (see above).
Chap. III.
BRAGG, W. H., and W. L. BRAGG: "X-rays and Crystal Structure," Bell.
SIEGBAHN, M.: "Spectroscopy of X-rays," Oxford University.
COMPTON, A. H.: "X-rays and Electrons," Van Nostrand.
CLARKE, G. L.: "Applied X-rays," McGraw-Hill.
For those interested in x-ray practice.
RUARK and UREY: (see above).
Chaps. VIII and IX.
"Encyclopaedia Britannica."
Spectroscopy, X-ray (Siegbahn).
X-rays (Bragg).
Atom (Bohr).

Chapter XXIII

SOMMERFELD: (see above).
Chap. VII. Gives a fuller discussion of band spectra.
KOHLRAUSCH, K. W.: "Der Smekal-Raman Effect," Springer.
For those interested in Raman effect and chemical forces. No equivalent work in English.
"Encyclopaedia Britannica."
Band Spectra (Curtis).

Chapters XXIV to XXV

RUTHERFORD, CHADWICK, and ELLIS: "Radiations from Radioactive Substances," Macmillan.

SODDY, F.: "Interpretation of Radium," Putnam.
Popular account of elementary phenomena.

ASTON, F. W.: "Mass-Spectra and Isotopes," Longmans.

FEATHER, N.: Collision of Neutrons with Nitrogen Nuclei, *Proc. Roy. Soc.*, Vol. 136, p. 709, 1932.

BAINBRIDGE, K. T.: Atomic Masses and Structure of Atomic Nuclei, *Jour. Franklin Inst.*, Vol. 215, p. 509.

DARROW, K. K.: Contemporary Advances in Physics, XXVI, The Nucleus, *Bell Tech. Jour.*, July, 1933.

"Encyclopaedia Britannica."
Radioactivity (Rutherford).
Nucleus (Andrade).

Chapter XXVI

COMPTON, A. H.: "X-rays and Electrons," Van Nostrand.

"Encyclopaedia Britannica."
Compton Effect (Compton).

Chapters XXVII to XXVIII

DARWIN, C. Y.: "Recent Developments in Atomic Theory," Oxford University.

JEANS, J. H.: "The New Background of Science," Macmillan.

SWANN, W. F. G.: "The Architecture of the Universe," Macmillan.

SLATER and FRANK: "Introduction to Theoretical Physics," McGraw-Hill.
Gives the mathematical background for the new mechanics.

FRENKEL, J.: "Wave Mechanics," Clarendon.

QUESTIONS

Chapter I

1. Where in the space-time diagram would the following events lie (*a*) The printing of my copy of yesterday's *New York Times.* (*b*) The printing of today's copy of the *New Orleans Picayune;* suppose the printing occurs at the present moment.

Could either of the following be properly maintained: (*a*) The *New York Times* which I am reading was printed yesterday exactly where I am now. (*b*) This *New York Times* which I am reading today will be printed in New York tomorrow?

2. If two battleships are traveling parallel so as to be without relative motion, must this motion be allowed for when one ship opens fire on the other?

3. How many einsteins or centimeters is the separation between the two ends of a meter stick? Between two ticks of a clock? A beam of light which I see left the sun (150 million kilometers away) 500 sec. ago. Show that the leaving the sun and the arrival here are not "separated" events.

4. Does the world return to the same place in space after the lapse of a year?

5. Perhaps all things, the earth and stars, you and I, and meter sticks are a hundred times smaller today than yesterday. Who could tell? What do you think of this suggestion? What do you mean by the size of a thing? Is the proposition (*a*) possible, (*b*) meaningless, (*c*) a contradiction of terms?

6. How much will a 1-gm. bullet traveling 500 meters per second increase in mass because of its motion?

7. A swimming pool is $10 \times 5 \times 2$ meters. Hence it contains 1000 by 500 by 200 cc. (or gm.) of water. Suppose it is heated 100°C., how many grams does it gain in weight? (1 cal. is equal to 42 million ergs.)

Chapter II

1. What is meant by distance and by a straight line? If we made meter sticks of rubber instead of steel, would it affect the meaning of straight line? Why do we not use rubber meter sticks?

2. If a person continues to travel in a straight line, may he eventually return to his starting point or could you be sure he would not do so without trying the experiment?

3. It has been said that the Copernican system with the revolving earth is not more true than the Ptolemaic system where sun and stars moved about the earth. It is only vastly simpler. What do you think of this point of view?

4. The area of Iowa is 150 billion square meters. How much radiant mass is received from the sun per second? What is the total force of this radiation pressure? (Get the force as the rate of change of momentum.)

5. Will the gravitational attraction cause the star image to appear nearer to or farther from the sun?

Chapter III

1. Show why the atomic weights 8 for oxygen, 4⅔ for nitrogen, and 3 for carbon fitted Dalton's theory as well as the correct values.

2. Prove that, if 1 volume of chlorine and 1 volume of hydrogen unite to form 2 volumes of hydrochloric acid, hydrogen and chlorine must each be diatomic.

3. Find the weight of the gram molecule of each of the gases listed in Table 2.

4. How many of the earlier elements differ from whole numbers by 0.1? Is this relation probable as a matter of chance?

5. How much kinetic energy is possessed by a cubic centimeter of nitrogen? Of hydrogen?[1] Does this depend upon the temperature? Explain.

6. What will happen to ρ and to v in Eq. (5) if the pressure is doubled by compressing the gas without changing the temperature?

7. What is the mean speed of helium and of nitrogen molecules? (Helium is a monatomic, nitrogen a diatomic molecule.)

8. How does the velocity of sound in air compare with the speeds of the molecules?

9. Find how fast water molecules travel at the boiling point.

10. Find the kinetic energy of a single molecule of the air at room temperature, 300° abs. How much energy would a hydrogen molecule and a mercury molecule have at this same temperature?

11. If the diameter of the capillary is 1 mm. and of the bulb is 400 cc. (in a McLeod gage), what is the ratio of compression when the gas is compressed to a column only 2 mm. long? Supposing the column in a is 2 mm. higher, *i.e.*, even with the top of the closed tube, compute the original pressure in millimeters.

12. Compare a pressure of 0.001 mm. and 1 bar.

13. How many molecules are there per cubic centimeter at 1 bar pressure? Suppose the residual gas is air, what will be the mean free path?

Chapter IV

Use *atomic units* in the following problems.

1. What is the weight of a mercury atom; of an alcohol molecule (C_2H_6O); of hexacontane ($C_{60}H_{122}$); of Perrin's smallest particle (page 65); of a gram weight?

2. What is the volume of a cubic centimeter? What is the density of water in protols per cubic angstrom? What is the wave length of yellow light (six ten-thousandths of a millimeter).

3. How many subseconds in an "einstein"? How far would a bullet traveling with a speed of 1 km. per second go in a subsecond?

4. Find the atomic unit of acceleration and the value of g in atomic units.

[1] Use standard conditions of pressure and temperature except when otherwise specified.

5. What is the kinetic energy of a helium molecule traveling 1 km. per second? What is the average kinetic energy of translation of any gas molecule at 300°C.? How much rotational energy for a diatomic molecule?

6. In the glucose molecule ($C_6H_{12}O_6$) the six C are in a straight chain 1.5 angstroms apart, H and O almost evenly distributed along the chain. Find its moment of inertia and the angular velocity. (I for a rod of length L about its center is $\frac{1}{12}mL^2$).

7. Estimate from the D-P law the specific heat of copper, silver, and tungsten. The specific heat of beryllium is 0.425; does it obey the D-P law?

8. How fast did Perrin's smallest particles move?

9. Perrin with his microscope could detect only rotations in the horizontal plane (about a vertical axis). How much would the actually observed average rotational energy be?

Chapter V

1. What proportion of the molecules of hydrogen are going 2 miles a second or faster?

2. How would the velocity scale in Fig. 26 be changed to have it apply to oxygen?

3. Using Eq. (8′), compare the number of hydrogen molecules at 300° abs. (27°C.) moving upward with a speed of 0, 1, 2, km. per second.

4. Using the Boltzmann law, find the expression for the relative numbers of water molecules per cubic centimeter in the vapor and liquid states at the boiling point. Use the value of P.E. from Table 7. (The Boltzmann law cannot, however, be directly applied to such cases without further considerations which are beyond the scope of this book.)

5. At what height would an atmosphere of the smallest of Perrin's particles (mass 7.2 billion protols, page 65) drop to half pressure? [Note that the exponent in Boltzmann's formula must equal -0.7. When the particle is in an emulsion, only that part of the weight which is not supported by the water is effective. In this case ($\rho = 1.1$) the effective weight is $\frac{1}{11}\,mg$. The value of g in atomic units is 9.8×10^{20}.]

Chapter VI

1. You have 1 gm. of carbon dioxide. Its temperature is 21.5° and its volume is 2 cc. Describe it further (Fig. 27).

2. The volume of the substance in problem 1 is (*a*) increased isothermally to 6 cc.; then (*b*) at constant volume the pressure is raised to 90 atm., then (*c*) at constant pressure the volume is decreased to 0.8 cc.; then (*d*) the pressure is lowered to 60 cc., and then (*e*) the volume increased its original value. Describe how these processes can be carried out. Trace this out on the PV diagram. Is it possible to specify the substance at all times as either "liquid" or "gas"?

3. Find the boiling points of familiar substances from Fig. 28.

4. The electrons appear to be the most important agents in conducting heat in a metal. One end of a copper rod is in steam, the other in ice. Describe the process of heat transfer.

Chapter VII

1. Show instances in Dalton's table (*a*) of incorrect valence, (*b*) of incorrect chemical analysis, (*c*) of mistaking compounds for elements. What is azote? What do his Figs. 22, 23, 28, and 29 represent? What do you think of his analysis of alcohol (Fig. 33)?

2. In what instances is the order of ascending atomic weights violated in Mendeleef's table?

3. In Fig. 93 x-ray lines of rhodium are shown but traces of ruthenium lines also appear. In Fig. 87 along with the cobalt lines appear lines of iron and nickel. Why?

4. What are the chemical properties of radium? Of masurium?

Chapter VIII

1. Make a table giving for the different parts of the spectrum: (*a*) wave-length range, (*b*) frequency, (*c*) means of production, (*d*) of detection, (*e*) absorption in common substances, and (*f*) principal properties.

2. Some think of an electron as nothing but the beginning of lines of force which spread out to infinity in all directions. Does it seem plausible that such lines of force should be in equilibrium when the electron is moving steadily but that a disturbance of the wave should travel out the lines of force when the electron is suddenly started or stopped? (Electromagnetic theory of light.)

Chapter IX

Charge on electron $= 4.77 \times 10^{-10}$ e.s.u. or 37.1 atomic units

1 coulomb or 1 amp. $= 10^{-1}$ e.m.u. $= 3 \times 10^{9}$ e.s.u.

1 atomic unit of charge $= 1.28 \times 10^{-11}$ e.s.u.

1 volt $= \frac{1}{300}$ e.s.u. $= 2.6$ atomic units

1. One thousand ions per cubic centimeter in air, 10 ions formed per second, how long does the average ion remain uncombined?

2. Ten ions per second in a cubic centimeter, what is the chance of some particular air molecule becoming ionized during the next year?

3. What is the chance that some chosen molecule will collide with an ion in the air; *i.e.*, with how many ions will it probably collide in a second or in a year?

4. Why should you expect the mean free path of an electron in a gas to be greater than that of a gas molecule? Why are two opposite ions much more apt to combine than two chosen air molecules are to collide?

5. Two condenser plates in air are 2 cm. apart; area 100 sq. cm. How many ions are between them and how many new ones are formed per second? How large a steady current can be caused to flow between them?

6. If the potential difference on these plates is 100 volts, what is the strength of the field? How long before the original ions are swept out? Are the ions constantly accelerated in this field? Explain.

7. What is the force on an electron placed between these plates and how much work is done as it goes from one plate to the other?

8. If the field in problem 6 were removed, would the number of ions in the air quickly return to the original value? Draw curve showing the change in the number as a function of time.

9. An electrometer has a sensitivity of 10,000 divisions per volt. Its capacity is 20 micromicrofarads. How many electrons are required to give 1 mm. deflection?

10. A Geissler discharge tube carries 1 milliamp. How many electrons pass a given place in the tube in 1 subsec.?

Work the following problems using electrostatic units.

11. How much work is done for each electron carried from one plate to another in a dry cell? (1.5 volts c.m.f.).

12. The normal cathode fall in hydrogen (platinum electrode) is 300 volts; what speed has an electron in the cathode glow? Also compute the speed of an H_2 ion as it strikes the cathode.

13. Find the kinetic energy and speed for an electron corresponding to 1 volt; 100 volts.

14. Find the force acting on an electron as it moves across a magnetic field of 1280 gauss with a speed of 6000 km. per second.

15. Suppose 10 coulombs (1 e.m.u. or 3×10^{10} e.s.u.) of electricity move with a speed of 1 cm. per second (as the drift of electrons in a wire) across a magnetic field of 1 gauss. What will be the force?

16. Work problems 11, 12, 13, 14 using atomic units.

Chapter X

VELOCITY OF FALL OF OIL DROPLETS
($\rho = 0.85$)

Weight of drop, grams $\times 10^{-12}$	Radius, microns	Velocity of fall, millimeters per second	Corrected velocity of fall
0.46	0.5	0.025	0.029
3.7	1.0	0.1	0.108
29.6	2.0	0.4	0.416

1. Check the value of velocity of fall for the 0.001-mm. drop. Viscosity of air: 0.000185 at 24°C. (NOTE.—The corrected velocity is computed using a slight correction to Stokes law.)

2. A student performing the oil-drop experiment finds the rate of fall of his drop 0.108 mm. per second. With an electric field of 1150 volts per centimeter he finds the drop rising with a speed of 0.108, 0.216, 0.108, 0.054, and (just balanced) 0. How many electrons did the drop hold in each case?

3. Take the case of the balanced drop in problem 2, (*a*) what is its weight (in dynes); (*b*) compute the charge on the drop; (*c*) compute the charge on the electron.

4. An ink mark has a resistance of 10^{10} ohms. If a difference of potential of 1 volt is applied to it, how many electrons will traverse it in a second?

5. Find the force between two electrons 1 angstrom apart. (Use atomic units.)

6. A cross-magnetic field of 5 gauss and cross-electric field of 150 volts per centimeter exactly balance each other in their effect on a cathode ray. What is its speed?

7. What will be the radius of curvature of the ray path in problem 6 due to either field separately?

8. In problem 6 how far does the electron go in 10^{-7} sec. and through what angle (in radius) will it be turned in that time?

Chapter XI

1. What is the speed of an electron as it reaches the plate of a radio tube if the plate is 25 volts higher in potential than the filament? If a current of 0.01 amp. (3×10^7 e.s.u.) flows, how much heat will be released at the plate per second?

2. Positive ions are often set free when a salt is heated. If a potassium ion (mass 40 protols) is released, what velocity will be given it by a potential difference of 100 volts?

3. At what potential must the grid be maintained in a rectifying tube? In an amplifier? Does it depend on the plate potential?

Chapter XIII

1. How much energy is radiated per second from a black surface (area 2 sq. cm.) at 1500° abs.? What is the predominant wave length?

2. What is the value of the quantum of energy for the green line of mercury (Fig. 48)? Assuming Einstein's theory, what would be the mass of a photon of this light? What would be its momentum?

3. What would be the slope of the curve (Fig. 48) if it were plotted in c.g.s. units?

4. A certain incandescent lamp gives out visible energy at the rate of 1 watt (10^7 ergs per second). Supposing that the average visible wave length is 6000 angstroms (yellow), how many of these visible photons are emitted per second?

5. State the three experimental facts which are mentioned in this chapter which demand the quantum theory.

6. From Table 19 compute the threshold frequency of caesium.

Chapter XIV

1. Find the frequency in c.g.s. and atomic units of the $H\alpha$ line of hydrogen.

$\lambda = 6563$ angstroms

2. Find the approximate wave lengths of the mercury lines used by Millikan (Fig. 48).

3. Compute the wave length of the fourth line of the Lyman series.

4. What is the greatest percentage difference between theoretical and observed lines in the Balmer series?

5. From Table 26 find the wave lengths of the first few lines of the principal and sharp series of sodium (compare with Fig. 52).

6. What two series in alkalis have a common limit, and why?

7. Does the defect for sodium ever change (as n increases) by more than 1 per cent?

8. Estimate the value of the $5S$ term of sodium.

Chapter XV

1. Compute the radius of the normal orbit, the velocity and frequency of the electron in its rotation, and the energy in the normal orbit of hydrogen and of ionized helium.

2. With the hydrogen considered as a solar system, how long is a "year" for the planetary electron? Kepler's law is that the periods of the planets are proportional to the three-halves power of their orbital radii; show that this holds for the orbits of hydrogen.

3. Draw an energy-level diagram for ionized helium. Indicate the transitions which will give practically the frequencies of the Balmer series.

4. Compute several wave lengths and the limit for the series of shortest wave lengths of He^+. What is the ionizing potential of He^+?

5. Draw a diagram of elliptical orbits showing all the possible transitions which contribute to $H\alpha$. (It will be shown that k can change only by ± 1. Omit all transitions from your diagram representing changes of k of 0 or 2.)

6. Under ordinary conditions the Lyman series, but not the Balmer, Paschen, or Brackett series, of lines can be obtained as absorption spectra. Why? The Balmer lines appear in the solar absorption spectrum, which proves what?

7. What is the least value (other than zero) which the angular action of a hydrogen atom can assume? What is the least value (other than zero) of the angular momentum? (Give in both atomic and c.g.s. units.)

Chapter XVI

1. Neglect the penetration of orbits and draw a simple diagram (as Fig. 56 or 57) indicating sodium orbits, giving energies (Table 26).

2. How many e-volts must an electron have to displace an electron in sodium to the $2P$ orbit? How much to ionize it? (Fig. 61.)

3. Estimate from Fig. 61 the frequency of the first lines of the principal series and of the sharp series of sodium (compare with Fig. 52).

4. In Fig. 61 three transitions are shown between the $3D$ and the $2P$ levels. What are these transitions? (Indicate as $2^2P_{1/2} - 3^2D_{3/2}$, etc.)

5. What are the frequencies of the following mercury lines: $2^3P_2 - 3^3D_1$; $2^3P_2 - 3^3D_2$; $2^3P_2 - 3^3D_3$; $2^3P_2 - 4^3D_3$; $1^1S_0 - 2^3P_1$?

6. By what letters are the following series represented in Fig. 68? Singlets: principal, sharp, diffuse. Triplets: sharp, diffuse. Combination: sharp, diffuse.

7. Which are the five most probable transitions in mercury (see Fig. 68)?

8. What kind of multiplicity is found in the spectrum of thallium, in Al^+?

9. From the data in the "International Critical Tables" (Vol. V, pp. 392 *ff.*) plot the energy-level diagram of some element. (Potassium or cadmium may be compared with sodium and mercury of text. Helium is perhaps most interesting with its singlets and doublets which latter are really triplets; there is a selection principle here which prevents combination series.)

Chapter XVII

1. Draw the ionization and inelastic collision curves as they would appear for sodium vapor.

2. Suppose the cell on P (Fig. 66) were reversed. How would the curves of Fig. 67 look?

3. How much energy must an electron have to strip helium of both its electrons?

4. What color will the single-line spectrum of potassium be?

5. Sodium heated in a flame gives the yellow lines (λ5890, λ5896) and no others. Why?

6. What voltage is necessary to excite the familiar green line of mercury ($2^3P_2 - 2^3S_1$)?

Chapter XVIII

1. How strong are the poles of a bar magnet 10 cm. long, magnetic moment 100? What is the magnetic moment of a circular loop of wire of 10 cm. radius, carrying a current of 5 amp. ($\frac{1}{2}$ e.m.u.)?

2. What is the mechanical and magnetic moment of the hydrogen atom (neglecting spin) in the $1S$, $2S$, $2P$ states?

3. Express 1 gauss in atomic units. What is the highest rate of precession attainable? If an electron is vibrating (*a*) parallel to the field, (*b*) normal to the field, how will the magnetic field affect it?

4. A mercury atom remains in the excited 2^3P_1 state for 10^{-7} sec. If it is in a field of 1.2 gauss, through how many degrees will it precess in that time?

5. What is the total magnetic moment of a sodium atom in the $1^2S_{\frac{1}{2}}$ state? Suppose sodium vapor of such a density that there are 10^{-17} atoms per cubic centimeter. What is the maximum magnetic moment attainable (when all atoms rotate in the same sense)? Reduce to c.g.s. units.

6. What positions can a mercury atom in the 2^3D_3 state assume in the magnetic field? What are the values of m? What is the value of the magnetic energy when the atom is parallel to a field of $\frac{1}{3}$ atomic unit?

7. What are the possible values of m if j is $\frac{1}{2}$; 1; $\frac{3}{2}$?

8. Draw the energy-level diagram for the Zeeman effect of the mercury line $1^1S_0 - 2^1P_1$.

9. Find the values of g and draw the energy-level diagram for the Zeeman effect in the mercury lines (*a*) $1^1S_0 - 2^3P_1$ and (*b*) $2^3P_1 - 3^3D_2$.

Chapter XIX

1. A soap film is 5000 angstroms thick. What color light will be reflected from it at a glancing angle of 30°?

2. Compute the wave length and frequency of an x-ray beam which is reflected with a glancing angle of 30° from calcite; at an angle of 5°.

3. The $K\alpha$ line of tungsten (λ = 0.20 angstrom) is reflected at an angle of 8° 40′ from a cleavage face of NaF. Compute the crystal spacing.

Chapter XX

1. Find the wave lengths of the $K\alpha$ lines of the elements shown in Fig. 88. The crystal used was calcite with a grating space of 3.028 angstroms.

2. Using the Moseley law, estimate the wave length of the $K\alpha$ line of uranium.

3. Compare the slope of the $K\alpha$ curve in Fig. 89 with the theoretical value.

Chapter XXI

1. What is the shortest wave length obtainable in a medical tube operating at 200 kv.?

2. What voltage is necessary to excite the $K\alpha$ line of tungsten? Figure 93 was obtained with a calcite crystal. Compute the limiting frequency obtained at 40 kv. and check with theory. Also compute the wave lengths of the characteristic K lines of rhodium.

3. Filters are often used to produce monochromatic x-rays. Suppose a piece of ruthenium is interposed between the tube and ionization chamber in the experiment illustrated in Fig. 93. Indicate in drawing how the 40-kv. curve would be modified.

4. In optics a given frequency is frequently absorbed and later reemitted. Can this happen in x-rays? Does Stokes' rule (page 108) hold?

5. Compare the absorption limits of silver and rhodium (Figs. 93 and 95).

6. What potential is required to excite the $M \rightarrow L_3$ lines of silver?

Chapter XXII

1. What is the wave length of the $L\beta$ line of uranium? What is the mass of this photon?

2. Draw the possible transitions between N and M levels (uranium).

3. What potential is necessary to excite the complete L radiation of uranium?

4. Name three orbits which have an orbital momentum of $\hbar$ and a total angular momentum of $1\frac{1}{2}\hbar$.

5. At which elements do the most pronounced (*a*) downward, (*b*) upward breaks occur in Fig. 98? Why?

6. Make a table showing the placing of the electrons in each of the chemical elements.

7. In Fig. 69 in addition to the major peaks occurring at 2, 10, etc., minor peaks occur at elements 4, 12, 20, etc. Can you explain this?

8. The Pauli exclusion principle forbids a 1^3S_1 state in mercury. Why is a 2^3S_1 state possible?

Chapter XXIII

1. From the data in Table 8 compute the energies in the lowest quantum states of oxygen and hydrochloric acid. How many of these states are apt to be excited at room temperature? (Take the center of mass as midway between the oxygen atoms and as in the chlorine atom. Is this latter exactly justified?)

2. How much force is required to stretch the hydrochloric acid molecule by 0.1 angstrom?

3. Compare the proportionality between energy and quantum number in (*a*) the electron in the hydrogen atom, (*b*) the angular motion of a molecule, and (*c*) the vibrational motion of a molecule.

4. Explain why light of frequency 3.3 is absorbed by hydrochloric acid vapor (Fig. 103).

5. Compare the stiffness of the binding in carbon tetrachloride and tin tetrachloride.

Chapter XXIV

1. What proportion of radium emanation will be extant after two weeks?

2. A wire has been given a fresh deposit of radium *A*. Plot a curve showing emission of beta rays as a function of time.

3. How much radium *D* and radon will be in equilibrium with 1 gm. of radium? How long after fresh radium is prepared before equilibrium is established?

4. Will freshly purified uranium contain U II?

5. How many alpha particles will be emitted during the life of a gram of radium?

Chapter XXV

1. Assuming the weight of radium exactly 226 gm., find the exact weight of radon. (Velocity of alpha particle from radium is $\frac{1}{20}$ *c*.)

2. What is the heat of reaction of $4He^4 \rightarrow O^{16}$?

3. Taking the mass of the neutron as 1.0067, find (Table 52) the reaction heat of B^{10} + neutron $\rightarrow B^{11}$.

Chapter XXVI

1. What proportion of its speed does a neutron lose when it makes a direct hit (elastic) with the nitrogen nucleus?

2. What is the wave length of a photon the mass of which is as great as that of an electron?

3. In what respects does the Compton effect differ from the Raman effect?

Chapter XXVII

1. What is the speed of propagation of the matter wave of an alpha particle (speed $\frac{1}{20}$ *c*); of an air molecule (speed 500 meters per second)?

2. What is the wave length of an average air molecule; of an electron going 100 km. per second?

NOBEL PRIZES

The Swedish scientist Alfred B. Nobel, inventor of dynamite, died on Dec. 10, 1896, bequeathing $9,000,000, the interest of which should yearly be distributed to those who had mostly contributed to the benefit of mankind in the fields of physics, chemistry, medicine, literature, and peace. The physics and chemistry awards are made by the Swedish Academy of Science. The prizes are worth some $40,000 each. Below are given the awards in physics and a few in chemistry together with the page references.

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Four Americans are represented: Michelson, Millikan, Compton, and Langmuir.

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