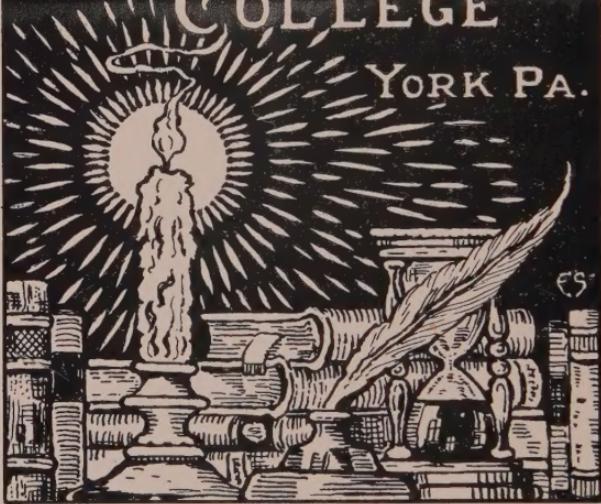




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# **THE INTERPRETATION OF THE ATOM**

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# THE INTERPRETATION OF THE ATOM

By

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NOBEL LAUREATE IN CHEMISTRY, 1921

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## PREFACE

This book has been written to take the place of *The Interpretation of Radium*, first published in 1909, the fourth edition of which has long been out of print. Like the earlier work, it is intended primarily for the general reader interested in the great advances in our knowledge of the nature of matter and the structure of the atom, which date from the discovery of the X-rays in 1895, of radioactivity in 1896, and the recognition of the electron in 1897. But it is hoped it may be helpful as a guide to the scientific student, both those who are commencing their studies and those whose main work lies in other fields and to all interested in the progress of atomic chemistry and the synthesis of the new with the older body of knowledge.

The fundamental reconstruction of our outlook upon the world of matter, energy, space and time which is now being attempted, mainly as a consequence of the successes of the theory of relativity, seems to neglect the ordinary phenomena of Nature in favour of the exceptional. It has not yet succeeded in giving us any consistent or complete mental picture in place of the older and more mechanical views. In this exposition these purely symbolic and physically meaningless conceptions enter only so far as they are unavoidable. The objective is rather the interpretation of the ordinary properties of matter which the new views singularly fail to account for.

Part I., *The Radioactive Elements and Isotopes*, deals fully and systematically with the remarkable series of spontaneous disintegrations of the atom which were recognised first by Professor Rutherford and myself in Montreal in 1902 to be the cause of all the varied phenomena of radioactivity, and which later, from 1907 to 1913, revealed the hitherto completely unsuspected existence of the different types of atoms of the same chemical element which are chemically *identical*, and which in 1913 I christened "isotopes."

Part II., *The General Progress of Atomic Chemistry*, deals with the wider application of these fundamental discoveries,

and of the conceptions of quanta, relativity and wave-mechanics, to the chemistry of the atom. Theories of spectra have their due place, but along with those dealing with electrolytes, chemical affinity, valency, the Periodic Law and molecular architecture. The recent work on the atomic nucleus and the modern form of Prout's hypothesis, as a consequence of Aston's Whole-Number Rule, and a chapter on cognate geological and astronomical aspects and the new cosmical radiation conclude the volume.

In the twenty-three years which have now elapsed since the earlier work first appeared, great changes have taken place in the public's attitude towards and appreciation of new scientific discoveries. The complete failure of the older inherited ideas and philosophies to account for the modern world and its problems is turning men more and more to the study of the facts of Nature. The study of the inanimate universe, as the study most difficult for man to distort and the most dangerous for him to neglect, is becoming recognised as the most human of all studies. But even it may be "sicklied o'er with the pale cast of thought."

Personally I more and more come to regard the purely formal and mathematical presentation of physical theories as a disguise and evasion of the real problems rather than as any solution of them. I have tried, in other fields, to show the incredible confusions, of which the whole world is now one seething example, that have followed from the invention by the Hindu mathematicians of negative quantities, and their justification from their analogy to debt. So that naturally I am not among those who can bow down and worship the square-root of minus one.

The real student, it seems to me, has little use for such short-circuits. They compel him in fact to extra labour in thinking things out anew right from the beginning, whatever he tries to comprehend, and they condemn him to eternal vigilance if he is to escape from the cobwebs with which the human mind seems ever trying to enmesh itself. It is to such this book is offered, whether to those in the wide sense, seeking an escape from the futilities of the past, or to those in the narrower academic sense, upon whom the rapid march of progress bears most hardly, expected as they are to inform their examiners

about all sorts of recent advances which very few as yet have had time to ponder over and try to understand.

I have to express my grateful thanks for the uniform courtesy with which authors and publishers have ungrudgingly allowed me to borrow numerous illustrations from their books, and my detailed acknowledgments for these are made at the end of the List of Illustrations.

FREDERICK SODDY.

OXFORD,  
*April, 1932.*



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**PART I**

**THE RADIOACTIVE ELEMENTS AND ISOTOPES**



## CHAPTER I

### THE DISCOVERY OF RADIOACTIVITY

**X-rays and Phosphorescence.**—The science of radioactivity began in 1896 with the discovery of M. Henri Becquerel, in Paris, that certain compounds of the element uranium emit rays of the same general type as the X-rays which Röntgen had discovered the year previously. The X-rays were a new type of radiation which is emitted when an electric discharge is sent through a highly exhausted vessel. It is capable of traversing objects opaque to ordinary light, such as thin sheets of metal, and of darkening the photographic plate when completely protected from light by opaque envelopes.

At first the real origin of the X-rays was not known, but it was observed that one of the conditions attending their production was a greatly enhanced fluorescence of the glass walls of the vacuum tube. This, we know now, was due to the invisible X-rays striking the walls and causing the glass to fluoresce. The important condition for the generation of the X-rays is that the vacuum must be sufficiently good, and Röntgen's success was probably due to his using a better vacuum than at the time was readily obtainable. The connection between the X-rays and the fluorescence of the tube, however, was the basis of a suggestion by M. Henri Poincaré, that it would be worth while to examine the rays from ordinary fluorescent and phosphorescent substances, in order to see whether any rays were produced by them similar in nature to the X-rays. Such rays were therefore deliberately looked for by Becquerel in the light emitted by these substances, a subject in which he, as his father and grandfather before him, had specialised.

It was his good fortune that, among the phosphorescent and fluorescent substances which he examined, he included some of the compounds of uranium. The element uranium is the last in the list of elements, arranged in accordance with the Periodic Classification, in order of atomic weight,

It thus possesses the heaviest and presumably the most complex atom known.

The phosphorescent substances, well known from their application to the manufacture of luminous paint, change the character of the light incident upon them to a different wave-length or colour. This secondary light persists after the extinction of the exciting cause, causing the substances to shine in the dark with characteristic colours. Fluorescence is essentially similar, but in this case the secondary luminosity does not persist long enough to be separately observed without special appliances, but it mixes with the primary and gives the illuminated substance a peculiar "fluorescent" glow. As good an illustration of fluorescence as any is afforded by the X-rays themselves, and by the rays given by the more powerful radioactive substances. All these rays are quite invisible to the eye, but they are made visible by causing them to fall on certain fluorescent substances. Barium platino-cyanide, which gives a bright green fluorescence, is the one most commonly used. A piece of card-board covered with a layer of crystals of this substance, protected by a coat of varnish, constitutes the ordinary X-ray screen, which is equally well suited for showing the penetrating rays of radium.

**Discovery of Radioactivity.**—In Becquerel's original experiment, a tray of thin metal containing one of the fluorescent uranium compounds was laid on the film side of a photographic plate enclosed in a black paper envelope, and the whole was exposed to bright sunlight for a considerable period. The plate after development was found to be fogged beneath the tray containing the fluorescent substance, which was thus shown to be emitting rays capable, like the X-rays, of traversing a sheet of metal. But one day, the sun being obscured, the experiment after having been got ready was set aside in the dark to await a more favourable occasion, and left for some weeks. Something induced Becquerel to develop the plate without its having been exposed to sunshine at all, and he was surprised to find that the action had gone on in the dark just as much as it did in full sunshine.



FIG. 1.—M. BECQUEREL'S ORIGINAL URANIUM PICTURE.

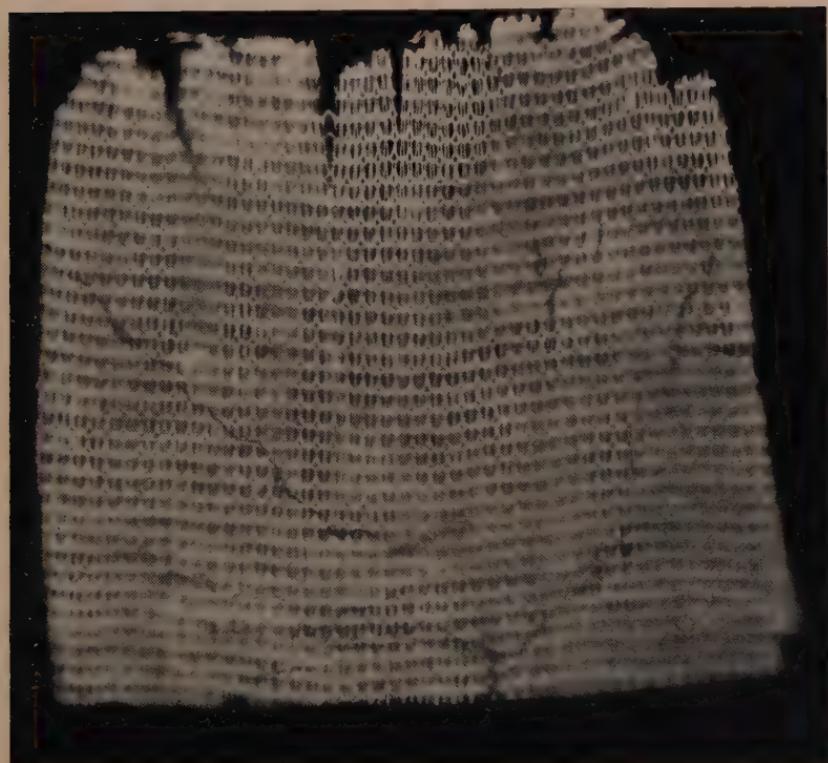


FIG. 2.—WELSBACH MANTLE IMPRINTED BY ITS OWN RAYS.

*To face p. 2.*



Such is the simple and oft-told story of the discovery of a new science, which in the thirty-five years that have elapsed has already exercised a more profound influence upon human thought and has been responsible for more progress in our knowledge of the material universe than any complete century prior to the scientific era. For it was quickly found that neither sunshine nor fluorescence had anything to do with the phenomenon. The property is a spontaneous and inevitable action of uranium, shown by it in the elementary form and in all its compounds, whether they are fluorescent or not, and not shown by other fluorescent substances which do not contain uranium.

Fig. 1 shows one of the earliest photographs by uranium rays obtained by Becquerel. Between the patch of uranium and the film, enclosed in a light-tight envelope, was placed an aluminium medallion, stamped with the head of a figure in relief, which partially shielded the film beneath from the penetrating rays. The impression under the thinner portions of the medallion is darker than under the thicker portions, thus causing the head of the figure to appear clearly in the photograph.

**Radioactivity an Inevitable and Spontaneous Process.**—So radioactivity was discovered. It is an entirely new property of matter shown, certainly, by only two of the then known elements. The intense scientific interest that it aroused was due to the fact that the radioactive elements are spontaneously and continuously emitting energy in new forms without any apparent external stimulus or supply. This was quickly and convincingly demonstrated to be due to the radioactive elements naturally undergoing veritable transmutations into other elements. The rays given out, though they correspond in general type more to the newly discovered rays artificially produced by the electric discharge *in vacuo* than to known forms of light, are, nevertheless, in quality of a higher order than any that can be artificially generated in the present state of electrical science. Just as they result without external stimulus or supply of energy, so no known process is able to produce them in non-radioactive matter. We cannot prevent their emission or affect in the slightest

degree the processes in which they originate in the radioactive substances.

The most distinctive feature of radioactivity is its inevitability. This reduces the experimenter to the rôle, unusual for the physical scientist, of a mere observer and disentangler of events and processes outside his power to influence and control. It is a rôle the astronomer, perchance, has had to accept, concerned as he is with the affairs of a distant universe. Whereas, the physicist and chemist, and their executive officer, the engineer, are more familiar with the rôle of controller of the affairs of the earth, though this till quite recently had almost completely escaped the notice of its inhabitants. Should the day ever dawn when from the position of observers and recorders they pass, by the growth of knowledge, to being able artificially to imitate and regulate radioactive processes—that is to say if ever they are in a position to transmute the elements at will—it would put into the hands of men physical powers as much greater than those they now possess as these are greater than the forces at the command of the savage. But of this particular contingency there is, perhaps fortunately, as yet no sign whatever. So far, at least, science in this quest has proved itself powerless.

**The Scope of this Book.**—The remarkable sequence of discoveries in the fields lying between physics and chemistry, that have followed so rapidly the original discovery of radioactivity in 1896, make it desirable, even at the risk of bewildering the non-technical reader, to try to give some sort of a bird's-eye view of the chief lines of advance. This will be attempted in the first three chapters, dealing, respectively, with the discovery of radioactivity and the new radio-elements, the interpretation of radioactivity by the theory of atomic disintegration, and isotopes.

The remainder of Part I. is devoted to the consideration of atomic disintegration and the rays of the radioactive substances systematically, as exhibited by the three long disintegration series of uranium, actinium and thorium. The radioactive changes in which  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays are spontaneously expelled prove to be veritable transmutations of the elements going on under our eyes. In two cases, dealt with in detail,

the production of helium from radium and other radio-elements, and the production of radium from uranium, it has been possible to demonstrate experimentally the continuous formation of one well-known element from another.

In Part II. the attempt is made to interpret for the general reader the rapid progress that has been made in our knowledge of the atom as a result of the discovery of radioactivity and of the electron and of the numerous novel and upsetting concepts, as to the nature of matter and energy, time and space, that have taken root in theoretical physics and chemistry during the present century. These are dealt with mainly from the point of view of their effect upon earlier ideas and generalisations concerning the nature of the chemical elements.

The concluding chapters deal with our knowledge of the nucleus of the atom, the prevalence of isotopes among the non-radioactive elements, and the application of the new knowledge of the atom to geology and astronomy, and, lastly, with the newly discovered cosmical rays.

**Mme. Curie's Generalisation.**—On the theoretical side, the conclusion that had most to do with the rapid progress made was the recognition that radioactivity is a fundamental and unalterable property of the atom, shown, it is true, by very few types of atom, but essentially unaffected by the state of combination of the element, or the conditions of its past and present environment. When you come to think of it there are very few such material properties, indeed, only one, and that is mass itself. This brilliant generalisation, at once clarifying and simplifying the whole subject, was made quite early, in the face of much apparent evidence to the contrary, by Madame Skłodowska Curie, also working in Paris. In spite of the discovery of many new phenomena, at first sight quite out of keeping with it, it has survived and remains as the central pivot on which the whole science turns.

Radioactivity being a property of the one element uranium, it was natural to ask whether it alone of the known elements was radioactive. This was the starting-point of Mme. Curie's illustrious researches. In a systematic enquiry she found only one other radioactive element—thorium, the element next in complexity and atomic weight to uranium. This important

discovery was also made by G. C. Schmidt. Thorium is, in the form of the oxide, thoria, of industrial importance in the manufacture of the Welsbach incandescent gas mantle, of which it is the main constituent. But the radioactivity seems to be unconnected with its action as a light generator in the gas mantle. More recently this oxide has found a use for coating the filaments of the so-called "dull-emitter" wireless valve. Here, again, although a sufficiently powerful radioactive substance might cause even a cold wire to act as the filament of the valve, it seems impossible that the very feeble radioactivity of thorium can exert any action in this connection, and the thoria probably acts as an earth oxide. Indeed, the precursor of the modern valve was the "Wehnelt cathode"—a hot platinum wire coated with lime.

To the electrical or ionisation test, thorium compounds have much the same activity as those of uranium, but to the photographic plate they are several times less active. This, as we shall see, is because two different types of rays are involved, the  $\alpha$ -rays which have most effect on the electroscope, and the  $\beta$ -rays which have most effect on the photographic plate.

The radioactivity of thorium compounds can be very easily demonstrated by anyone. If a gas mantle, after being cut open and pressed flat, is burnt off, and the ash carefully laid on the film side of a photographic plate, wrapped in an opaque envelope, and left for a fortnight or longer, the result, on developing the plate, will be something like that shown in Fig. 2 (facing p. 2). The negative, of which the plate is a positive, was taken with a very thin but completely opaque leaf of aluminium foil between the mantle and the plate, instead of paper.

Subsequent work has shown that the common element potassium and its rare analogue, rubidium, possess apparently a feeble radioactivity. It is entirely confined to the emission of  $\beta$ -radiation, and as it cannot be concentrated, it has proved very difficult further to elucidate. It appears to be spontaneous and atomic in character, but possibly it is not entirely on a par with the other known cases of radioactivity. But none of the other elements, known at the time radioactivity was discovered, possess the property to a detectable extent.



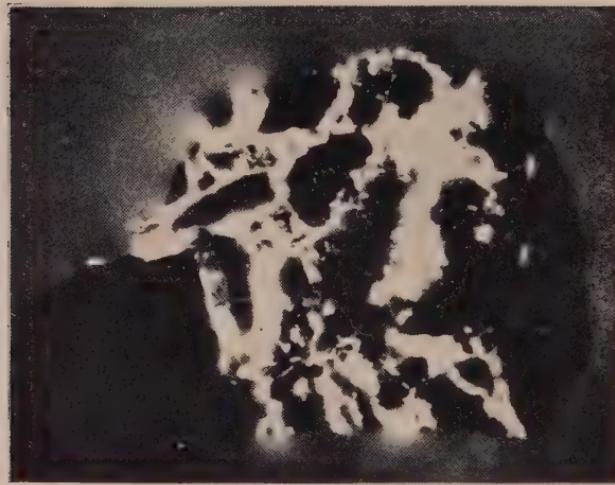


FIG. 3.—PICTURES OF PITCHBLENDÉ BY SIR WILLIAM CROOKES.

The left figure is a photograph by daylight, and the right was taken in the dark by the rays from the substance itself.

*To face p. 7.*

**Discovery of the New Radio-Elements.**—In investigating further the radioactivity of uranium, Mme. Curie made the observation which was to open up the field of work in which she is renowned and to bring the subject from its very small beginnings instantly into world-wide prominence and interest. It was the first complete and striking vindication of her fundamental generalisation. She found that the natural uranium minerals are many times more radioactive than the uranium in them accounts for, whereas artificial minerals which she made, of the same chemical composition, are not in this respect abnormal. Herself a chemist, she worked with her husband M. Pierre Curie, a physicist, in the new field which, in its early stages, called for all the help it could get from both sciences. Now the subject is getting worked out as far as the chemist is concerned, and even the physicist is being subordinated to the modern transcendental mathematician and his strange ways of economising, not to say avoiding, thought. That is real progress, if you will, for in the rest of the physical sciences the more that is done, the more there seems still to be done!

At that time the world's uranium supplies came practically entirely from the celebrated St. Joachimsthal mine in Bohemia. It is a State mine that originally had been worked for silver—hence the word “thaler” for the Austrian florin, of which word the almighty “dollar” is a corruption. Now, under the Czechs, its name has been changed to Jachymov, which seems a pity, as there are few place-names with more interesting and varied historic associations. The ore mined in recent years is called “pitchblende,” and it is one of the varieties of the uranium minerals, known as the uraninites, of comparatively recent secondary origin. Selected pieces may contain more than 50 per cent. of their weight of uranium in the form of oxide, but for many years now this source has ceased to be very important.

The radioactivity of a selected lump of pitchblende to the photographic plate is beautifully shown by two photographs taken by Sir William Crookes (Fig. 3). The lower one is an ordinary daylight photograph of a polished face, and the upper is a positive of its own radiograph, taken by leaving it some weeks on a photographic film placed inside an opaque envelope. The lighter portions in the impression

clearly show the veins of the rich mineral among the inactive gangue.

These pitchblendes may be as much as three to four times as radioactive as pure uranium oxide. If Mme. Curie was right in her generalisation, this could only be the case if the mineral contained elements more powerfully radioactive than uranium. Analysis of the mineral and separation into its component elements showed that two of those present, the bismuth and the barium, were strongly radioactive, though ordinary bismuth and barium are not radioactive. The activity proved to be due to very minute quantities of two intensely radioactive elements. The one chemically resembling bismuth was first discovered and named Polonium, after its discoverer's native country, Poland. The other, next discovered, is the one chemically similar to barium and was felicitously christened Radium. Yet a third, named Actinium, was discovered in the same mineral by M. Debierne, working with the Curies. It is chemically similar to the rare-earth elements and is separated along with them.

**Radium.**—Uranium and thorium, if not very widely known elements, are fairly abundant, and, therefore, as will soon be made clear, proportionately feebly radioactive. In contradistinction, the new radio-elements exist only in absolutely infinitesimal quantities, and, since the greater part of the activity of the original mineral is due to them, when separated they are correspondingly intensely active. Radium has this outstanding advantage over all the numerous types of new radio-elements now recognised. Not only is it outstanding for the intensity, variety and arresting character of its radioactivity, but it exists in just sufficient quantity for the chemist to work with as a distinct substance and to separate its compounds in the pure state. The others either exist in totally unweighable amounts, like polonium and actinium, or they cannot be separated from their admixture with known elements present in the mineral, or, if capable of separation, their radioactivity is neither so intense nor so varied as that of radium. For these reasons radium has achieved well-deserved pre-eminence, and it may be said to epitomise the whole subject of radioactivity. But, from the strictly sci-

tific point of view, it is only one example of a great number.

It is present in pitchblende and other minerals in the definite proportion of three parts per ten million of uranium for reasons that will be later made clear. It is convenient to remember that the British ton, 2,240 lbs., is very nearly a million grams, so that a ton of 50 per cent. uranium ore yields only one-sixth of a gram—166·6 milligrams or about two and a half grains—of radium element. Although the element radium itself has been prepared on only two or three occasions, and it is, of course, sold and used as some compound, such as the bromide, it is always measured now in terms of its content of the element. Hydrated radium bromide,  $\text{RaBr}_2\text{H}_2\text{O}$ , contains for example 54·88 per cent. of radium. In 1910 an International Radium Standards Committee set up, as the radium standard of measurement, a tube of radium chloride prepared by Mme. Curie, and caused substandards to be issued to the principal official testing institutions of various countries. So that now there is no more indefiniteness about the strength and quantity of this, the most precious and costly substance it is possible to buy by weight, than there is about gold or diamonds which, in similar quantities, are hardly worth having. The cost of radium element has varied from £1 when first made to as much as £80 per milligram, and now is about £12, but a milligram of gold is worth only one-thirtieth of a penny. Nor is there any hope that one day radioactive substances will become plentiful, as gold well might by some chance discovery. Radioactive substances are rare in proportion as they are radioactive, because their radioactivity is a measure of the rate at which they are destroying themselves.

Mme. Curie's separation of radium compounds in the pure state, although unique in chemistry on account of the infinitesimal quantity of the material separated, was technically a straightforward chemical operation. The increasing activity of the successive concentrates obtained gives a sure and easy method of knowing the progress and perfection of the separation. As has so often happened since, the new element was found to be very closely similar in chemical character to a known element, in this case barium, and the

operations consist in (1) separation with (2) separation from the analogous element.

It was not till about 1903 that sufficient had been laboriously accumulated for a thorough chemical examination. It was then found that the new element, in all respects, conformed in its chemistry to the alkaline earth elements, of which the other members known were calcium, strontium and barium. It occupied, in the Periodic Table, the vacant place at the end of this (the IIInd) family, two places horizontally removed from thorium in the IVth family as thorium is two places removed from uranium in the VIth family, the end places of the IIIrd and Vth families being then vacant. A chart of the Periodic Table of the chemical elements will be found at the end of the volume.

Its atomic weight, in terms of oxygen=16 as standard, was found to be 226, that of thorium being 232 and of uranium 238 to the nearest integer, these being the three largest known. In spectrum, as in its chemical properties, it is analogous to barium, and the only feasible way found of separating radium from barium is by a long and somewhat tedious fractional crystallisation of the salt, usually the bromide or chloride. In fact, chemically it comports itself with the utmost propriety exactly as the missing element occupying this vacant place could have been predicted beforehand to behave, from our general knowledge of the nature of the analogies between the elements shown by the Periodic Classification.

**Origin of the Energy of Radium.**—On the radioactive side, however, its mere existence was a challenge which physical science had instantly to answer or to declare itself hopelessly at fault. For it seemed to defy with impunity the validity of no less well established a doctrine than the law of the conservation of energy. The emission of its rays keeps it permanently at a perceptibly higher temperature than its surroundings. Accurate measurements, in due course, showed that it emits every two days more energy than can be obtained from a similar weight of any combustible or explosive substances in the most energetic changes till then known. This it keeps up from day to day and year to year without as yet, in the quarter of a century that it has been known, any apparent



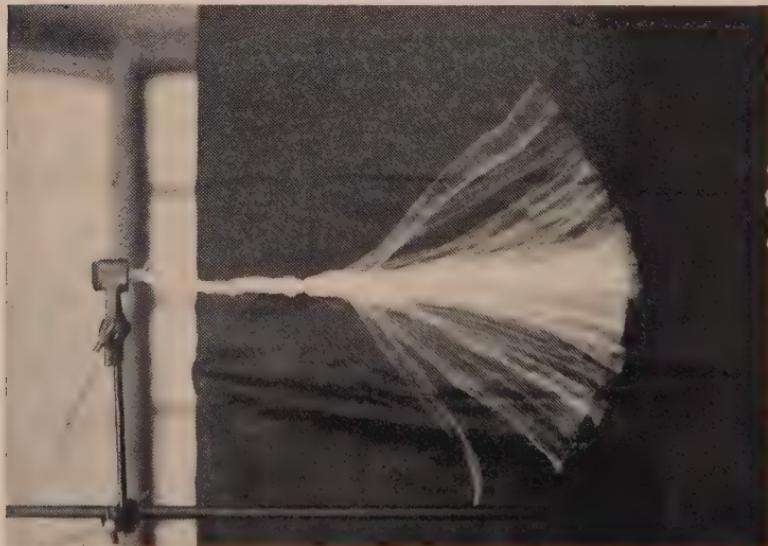


FIG. 9.—SILK TASSEL ELECTRIFIED.

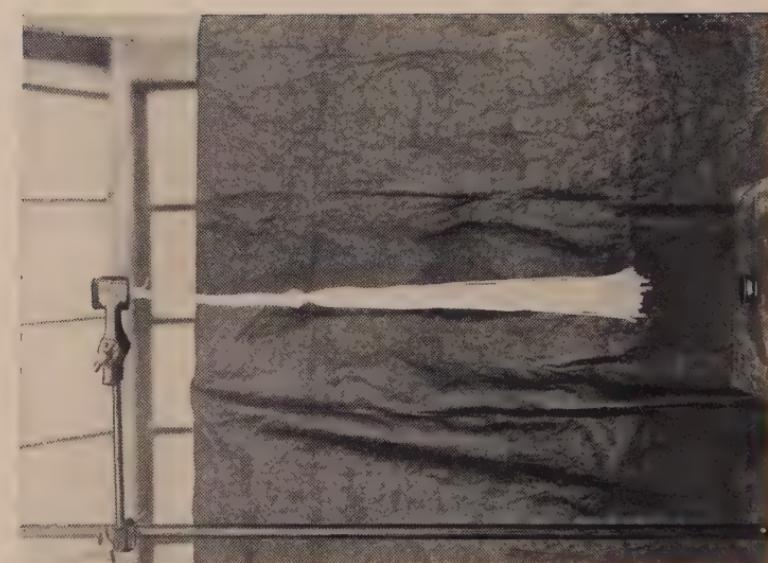


FIG. 10.—SILK TASSEL DISCHARGED BY RADIUM.

*To face p. 17.*

intensity of the radiation. This property is at the basis of the rapid, accurate and quantitative electrical methods of measurement, which have contributed so materially to the triumphant progress made in these new fields. Radioactivity was fortunate in the development of quantitative experimental methods at once simple, sensitive and accurate.

The discharging action of the new types of rays was accounted for in 1896 by a theory of gaseous ionisation put forward by Thomson and Rutherford, primarily for the action of the X-rays, but equally applicable to the other cases. It regards the rays as dissociating the neutral molecules of the gas into the positive and negatively charged particles called ions, and these positive and negative ions go to and from the charged body according as to whether it is negatively or positively charged, neutralising the charge. The action is essentially the same as in the theory of electrolysis of liquids developed much earlier by Faraday, and discussed in Chapter XII. The passage of an electric current through aqueous solutions of metallic salts frequently causes the metal to be deposited on the negative electrode or cathode. This is of course the basis of all the common electroplating processes.

But there is one very important distinction between the two cases. According to modern views, in the solution the ions already exist, and the electric force merely directs them to the oppositely charged electrode where they give up their charges. For gases, the molecules are normally neutral, and it requires energy to ionise them. The degree of ionisation is an electric measure of the intensity of the rays, and of the energy which is abstracted from them in producing the ions. Left to itself, an ionised gas almost instantly reverts to its pristine non-conducting condition, by the recombination of the oppositely charged ions, one with another.

The ionisation of the air by X-rays or a sufficiently powerful radioactive substance, such as radium, can be shown very simply by the means indicated in Figs. 9 and 10. A tassel made of floss silk is electrified by stroking it with a dry tobacco pouch of rubber, when the threads all stand out and repel one another as seen in the first figure. It is in fact a rough and ready, but quite useful, electroscope. The moment the air in the neighbourhood is irradiated by X-rays, or the

rays of radium, the tassel is almost instantly discharged, and resumes its original state as shown in the second figure. This electrical, or ionisation, method of investigating the new types of rays is usually much more accurate, sensitive and convenient than the methods based upon the photographic and fluorescent actions.

## CHAPTER II

### THE INTERPRETATION OF RADIOACTIVITY

**The  $\alpha$ -,  $\beta$ - and  $\gamma$ -Rays.**—The interpretation of the phenomenon of radioactivity, as a veritable process of spontaneous transmutation of the radio-elements proceeding before our eyes, was due to a series of researches carried out for the most part in the Physical and Chemical Departments of McGill University, Montreal, 1898-1902, by Professor Ernest Rutherford<sup>1</sup> and the author. Before considering these the state of knowledge with regard to the nature of the rays emitted will be reviewed.

The Continental physicists had shown that the ordinary penetrating rays of uranium and thorium are deviated by electric and magnetic fields in the same sense as, but with more difficulty than, the cathode-rays, and that they therefore consist of electrons travelling at a very high velocity, which may be nearly that of light itself. Rutherford, whose theory of gaseous ionisation, jointly with Sir Joseph Thomson, was referred to in the last chapter, was the first to recognise in the radiation of the radio-elements, besides this penetrating type deviable by a magnet, a non-penetrating type, absorbed by only a few inches of ordinary air, which did not appear to be deviable by ordinary magnetic fields. He called this type the  $\alpha$ -rays in contradistinction to the other type which he termed the  $\beta$ -rays. The latter have much the same penetrating power or "hardness" as X-rays of moderate penetrating power, and, by comparison, the  $\alpha$ -rays are, at first sight, less interesting. They have, for feebly radioactive elements like uranium and thorium, practically no photographic action, though for intensely active radio-elements this is not true. But to the ionisation test, by the gold leaf electroscope, they exhibit far more powerful action than the  $\beta$ -rays, both on account of their greater energy and on account of their easy absorbability.

<sup>1</sup> Created a Knight in 1913. Elevated to the Peerage with the title Baron Rutherford of Nelson, 1931.

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Closer examination revealed them to be of dominating interest, as they represent by far the greater part, usually over 90 per cent., of the total energy of radiation. This, coupled with their easy absorption by the air and other gases, accounts for their great ionising power, as shown by their discharging action on the electroscope, even when they are too feeble to affect the photographic plate at all. It was suggested by several investigators that they might be "positive" rays corresponding to the negative  $\beta$ -rays. It was then beginning to be understood that, in all cases, the positive charge is never associated with less mass than that of the hydrogen atom. It is impossible to divorce positive electricity from matter in the same way as negative, and the failure to deviate the  $\alpha$ -rays might be due to their much greater mass and kinetic energy.

This view was, in 1902, proved to be correct. Rutherford found that a magnetic field, sufficiently intense to coil up the cathode-rays of the vacuum tube to circles of only  $1/250$ th of an inch radius, sufficed to coil the  $\alpha$ -rays of radium into the arc of a circle of about 16 inches radius. Later, success attended also the attempts to deviate the  $\alpha$ -particle by electric fields, and the combination of the results showed that the ratio of the mass to the charge of the particle was about twice that of the hydrogen ion,  $H^+$ , and about four thousand times that for the negative electron. It was thus clear that the  $\alpha$ -rays are composed of positively charged radiant atoms expelled with great velocity. This varies in different cases from one-thirteenth to one-twentieth of the velocity of light, that is from 9,000 up to 14,000 miles a second. No material projectile of anything like this speed had ever been available before, and this new weapon has told us much as to the inner structure of the atom. In due course the  $\alpha$ -particles were proved to be helium nuclei, that is to say, helium atoms shorn of their two satellite electrons and carrying two positive charges. But that is a story in itself which will be told in Chapter IV.

So soon as radium became available for exact physical investigation, a third type, the  $\gamma$ -rays, was discovered, and later this type was recognised also in the radiations from the feebler radio-elements. Though in relative intensity it is always much the most feeble of the three types, at least as regards the three

common tests—the ionisation, photographic and fluorescent effects—it is most extraordinarily penetrating, easily surpassing the very hardest X-rays that can be produced by the most powerful modern appliances. The  $\gamma$ -rays from a few milligrams of radium can be still detected by the electroscope after they have passed through 8 or 10 inches of lead or mercury. They were first thought to be a type of X-rays which accompany the  $\beta$ -rays, much in the same genetic relation as the X-rays of Röntgen to the cathode-rays. Even their unique penetrating power has now been overshadowed by the discovery of the new cosmical rays, which find their way to this earth apparently from the depths of empty space, and some of which are at least ten times as penetrating as the  $\gamma$ -rays of radium, the main component being at least five times as penetrating. The trajectory of the  $\gamma$ -rays is completely unaffected by electric or magnetic fields.

**Effect of the Magnetic Field.**—The salient features of the effects of these fields upon the three types of rays is very clearly shown by a diagram due to Mme. Curie (Fig. 11). A lead container, B, with a small quantity of a radioactive preparation,

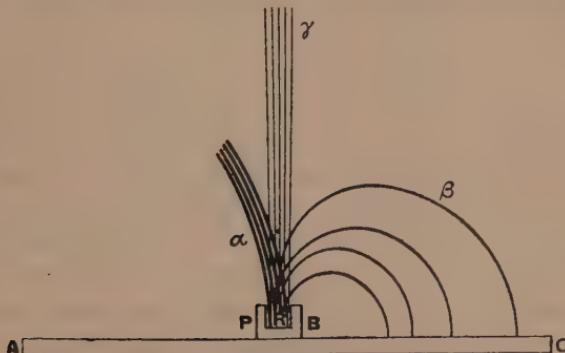


FIG. 11.

R, contained in a deep hole in it, is resting on a plate, AC, and is supposed to be emitting a pencil of rays upwards in the plane of the paper. Passing through this plane at right angles to it there are supposed to be lines of magnetic force produced by an electromagnet, not shown, with the S-pole below the plane of the paper and the N-pole above it. The faint and

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feeble  $\gamma$ -rays pursue their course unaffected by the field. The  $\beta$ -rays are easily coiled up into circles of varying radii, the smaller circles corresponding with the less swift  $\beta$ -rays. The powerful  $\alpha$ -rays are very slightly deviated in the opposite sense, but the curvature shown is very much exaggerated in the diagram for clearness. If it be supposed that the layer of radioactive substance is practically without thickness, so that no absorption takes place in the substance itself, the diagram illustrates also another characteristic feature of the  $\alpha$ -rays discovered by Sir William Bragg. Those from a single radioactive substance all travel the same definite distance or "range" in air, or other absorbing medium, and all end at practically the same point. It has been said, whether truly or not time alone can judge, that the three directions at right angles which the diagram interrelates, (1) the direction of the force, (2) the direction of the motion, (3) the direction of deflexion, or acceleration, give us the reason for the three dimensions of space, that is, that space is three dimensional because of this fundamental relation governing all electromagnetic phenomena.

**The Thorium Emanation.**—The discovery which now stands out as the true starting-point of the interpretation of radioactivity had to do with a slight difference in the general character of the radioactivity of uranium and thorium. Whereas the first is quite constant, so that, to this day, the standards used for  $\alpha$ -ray measurement are usually made out of uranium oxide, that of the second is capricious *and dependent on draughts*. By 1900 this difference had been traced to the power possessed by the compounds of thorium of giving out not only  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays, like those of uranium, but also an "emanation" itself radioactive and giving out  $\alpha$ -rays. This emanation, as it was termed by Rutherford, behaved in fact like a radioactive vapour, diffusing through porous substances such as paper, but stopped by the thinnest film of mica or other impervious septum. It was the first example recognised of ephemeral radioactivity. It could be entirely separated from the thorium compound by passing a stream of gas through it, and, when this gas was left undisturbed, the radioactivity of the contained emanation regularly decayed in a geometrical

progression with the lapse of time. At the end of any minute the activity would be found to be only one-half as great as at the beginning of that minute. As we now express it, its period of half-change is about a minute. Henceforth, for brevity, we shall speak of this period as the period of half-change or "half-period," to indicate the time it takes for an ephemeral radioactive substance to lose one-half its initial activity.

**The Active Deposits.**—The emanation of thorium, however, had another very surprising property. It conferred on the walls of the vessel containing it, as indeed on any solid object with which it came into contact, another new kind of ephemeral activity, in this case with a period of half-change of 11 hours. Simultaneously M. and Mme. Curie noticed a similar phenomenon for radium compounds, without however discovering the corresponding radium emanation which is responsible for it, which was discovered later by Dorn. Actinium is the third radio-element to give an emanation and a characteristic "active deposit," as the activity produced by the emanations is now termed.

These three pairs of emanations and active deposits are all quite different in their radioactive character, which in each case is characteristic of the particular radio-element producing them. With the growth of the subject, the old name "emanation" has been retained as a general term to signify all three, and the names "thoron," "radon" and "actinon" have been coined to signify, respectively, the thorium, radium and actinium emanations. From this point the numerous products, called collectively the "active deposit," are named in alphabetical sequence by the letters A, B, C, following the name of the element from which they come. Thus it is known that the "active deposit" of radium undergoes, after deposition from radon, a sequence of changes indicated by the letters A to G, the successive bodies being termed radium A, radium B, and so on.

The half-period of radon is about 4 days and of actinon only as many seconds. The half-period of the radium active deposit, considered as a group up to and including the C-member, is of the order of half an hour and of the actinium active deposit rather longer. The very definite and character-

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istic rates of decay, in all these cases, themselves furnish most unequivocal and infallible tests of the identity of the ephemeral radio-elements. They are regularly used to identify them and the parent elements from which they come and to distinguish the one from the other, even in almost infinitesimal quantities, completely beyond detection by chemical or spectroscopic methods of analysis.

**The Radioactive Emanations are Argon Gases.**—In 1899 the author, then a Demonstrator in Chemistry at McGill University, was invited by Rutherford to join him in the new field of work he had opened up. The first result was, to a chemist, not a little intriguing. An examination was made of the chemical character of the thorium emanation, or thoron, and it gave the most amazing result that it must be a member of the entirely new family of chemically inert gases, the first of which, argon, had been discovered in the air by Lord Rayleigh and Sir William Ramsay only four years previously. The latter and his collaborators had followed this up with the discovery of four other similar gaseous elements, helium, neon, krypton and xenon, which are present, in infinitesimal quantity only, in the atmosphere. Argon is present to nearly 1 per cent. in the air, but the others only from twelve parts per million for neon, the most abundant, to one-twentieth part per million for xenon, the rarest. Helium, as the name implies, had been discovered by its spectrum in the sun before it was known as a terrestrial element. Ramsay in 1897 had first tracked it down to earth in the uranium minerals, but it was then found to exist in the air to the extent of four parts per million. But of this we shall have more to say later.

The most interesting or uninteresting thing about this new family of gases was their complete absence of chemical affinity or combining power of any kind. They, alone of the elements, form no compounds. Hence they alone remain as gases after drastic chemical treatment by sufficiently powerful absorbents. All the other known gases combine with, and are absorbed by, one or other of the reagents available. But on treating the radioactive emanations given off by thorium and radium compounds with all the most powerful reagents and absorbers in the chemist's battery they were not absorbed, or in any way

affected. This conclusion was subsequently much more thoroughly and completely established for radon by Ramsay and the author, using the methods the former had relied upon in his work on the argon family of gases. It was a most extraordinarily lucky chance that this first chemical experiment on the thorium emanation was in itself sufficient to prove the doctrine of atomic disintegration, to which all the subsequent experiments led. For unless the observation was wrong, which it was not, it proved that the element thorium produces an argon type of gas. This was the first chemical evidence of a real transmutation.

**Condensation of the Emanations by Cold.**—Somewhat later, the observation was made that, though unabsorbable by any known reagent, the emanations, both radon and thoron, are readily condensed to the non-volatile state by extreme cold, by passing them with a stream of non-condensable gas through a tube cooled by liquid air. This showed them to possess specific physical properties and to behave as gases of high molecular weight or density. Diffusion experiments led to the same conclusion. Now of course we know that all three emanations are isotopes, occupying the last place in the zero family of inert gases, two places horizontally removed in the Periodic Table from radium, just as radium is from thorium and thorium is from uranium. Actually the emanations were the first isotopes to be severally recognised. This was possible because of the entirely different characters of their radioactivity.

The property of the emanations of being condensed at liquid air temperature has proved invaluable, especially in the case of radon, both for its investigation in a pure state, in the almost infinitesimal quantities in which it exists, and in the commonest application of radium in surgical treatment. It is much better, instead of using radium itself for this work, to use it simply as a generator of radon, which gives all the useful rays given by radium itself. The radium, in medical institutions properly equipped for this work, is kept in solution in a safe place, and the radon, as it grows, is pumped off from the solution, condensed by liquid air in capillary glass tubes, which are then sealed off. These radon "seeds," as they are

called, can be inserted into the body where required by means of a surgical needle and need not necessarily be removed again, but may be left in the body to do their work. In a few weeks, their activity decays practically to zero, and meantime the radium has grown a fresh crop of radon for further use. Not only is all risk to the precious element thus avoided, but the surgery required is much less drastic.

**Uranium X.**—In 1900, Sir William Crookes, by means of several elegant chemical methods still in use for the purpose, succeeded in separating completely from uranium something, which he termed uranium X, which causes the photographic part of the radioactivity of the uranium. This at first seemed to upset Mme. Curie's generalisation that radioactivity is an atomic property of uranium. Becquerel, independently and simultaneously, but by a different chemical method, also separated uranium X from uranium. Both thought that the uranium, so purified, was inactive. However they had really only separated the constituent responsible for the  $\beta$ -rays, which are the photographically active rays. The much more powerful  $\alpha$ -rays of uranium, it was later found, are quite unaffected by any known chemical treatment, and are an atomic property of uranium.

Then Becquerel, re-examining his preparations a year afterwards, found that the activity of the uranium X had in the interval practically completely disappeared, while the uranium, before completely inactive to the photographic plate, was now again as active as at first. Uranium X is thus another example of ephemeral radioactivity, the half-period in this case being 24·6 days. At this time Becquerel was under the influence of a false interpretation which he had advanced to account for the phenomena observed by the Curies for radium, due to the active deposit produced by radon. Through the latter not being recognised as essential to the effect, the view had been taken that radioactivity may be "induced" in non-radioactive matter by the rays from radioactive matter. Whereas experiments with the thorium emanation had already proved that the active deposit effect is entirely prevented if the radioactive material is contained in an airtight vessel, however thin the walls, and the same

is true for radium. The active deposit is, in fact, produced by the gaseous emanations and deposited on any available solid surface in the neighbourhood. It is attracted by a negatively charged surface and repelled by a positively charged one, and in this way it can be concentrated on very small surfaces, such as a needle point, the rest of the vessel in which it is contained receiving little or none.

But Becquerel thought that uranium X owed its temporary activity to "induction" by the radioactive uranium, and so he missed the fundamental significance of his own observation of the regeneration of uranium X after chemical separation, by the uranium when left to itself for a year. He regarded the decay of the activity as analogous to the decay of phosphorescence, after the exciting stimulus is withdrawn.

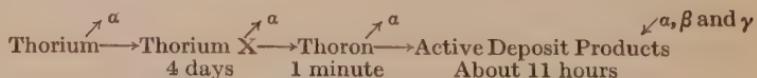
**Thorium X.**—In Montreal, in 1902, the continuation of the work already described for thoron led to a discovery being made for thorium, complementary to that described for uranium. In making a chemical examination of the emanating property of thorium compounds, it was found that simple chemical treatment of the latter may remove something which entirely accounts for the production of the emanation. So that thorium compounds may be entirely freed from their property of producing the emanation, which property is concentrated in the minute quantities of impurities separated in the treatment. This something was termed thorium X, as it seemed in many ways to be analogous to uranium X. Its removal is simply effected by precipitating the thorium from solution by ammonia. The thorium X remains in the solution, and is left behind as a minute impurity when the latter is evaporated to dryness and ignited. Its removal not only completely takes away the emanating power of the thorium, but also 75 per cent. of its  $\alpha$ -rays and the whole of its  $\beta$ - and  $\gamma$ -rays. So that, after thorough treatment, the thorium retains only one-fourth of its original  $\alpha$ -activity. *But all this activity, so removed, rapidly comes back again, and, just as rapidly, the thorium X separated loses all its radioactivity.*

These changes, conveniently, are much faster than in the analogous case of uranium and uranium X. The half-period of thorium X is only 4 days, and, after 3 weeks or a month,

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its activity completely disappears, while the thorium from which it was made is again as active in every way as at first. One can go on repeating the process on the same quantity of thorium indefinitely, at daily, weekly or monthly intervals. As fast as the thorium X loses its activity, the thorium regains it. If, at any time, the two parts, into which the thorium compound has been separated by chemical treatment, are mixed together again, the mixture is, in all radioactive respects, exactly the same as the original before separation. This proved that the chemical treatment had nothing to do with the cause of the phenomenon. It merely revealed profound changes that are occurring naturally and spontaneously, but which are not obvious before chemical analysis. We have two processes, always going on together, a steady formation or production of thorium X from thorium, and a steady decay and disappearance of the thorium X that is produced. In the normal state, these two opposed processes exactly balance—they come into radioactive equilibrium, as we say—when as much fresh thorium X is formed each instant as disappears each instant, so that the quantity of thorium X and the radioactivity appear constant. At this stage it became clear that radioactivity consists, not merely in the continuous emission of  $\alpha$ - and  $\beta$ -rays or particles, but also in the continuous production of chemically new types of matter distinct from the parent, and which in turn go on emitting rays and producing yet other types in a long cascade of changes.

**Theory of Atomic Disintegration.**—It was most fortunate that the very complexity of the processes in thorium revealed what was taking place far more clearly than in any of the other cases. The picture that was formed at this stage is illustrated in the diagram—



One atom of thorium disintegrates, expelling one  $\alpha$ -particle and changing into an atom of thorium X, which in turn disintegrates again, expelling an  $\alpha$ -particle, and becoming an atom of thoron, an argon gas. This in turn rapidly expels yet another  $\alpha$ -particle and changes into the active deposit, a

non-volatile form of matter, which breaks up, in what we know now is a complex series of further consecutive changes, and expels  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays in the process.

So it is in the other cases. The atom of uranium expels an  $\alpha$ -particle and becomes an atom of uranium X, which then proceeds to disintegrate again and to expel a  $\beta$ -particle. The atom of radium expels an  $\alpha$ -particle and becomes an atom of radon, an argon gas, which then, much as thoron but at characteristic rates, proceeds to disintegrate again and again. In all of these cases the changes are revealed by the rays expelled, and when you come to the last change, if it is the last, the product becomes inactive and passes beyond detection. One must turn as it were from observing a shower of shooting stars to finding the meteors afterwards, a much more arduous task. In the course of it, radio-chemistry was to make a discovery, the discovery of isotopes, with a stranger and more fascinating history perhaps than almost any other discovery in regard to the nature of matter. This will be introduced in the next chapter. We may observe here that, complex as the changes in thorium proved to be even in 1902, three of the steps were missed, inevitably as it now appears, in the first examination. Their discovery was in fact the first positive step towards the recognition of isotopic elements.

The discovery of the continuous reproduction of new kinds of radioactive matter by the radioactive elements, as fast as those present were removed, though now familiar enough, was, at the time it was made, probably one of the most upsetting and unlooked-for experimental results ever obtained. To a chemist it was just as though he were to purify, say, lead from silver, and then, re-examining the lead some time after, were to find silver in it again, and, repeating the process again and again, were always to find that, though absent when freshly purified, always after sufficient lapse of time, *more silver had grown*. Most certainly this sort of thing does not occur with the ordinary elements, at least on a scale experimentally detectable, and it is for this precise reason that the elements came to be regarded as unchanging and unchangeable. That it does demonstrably occur with the radio-elements is, equally precisely, the reason, if not the only reason, why the doctrine of the unchangeability of the elements had to be modified,

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so far as concerns the radio-elements. Other lines of evidence that the radioactive changes were really transmutational were derived from (1) the law of the changes, which the chemist terms "the law of monomolecular reaction," only one changing particle being involved and not a number as in any combination; (2) the unparalleled energy evolution, which is of the order of a million times greater than in the most energetic chemical changes known; (3) the total absence of dependence of the rates of disintegration upon all physical influences such as temperature, pressure, concentration and other factors which modify chemical reactions; (4) Mme. Curie's principle that radioactivity is an atomic property.

**Earlier Anticipations of the Theory.**—With regard to the last, if Mme. Curie were correct in this view, then the interpretation of the remarkable sequence of changes occurring in uranium and thorium, as veritable transmutations of these elements into others, was the only logical conclusion. Even before 1903, some suggestions of a very vague and general character had been made, in discussing all the possible explanations of radioactivity, that it might be due to some kind of transformation or change of the substance and even of the atom. The expulsion of electrons as  $\beta$ -particles (the nature of the  $\alpha$ -rays was not then known) was not of itself at the time any valid evidence whatever of transmutational change. The emission of electrons from the cathode during the electric discharge, and in numerous other phenomena which were well known at the time, does not involve any "atomic" change whatever. The spontaneous emission of energy certainly suggested that some kind of change was in progress. Elster and Geitel, two German physicists, in 1899 ascribed radioactivity to a possible change in the atom of the radio-element analogous to that of the molecules of an unstable compound passing into a more stable state with loss of energy. They suggested that the active substance might be gradually changing into an inactive form with consequential change in its elementary properties, always provided that the energy emitted really did come from the radioactive substance, and not from the outside.

Of these early anticipations of the theory that radioactivity

was due to veritable transmutations of the elements, it is interesting to note that Mme. Curie's was the closest and most precise. In 1900, discussing all the conceivable explanations, she reduced them to two groups, according as to whether the energy given out was or was not provided internally from the substance itself. If it was so provided, she argued, then the radioactive matter must be undergoing a chemical transformation, which furnishes the energy radiated away. But this chemical transformation cannot be an ordinary chemical change which leaves the atom inviolate. She said, "If anything changes it must be the atom, since it is the atom to which is attached the radioactivity." Considering that at the time there was no unequivocal evidence whatever of any material changes, nor even that the energy of the change was supplied from the substance itself, Mme. Curie went just as far as it was then possible to go. When evidence of material changes was obtained, she rightly claimed the disintegration theory as the logical sequence of her fundamental view-point that radioactivity is an atomic property.

**Transmutation in Ancient and Modern Times.**—Ever since the day of Robert Boyle, the author in 1661 of *Chemista Sceptica*, the true chemist had perforce to be a sceptical chemist. Even to speak of transmutation at all was apt to be considered a breach of good taste. The inherited memories of the infamous origins of his science among the alchemists, poisoners and other professional charlatans and rascals of the Courts of ancient Egypt and of medieval Europe, die hard. From the beginning of chemistry as a science, the true chemist had become very sceptical of the facile and superficial generalisations of the ancients regarding the unity of matter. He came to regard all claims to have effected transmutation as evidence either of criminal tendencies or of an egregious lack of the first elements of decent chemical cleanliness. Now, largely owing to the opportunity which radioactivity has afforded of studying experimentally a *real* case of natural transmutation, it will be admitted that the intuitive instincts of chemists towards this question were fully justified.

Possibly it may come as a surprise to the up-to-date reader to learn that, outside the narrow field of the radioactive sub-

stances, there is still no unequivocal evidence of any transmutational changes at all. As a speculation or guess, such changes are of course continually being assumed and never more lightly than to-day. From the very earliest times, and in definite form as Prout's hypothesis since the beginning of last century, it has been supposed that the elements are all built up of the same stuff—that they are compounds of varying degree of complexity of one fundamental element or " protyle." In Prout's hypothesis this was hydrogen, and the atoms of the other elements were supposed to be made out of a number of hydrogen atoms condensed together into a more intimate union than occurs when the elements combine with one another to form ordinary chemical compounds. We shall have more to say of this particular idea in the next chapter and in Chapter XVIII.

Coming to more recent times, in the concluding decades of last century, some kind of transmutational process was invoked both to explain stellar phenomena, as then being revealed by the spectroscope, and with regard to each new development in electricity. Sir Norman Lockyer, upon the observation and study of the so-called " enhanced lines " in stellar spectra, advanced a theory of cosmical evolution based on the supposed continuous formation of the heavier elements from the lighter ones, hydrogen and helium, as new stars grow old and cool. Sir William Crookes, largely on the phenomena that occur in the passage of electricity through highly rarefied gases, based many speculations concerning matter in a new and fourth state, the genesis of the elements and the existence of " Meta-Elements " as transition forms between the stable elements.

The discovery of the electron, and the determination of its mass as  $1/1840$ th of that of the hydrogen atom, till then the smallest entity known to science, was widely regarded as revealing the actual protyle out of which the material atoms are built up. The view that science had resolved matter into electricity—the so-called electrical theory of matter—was widely, if not very critically, discussed.

Now it has become abundantly clear that these views, in so far as they invoked material changes more deep-seated than the ordinary changes of matter with which the chemist is familiar, were quite at fault. Conversely, there has been

going on a basic reinterpretation of the common ideas and phenomena of chemistry in terms of the electron. Chemical affinity, bonds of union, valency and the like appear as resultants of the combination of the negative electrons with the positive atoms or ions of matter. A much closer connection has been established between chemical character and physical properties, such as the various types of spectra emitted by the same element, and the "enhanced" lines which misled Lockyer.

Speculation and hypothesis go merrily on. All modern cosmogonists resort, as a matter of course, to some form of transmutational processes to explain the origin and maintenance of the energy of the sun and stars over cosmical periods of time. Starting from the old classical conception of Clerk-Maxwell of radiation as a wave-motion propagated uniformly in all directions over a continuous spherical wave-front rather than from the newer conceptions of light as composed of quanta or photons, no known transmutational process even is adequate to account for the apparent outpourings of energy from the sun and stars over the vastly extended scale of cosmical time which radioactivity has proved to be necessary.

In consequence, resort has been had to supposed processes of condensation of hydrogen into helium to supply the energy, which on the transcendental theorem of relativity and the equivalence between mass and energy to which it leads, ought to supply even more energy than that afforded in the radioactive disintegration of the heaviest elements. But as even this falls short, following the same hypothesis, a veritable annihilation of matter into radiation has been postulated as the only really sufficient source of the energy the stellar universe seems so profligately to dissipate in every direction over inconceivable æons of time. Also, in the latest and most interesting of the experimental discoveries in this field, that of the ultra-penetrating cosmical radiation reaching us uniformly in all directions from apparently empty space, a synthesis or rebirth of the heavier elements out of hydrogen has been suggested as the cause. May time deal with these cosmogonies more kindly than it has done with those of the past.

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But as regards this earth at least, and the phenomena directly amenable to experimental investigation and enquiry, it still remains true that, so far, it is only in the extremely restricted field of the radioactive elements that the limits to the analysis of matter into atoms and elements set by the chemist have been overstepped, and the Rubicon which the human mind has so lightly vaulted over in imagination from the dawn of civilisation has as yet actually been crossed by science.

## CHAPTER III

### ISOTOPES

**Implications of Atomic Change.**—Until the interpretation of radioactivity, the atoms had been, as Clerk-Maxwell put it in 1873, the permanent foundation stones of the universe. A new world was opened up when it was discovered that the two heaviest and most complex of the atoms were spontaneously breaking up and passing through a long succession of unstable and more or less ephemeral forms. Discoveries, such as the discovery of the production of helium from radium and the production of radium from uranium, any one of which would have startled the chemists of any earlier century, now followed from the theory of atomic disintegration as a matter of course, being predicted beforehand, much as a skilled billiard player will declare his stroke before he plays it. For the sake of trying to get a general view of the subject, let us postpone their more detailed consideration, and pass on at once to what was the strangest result of all. For even the chemist, of all people the one most familiar with the meaning and implications of that little word—change—not only did not foresee this one, but took some considerable time and the accumulation of a wealth of examples before understanding it. In 1911 to 1913 three or four converging lines of evidence, drawn from both the physical and chemical developments of the subject, revealed a new type of complexity in the chemical elements which had never before been even suspected.

If at the end of the summer, after the garden bulbs had been dug up to be stored indoors against the winter frost, they had the misfortune to become all mixed up, a skilled gardener, no doubt, might easily sort the crocuses from the tulips and the tulips from the hyacinths, but he would be a very remarkable one if he could sort each of the various bulbs into their several varieties, the white, the yellow, the blue and so on. Yet next year, after they had flowered again, anyone not colour-blind could do it. So it has proved for—of all

unlikely things—the chemical elements. “By their fruits ye shall know them.”

The chemist dealing with unchanging elements sorts them easily enough into their several varieties. But let them change into one another and what subtle internal distinctions between the different atoms of the same element are at once disclosed! So it was left for the radio-chemists to discover, first, that many of the new radio-elements, which are produced by different parents and which in due course change quite differently into different products, are chemically indistinguishable and identical. Once mixed together they cannot be separated again from one another by any process of chemical analysis whatever.

**The Discovery of Isotopes.**—The first indication that there was some unknown factor at work arose out of the very large number of disintegration products. At the present time some forty are recognised, which is nearly one-half as many as the total number of chemical elements. There certainly did not appear to be nearly enough vacant places in the Periodic Table to accommodate them all. As it happened, for the first three new radio-elements, radium, polonium and actinium, discovered in the uranium minerals, the difficulty did not arise, because each does occupy a place in the latter part of the Periodic Table formerly vacant. Each is a chemically new as well as a radioactively new species. But this could not go on. As new radioactive disintegration products continued to be recognised, it was found that they were new only in the nature of their radioactivity. In their chemical character they proved to be *identical* with other elements already known, either with one of the radio-elements already discovered or with one of the known inactive elements.

Thus, in 1907, B. Boltwood showed that another new radio-element, which he named ionium, is present in the uranium minerals. It had before been separated with actinium, but not separated from it or recognised as a distinct radio-element. It is a long-lived element, giving  $\alpha$ -rays only, which by its disintegration produces radium. The rate of change is exceedingly small, the period of half-change being of the order

of 75,000 years. It is intensely radioactive, and it acts as the direct parent of radium, but of this we shall have more to say in Chapter V.

Now Boltwood separated ionium from actinium and the allied rare-earth elements very simply and effectively by adding a little thorium, which was then separated and purified by well-known methods. The thorium and ionium remain always together once mixed, and no chemical process is capable of separating them again. The two are chemically identical, or as we now say, isotopes.

Even more interesting was the actual path by which historically the conception of isotopes first entered the world. It was through a series of discoveries (1905-1907) for the thorium minerals complementary to those made by Mme. Curie for the uranium minerals. Sir W. Ramsay and O. Hahn in 1905, in the course of the separation of radium from a new Ceylon mineral, thorianite, which contains some uranium but is mainly thorium oxide, noticed in the final fractionation of the barium from the radium that the radioactivity separated into two parts, instead of being wholly concentrated with the radium, leaving the barium inactive, as it should do. From the latter they easily separated a new radio-element, which was intensely active like radium, and to which they gave the name radiothorium. Chemically it behaves as thorium, but, weight for weight, is incomparably more active. It undergoes an  $\alpha$ -ray change and produces, as the first product, thorium X, the discovery of which had in 1902 led to the first formulation of the theory of atomic disintegration. Clearly Ramsay and Hahn had separated a new member of the disintegration series intermediate between thorium and thorium X, and of course chemists immediately set about trying to separate radiothorium from thorium compounds.

Then arose a very curious and involved situation. Although Ramsay and Hahn had had no special difficulties in separating radiothorium from thorium minerals, the chemist did not live who was clever enough to separate it from the ordinary thorium salts and compounds of commerce. That radiothorium was there was, of course, shown by their producing thorium X, but the most elaborate and prolonged efforts failed to effect even the least concentration from thorium of the constituent

producing the thorium X. McCoy and Ross, two American chemists, after describing many unsuccessful efforts, in 1907 had the courage of their convictions and boldly concluded that the two substances are entirely inseparable by chemical processes.

**Radiothorium and Mesothorium.**—In the meantime Hahn had followed up the discovery of radiothorium by another. Two other closely related bodies were discovered in the disintegration series intermediate between thorium and radiothorium, which he named mesothorium I and II. The former is fairly long-lived and changes without the emission of any detectable radiation—though probably a  $\beta$ -ray too low in velocity to be detectable is expelled—into the latter, which is short-lived and emits a powerful  $\beta$ - and  $\gamma$ -radiation.

These new radio-elements, mesothorium and radiothorium, are of commercial and technical value, like radium. For although not nearly so long-lived as the latter, they last sufficiently long to be very useful substitutes for radium, particularly for the manufacture of luminous paints for watches and the like, where the useful period of life is determined rather by that of the phosphorescent paint than of the radioactive substance incorporated with it. Being obtained as a bye-product from the residues of thorium minerals, enormous quantities of which are worked up to provide the thorium required by the gas mantle industry, the raw material is costless and practically unlimited in amount. But the extraction appears to be too costly to make the new radioactive substances, as was at one time hoped, a real rival to radium, which still enjoys a monopoly value. The half-period of mesothorium I is 6.7 years, of mesothorium II, 6.2 hours, and of radiothorium, 2 years.

After these new discoveries it began to dawn upon the radio-chemical world that Ramsay and Hahn had *not* separated radiothorium from the thorium minerals at all. What they had done was unwittingly to separate the still unknown mesothorium I along with the radium and barium. Then this, *in the course of time*, had produced the radiothorium which they ultimately obtained. It is easy to separate mesothorium from thorium, and radiothorium from meso-

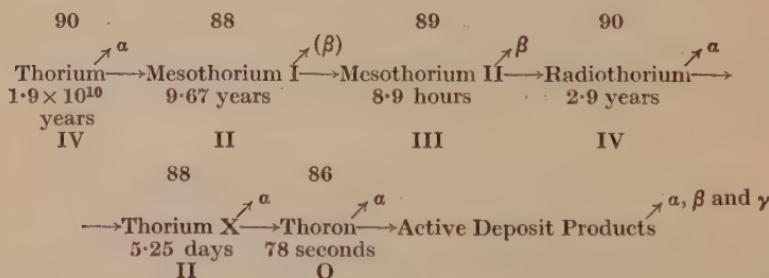
thorium, whereas it is quite impossible to separate radiothorium from thorium. The radiothorium separated is not that present in the mineral at all, as that of necessity remains together with the thorium. It is that subsequently grown from the mesothorium originally present in the mineral.

**Philosophical Implications.**—The philosophical interest and importance of this could hardly be exaggerated. A combination of two chemical analyses, and of appropriate waiting in between for a crop to grow, first revealed the existence of isotopes among the radio-elements, because they are in process of continuous spontaneous change. But when we come to deal with the common unchanging elements it cannot be applied. The only thing that can be averred with regard to these is that, if similarly, the ordinary elements are such mixtures of different chemical identities, the one thing certain is that the older methods of analysis would have failed completely to reveal their complexity. Strömholm and Svedberg in Sweden were the first to suggest such a general complexity of matter, concealed under a merely chemical identity of the different elements. They were the first also to try to fit all the disintegration series into the Periodic Table, though the attempt was then premature because of important lacunæ in our knowledge both of the numbers and of the chemistry of the various members. But, to do so, it was clear that many of the members had to be put into *the same place*. Thus, the three emanations must occupy the same place, and thorium, radiothorium and ionium another single place. To this extent they anticipated the modern doctrine of isotopes.

**Chemical Identity of Mesothorium and Radium.**—In 1910, yet another outstanding case of chemical identity revealed itself, for Hahn's mesothorium I proved to be chemically identical with radium. Since the first is a product of thorium and the second of uranium, and since the greater number of radioactive minerals contain both these elements in appreciable quantity, this means that the radium derived from them must necessarily be contaminated to a greater or less extent with mesothorium. The only way to get radium pure and free

from mesothorium is to start with a uranium mineral that is substantially free from thorium. It may be considered a singular chance that all Mme. Curie's original work on radium was derived from the pitchblende of St. Joachimsthal, which in this respect is easily the purest of known uranium minerals. By the same principles, the ionium separated from a uranium mineral must always contain the whole of the thorium originally in the mineral, ionium and thorium being inseparables. In the Joachimsthal pitchblende the quantity of ionium is almost the same as the quantity of thorium, so that from it one gets a fifty to fifty mixture of ionium and thorium. This makes it possible to calculate the actual amount of thorium in Joachimsthal pitchblende, and it proves to be only about fifteen parts per million of the contained uranium, a quantity quite below detection by any ordinary method of analysis. For this reason, radium to be used as standards of measurements should preferably be made from Joachimsthal pitchblende, as it is essentially free from mesothorium. The activity of the latter decays so rapidly that, if present, it would invalidate the standard.

**The Thorium Series.**—The thorium disintegration series, in which in 1902 thorium X appeared as the direct product of thorium (as shown on p. 28), has now to be extended by the discovery of these three additional intermediate members, and runs<sup>1</sup>—



A period of steady work on the chemistry of the numerous disintegration products followed, notably by A. Fleck in the

<sup>1</sup> The Arabic numerals are the Atomic Numbers (see p. 46), and the Roman numerals refer to the Families in the Periodic Table as shown in the Chart at the end of the volume. The times given are the periods of average life, which are 1.445 times the half-periods (see p. 68).

writer's laboratory at Glasgow, definitively to ascertain which known element each most resembled, and whether or not it was chemically inseparable from that element. As methods were developed to examine the shorter-lived bodies, more and more were found to be inseparable from other known elements. Uranium X and radioactinium proved to be inseparable from thorium; thorium X and actinium X from radium; mesothorium II from actinium; the B members of the active deposit groups and also radium D from lead; the C members and also radium E from bismuth, none of those examined having a chemistry entirely new.

**The Displacement Law.**—So soon as the very complicated sequences of changes were sufficiently unravelled, and the chemistry of the successive products sufficiently studied, a very simple and comprehensive generalisation was found to connect the type of change the radio-element undergoes—whether an  $\alpha$ -ray change or a  $\beta$ -ray change—with the chemical character of the product. It is now known as the Displacement Law. As regards the  $\alpha$ -ray change it dates from 1911, when it was pointed out by the author that the product in this case has the chemical nature of the element *two places preceding* the parent in the Periodic Table. The complete generalisation dates from February, 1913, when K. Fajans in Germany, and A. S. Russell and the author in this country from the results of Fleck's researches already described, all independently extended the generalisation to the case of  $\beta$ -ray changes. So extended, it fitted the whole of the known disintegration series into the Periodic Table without any definite exception. In the  $\beta$ -ray change the product has the chemical nature of the element *one place after* the parent in the Periodic Table.

A chart exhibiting this simple generalisation is given at the end of the volume, but the details may be left for the present. Its general character will be obvious from a few examples already discussed. Taking first the  $\alpha$ -ray change, the Displacement Rule explains at once how mesothorium I, the product of thorium in the IVth family of the Periodic Table, by an  $\alpha$ -ray change, must come into the place occupied by radium in the IIInd family, and how radon, the product of radium in an  $\alpha$ -ray change, must come into the Zero family

of inert gases. As regards  $\beta$ -ray changes, the product of mesothorium I in the IIInd family, mesothorium II, must be in the place in the IIIrd family between thorium and radium, which is occupied by actinium, and, since mesothorium II undergoes a second  $\beta$ -ray change, its product, radiothorium, must be in the place in the IVth family occupied by thorium.

Thus from the type of ray expelled we may at once predict the chemical nature of the product, and *vice versa*. Many such predictions were at once made from the generalisation and confirmed by experiment, so that all the lacunæ in this part of the subject were in 1913 cleared up in a flash. Thus it predicted that some of the members of the active deposits must be chemically identical with thallium, and so it proved. The advances so made were of paramount interest and importance to the subject of radioactivity proper, as will be dealt with in the sequel. But the real advance was on a far wider front. For the Displacement Law explained in the simplest and most direct manner that veritable cryptogram, the Periodic Table itself.

The  $\alpha$ -particle carries two elementary atomic charges or units of positive electricity, and its expulsion from the atom reduces the positive charge of the atom by two units so that it occupies a place in the Table two places preceding that occupied previously. The  $\beta$ -particle is the electron or atom of negative electricity, and its expulsion from the atom reduces the negative charge by one unit—which is the same, electrically, as increasing the positive charge by one unit—and the atom then occupies a place in the Table one place after that occupied previously. So that the successive elements in the Table differ from one another by the single atomic or unit charge of electricity. Going in the direction of increasing atomic weight, each place corresponds with one unit of positive electricity more than the last place.

We arrive at the fundamental conclusion that the successive places in the Periodic Table correspond with a succession of integers which represent, in a manner still to be elaborated, the numbers of unit positive charges of electricity in the atom of matter. The Periodic Law is itself nothing else but the most general consequence of the modern view that electricity is atomic. All of this in a general way was the obvious con-

clusion from the Displacement Law. But it was immediately linked up with and made precise by two notable independent developments that occurred respectively a little before and a little after, namely Rutherford's theory of the nuclear atom, and Moseley's researches on the wave-lengths of Barkla's characteristic X-rays of the chemical elements, still to be dealt with.

**Isotopes.**—According to the Displacement Law, after one  $\alpha$ - and two  $\beta$ -ray changes, in any order it is "As you were" with regard to the chemical character. We get back again, after an  $\alpha\beta\beta$  triple change in any order, into *the same place* in the Periodic Table as we started from, and, whenever this occurs, the product is chemically inseparable from and identical with its great-grandfather. The product of the  $\alpha\beta\beta$  triple change is the isotope of the original parent, the word *isotope* being coined for this purpose as meaning simply "the same place." As such triple changes are frequent in the disintegration series we have at once the explanation of the curious atavism displayed by so many of the products, and their tendency to revert in chemical character to that of a previous member of the series, which at first seemed so puzzling and difficult to explain. Or, we may put it another way. The passage of the series through the Periodic Table is not straightforward but alternating, so that in the same series the same place may be passed through more than once.

Remembering that the most skilled chemists have absolutely failed by any method of chemical analysis, not only to separate any mixture of radioactive isotopes, but even to effect the slightest change in the proportion in which they are mixed, under conditions when even a slight alteration could readily be detected by radioactive measurement, these results clearly established a most important result. The chemical character of an element is entirely determined by a particular integral value representing in some way the nett positive charge of its atom, irrespective of its mass. After the triple  $\alpha\beta\beta$  change, the mass of the atom is reduced by four units, but its nett charge is unaffected. Again, mesothorium I is isotopic with radium, though the former, being produced from thorium of atomic weight 232 by loss of a helium atom, has an atomic

weight 228, whereas the latter is produced from uranium and has the atomic weight 226, two units less. Nevertheless, two such totally different elements are to the chemist identical and would be considered, but for their radioactivity, to be the same element.

The identity of the properties of isotopes is not confined to their chemistry. It extends also to all the usual physical criteria used for their characterisation, such as the melting-point and boiling-point of the element and its compounds, and to the ordinary arc, spark and X-ray spectra. But it does not extend to any physical property or constant—such as the density, the rate of diffusion and so on—which depends directly upon the mass of the atom or the molecule, unless, of course, it happens that the atomic weights of the isotopes are identical, that is to say that they are “isobaric” as well as isotopic. Most curiously, isotopes can be distinguished by their band spectra, since this, in contradistinction to the arc and spark spectra, is a molecular and not an atomic phenomenon and depends on the mass of the molecules. The wavelengths, or frequencies, of the bands are a function of the mass of the vibrating molecule producing them. Indeed, isotopes might have long ago been experimentally recognised by this property, but that formerly band spectra attracted little attention and interest in comparison with the spark, arc and X-ray spectra. Actually these advances much assisted the development of the theory of spectra (Chapter XIV) and were a necessary preliminary to it.

**The Nuclear Atom.**—This great clarification of the whole subject and the important new light it threw on the nature of the elements and the structure of matter, although first and most directly revealed by the Displacement Law, was supported by and in agreement with other more physical lines of speculation and experiment which converged in 1913 to the same broad conclusions. In the first place, Rutherford, in 1911, from experimental investigation of the trajectories of the  $\alpha$ -particles as they pass through the atoms of matter in their path, had tentatively put forward the well-known nuclear theory of atomic structure which still holds the field. The fact that an  $\alpha$ -particle can plough through millions of atoms

in its way, as though they were not there, without being deviated appreciably from its straight path, was discovered quite early by Sir William Bragg. But very occasionally the  $\alpha$ -particle may suffer a violent deflection and even be turned back the way it came. This pointed clearly to the atoms of matter being very open or empty structures with very minute but massive centres or nuclei. On the nuclear theory, a central highly charged nucleus, consisting of practically the whole mass of the atom, was supposed to be surrounded with concentric rings or shells of individual electrons, equal in number and opposite in sign to the charge of the central nucleus. This division of the atom, which is electrically neutral, into two separate parts, nucleus and shell, equally and oppositely charged, *both* of which charges vary unit by unit, in passing from one element to the next in the Periodic Classification, is the most essential feature of the Rutherford atom.

**The Nature of X-rays.**—Next, the discovery in 1912 by Laue, Friedrich and Knipping of Zurich, that the X-rays can be diffracted by natural crystals, very much in the same way as light is diffracted by a grating ruled with a plurality of fine parallel and equidistant lines, in due course completely elucidated the nature of the X-rays and also of the  $\gamma$ -rays. This showed them to be in all essential respects the same as light, but of frequency some thousands of times greater, and wave-lengths thousands of times less, than visible light. An X-ray spectroscopy, in all respects the counterpart of that of ordinary light, immediately developed, and was employed to determine the wave-length and frequencies of the X-rays.

Now in this field Barkla had already in 1908 shown the existence of a type of X-ray fluorescence of a highly important character. Every individual element when irradiated by X-rays, provided they are "hard" or penetrating enough for the purpose, *itself* emits a secondary or fluorescent X-radiation which is characteristic, not of the exciting ray, but of the chemical element. These characteristic X-rays of Barkla are homogeneous in quality. On the wave-theory, this means that they have characteristic wave-lengths, just as, for example, the  $D_1$  and  $D_2$  doublet in the yellow region of ordinary light is characteristic of the element sodium.

In December, 1913, Moseley determined the wave-lengths, or frequencies, of Barkla's secondary X-rays, for a number of successive elements in the Periodic Table. He discovered that they are simply related to the square of the integer which represents the place of the element in its order of sequence in the Periodic Table, beginning with hydrogen as unity, and going on to uranium as 92. Moseley, as it were, called the roll of the elements, so that for the first time we could say definitely the number of possible elements between the beginning and the end, and the number that still remained to be found.

**The Atomic Number.**—This integer is now called the Atomic Number. It is at once the nett value of the positive charge of the nucleus of the atom, and the number of the individual negative electrons that circulate in the outer system and neutralise this central positive charge. Whereas ordinary spectroscopy is concerned only with the outermost ring or shell of the electrons surrounding the nucleus, X-ray spectroscopy is concerned with the charge on the positive central nucleus. Ordinary chemical changes also are to be ascribed only to the outermost electrons in the atom. But in radioactive, as in any real transmutational change, it is the nucleus that changes. By each expulsion of the  $\alpha$ -particle from the nucleus, the Atomic Number, fixing the place of the element in the Periodic Table, suffers a reduction by two, while each  $\beta$ -particle expelled causes it to increase by one.

Thus, isotopes are simply elements with the external shells of electrons identical, because the nucleus in them has the same *nett* positive charge. But the nuclei are different, either in the gross number of the charges, + and -, contained in it, which causes their masses to be different, or, at least as a theoretical possibility, in the way in which the charges are structurally arranged. Isotopes may thus be colloquially described as elements, the atoms of which have similar outsides but different insides.

**Integral Atomic Weights and Prout's Hypothesis.**—Once the existence of isotopes had been revealed through the course of radioactive changes, it was natural to ask whether they did

not exist among the common elements. At first, all that could certainly be said was that if any of the common elements were really mixtures of isotopes of different atomic mass, the chemist, at least, would not have recognised it by his methods of analysis. At the same time, there were good reasons to believe that the discovery of isotopes might clear up naturally an exceedingly curious unexplained peculiarity about the atomic weights.

Prout's hypothesis, which was put forward at the beginning of last century, that all the elements are built up out of the condensation of hydrogen, would make the atomic weights integers in terms of that of hydrogen as the unit. Indeed, it was the desire to put this to a conclusive experimental test that underlay the long series of more and more accurate determinations of the atomic weights, which began with the classical determinations of Stas (1840), and for which last century was specially distinguished. The results were exceedingly curious. In the first place the fundamental ratio of the atomic weights of hydrogen and oxygen was against the view, for oxygen was found to be 15.88 if hydrogen is unity, or hydrogen is 1.00775 if oxygen is 16.

But, as accurate values were obtained for more and more of the elements, it was found that a large proportion of those known to the highest degree of accuracy were practically integral values in terms of oxygen as 16, though not in terms of hydrogen as unity. This is naturally the more likely to be true for the lighter elements. In the heavier, a whole integer may be only a fraction of 1 per cent. of the value, and, to test this point for these, much greater accuracy must be attained than is required for the lighter elements. Eight out of the first sixteen elements besides oxygen have practically exact integral values on the O=16 standard. They are helium, 4; carbon, 12; nitrogen, 14; oxygen, 16; fluorine, 19; sodium, 23; aluminium, 27; phosphorus, 31; and sulphur, 32. While some of the others, notably magnesium, 24.3, and chlorine, 35.45, depart from the integral value beyond all possibility of the deviation being due to error of experiment. Mallet in 1880 had calculated that the probability of this approximation to integral values being due to chance was over 1,000 to 1 against.

## ISOTOPES

So that, in a modified form, with oxygen, 16, or helium, 4, as the standard, Prout's hypothesis fitted about half of the best-known atomic weights. The probable explanation was made obvious by the discovery of isotopes. For the integral values would correspond to those elements which were homogeneous, and the fractional values to those that were mixtures, being then merely a mean value of the various individuals in arbitrary proportions. So it has proved, except for hydrogen itself and for bromine, an element with an atomic weight on the oxygen standard of almost exactly 80, but really a mixture in practically equal proportion of atoms of weights 79 and 81.

**Analysis of Elements by Thomson's Method.**—It is the superlative merit of Thomson's classic method of determining the mass of a charged particle that it would not, in the case of a mixture of particles of different masses, give the mean value, as all the chemical methods do, but the individual masses of the several varieties. The newer method is one of the very few experimental ways of looking for isotopes among the ordinary elements. After the original determination of the mass of the electron, Thomson took up the study of the positive rays by the same method. These rays can be got in the vacuum tube by the use of a perforated cathode. The positively charged particles, being attracted to the cathode, then in part go through the perforations and may be studied in the space behind the cathode. They were discovered by Wien and shown, by the effect of magnetic and electric fields upon their trajectories, to consist of positively charged particles never less in mass than the hydrogen atom. Already the atomic masses of several of the gases commonly occurring in the vacuum tube had been so determined, when, in 1913, Sir Joseph Thomson and F. W. Aston, examining neon by this method, found two groups of particles. The main group had a mass corresponding to 20, on the oxygen standard, and the other, very much weaker, to a mass of 22. The actual atomic weight of neon, determined from its density, is 20.2.

This was the first of a most striking series of successes in the discovery of isotopes among the common elements. After the War, Aston, improving the accuracy of the original method almost beyond belief, made of it the means for the determina-

tion of the individual isotopic weights even more accurately than the finest atomic weight determinations by chemical methods. He proved that the majority of the common elements so far examined are heterogeneous and consist of from two to a round dozen of isotopes, which differ in weight among themselves as much as 10 per cent.

But perhaps the most interesting and important result was to show that the values of the separate isotopes were integral, on the oxygen=16 standard, to a very high degree of approximation. However, to the newer and later determinations, a small but systematic departure has been established. Beginning with hydrogen, where the departure is greatest, being 7·75 parts per thousand in excess, it becomes steadily less and, in the middle of the series, reaches a minimum, about one part per thousand in deficit. Then the opposite occurs, so that for atomic weights in the neighbourhood of 200 the values become exact integers again. This may well prove to be one of the most important discoveries of the present century. For it is connected (up) with the Einstein principle of the equivalence of mass and energy, and these minute variations may in reality prove the measure of the internal energy of different elements, and of their relative stability to transmutational changes.

**Imagination versus Experiment.**—Thus, during the twentieth century, Nemesis has overtaken the most conservative of the sciences. The evidence that seemed to the nineteenth-century chemists so conclusively to disprove this facile speculation concerning the constitution of the elements, has now swung like a pendulum in exactly the opposite direction. Becquerel's observation, concerning some new rays given out by uranium, has not only led up to transmutation as an actually occurring natural process. It has shown that the methods of chemistry are inadequate to resolve into their constituents simple mixtures of different elementary things, which, once they are resolved, disclose integral relationships to exist between their atomic weights and, presumably at least, the nature of their internal structure.

So that after many vicissitudes and the most convincing apparent disproofs, the hypothesis thrown out so lightly by

Prout, an Edinburgh physician, in 1815, has, a century later, become the corner-stone of the modern theories of the structure of the atoms. Even in science, though not often, it happens that the prize is not always to the accurate, meritorious and deserving investigator, fully equipped and disciplined for the work in hand, but to the imaginative tyro. There is something, surely, akin to if not transcending tragedy in the fate that has overtaken the life work of that distinguished galaxy of nineteenth-century chemists, rightly revered by their contemporaries as representing the crown and perfection of accurate scientific measurement. Their hard won results, for the moment at least, appear as of as little interest and significance as the determination of the average weight of a collection of bottles, some of them full and some of them more or less empty. While upon a mere amateur, with natural imagination untrammelled by knowledge, descends the laurel crown of undying fame. The names of Marignac, Stas, Mallet and E. W. Morley, which the nineteenth-century chemists held up as examples to all who preferred experiment to speculation, may one day even be completely forgotten, while that of William Prout, so long as knowledge lasts, is certain of remembrance.

## CHAPTER IV

### HELIUM AND RADIOACTIVITY

**Some Early Problems.**—Naturally the recognition in 1903 that the radio-elements were undergoing transmutation raised a host of contingent questions as to how such apparently continuous and inevitable processes could be maintained over cosmical epochs of time. It was clear from the first that radium, for example, was changing too rapidly for the radium now in existence to have been that left over from an original store in the earth “when it was made.” The radium must be continually being reproduced in some process, or, long ago, it would all have disintegrated. But as regards the primary parent elements, uranium and thorium, the same question may of course be raised. Here, however, it was known that the rates of change are excessively slow, and that it would take thousands or ten thousands of millions of years for one-half of these primary elements to change. At that time, the highest estimates of the age of the earth were only of the order of hundreds of millions of years. So that, over this period at least, there was no immediate necessity for supposing that uranium and thorium are being reproduced in the earth in some still unknown process of atomic synthesis, complementary to radioactivity. Radioactivity itself was, in due course, to extend the geological time scale, and to show that some of the rocks of the earth are probably of the order of between one and two thousand million years old.

The question of the origin of the primary radioactive elements, uranium and thorium, and their possible continuous reproduction in some still unknown process, belongs to the same category as the insoluble problem of the creation generally, and so far there has been little if any progress made towards an answer. As regards radium, however, the case is entirely different. For there was good reason to believe from the very first that it was a long-lived product of the uranium series and that the break-up of uranium was the

source of radium, just as the break-up of radium is the source of radon. This was one of the first direct experimental tests of the correctness of the transmutation theory of radioactivity which the author attempted. But because of the intervention of the long-lived ionium between uranium and radium, as already mentioned, it was about the last to yield a positive result. This work has now been completed, but it is convenient to defer its more detailed consideration till the next chapter.

**Discovery of Argon.**—However, in 1903 there was an even more interesting possibility to be tested, which referred to the solar element helium, then newly discovered upon the earth. It came as an appropriate ending to a long series of discoveries, probably unsurpassed in dramatic interest and importance in the whole history of experimental science, and it was to furnish the first convincing and irrefutable evidence of the actual transmutation of one element into another by methods well known and practised long before the discovery of radioactivity.

The story really begins in the eighteenth century, with the work of the celebrated English chemist, Henry Cavendish, in 1785. For after Lord Rayleigh and Sir William Ramsay had discovered argon in the air in 1905, a search of the earlier literature by the latter revealed the astonishing fact that Henry Cavendish, 120 years before, had not only separated argon from atmospheric nitrogen by a method identical with that used by Rayleigh, but had determined fairly accurately its proportion in the atmosphere, which is about one in one hundred and twenty by volume.

The method consists in passing electric sparks through a mixture of oxygen and nitrogen in presence of an alkaline solution, when the nitrogen combines with the oxygen to produce nitrous and nitric acids, which are absorbed by the alkali. Cavendish had noticed that, after the above process, there is always a small bubble of gas left behind that could not be further reduced in amount, and he remarked that "if there is any part of the nitrogen of the atmosphere, different from the rest, it is not more than  $1/120$ th part of the whole." It was almost certainly pure argon. The spectroscope being then

unknown, it is difficult to see what more he could have done, and his observation remained completely forgotten till unearthed by Ramsay after the discovery of argon.

This process was also the one used to test, in the most drastic manner possible, the conclusion already arrived at that radon is an argon gas. It is also the older of the two competing processes for the "fixation of nitrogen," used for the large-scale production from the air of nitrogenous fertilisers for agriculture. This is an industry which has developed since the discovery of argon, and it illustrates the short step in these days between purely philosophical experiment and profound world-shattering economic achievement. For the process serves as well to make explosives as fertilisers—to feed the growing multitudes in time of peace and to blow up the surplus in time of war—a thoroughly typical example of twentieth-century science as directed by minds still in the pre-scientific age. That neither fertilisers nor explosives are being made, that millions of capital sunk in this new industry lie idle, and that people wanting employment are both poor and idle, because of misconceptions or preconceptions, now almost puerile, regarding money, are cruel anomalies even more typical of this time of transition.

**Discovery of Helium.**—A second anticipation touches the subject more nearly. Hillebrand, a distinguished American mineralogist, to whom we owe practically all that was known of the uraninite minerals, prior to the discovery of their radioactivity, had obtained from them, by heating or solution in acids, a gas which he, most unfortunately, took to be nitrogen. He certainly proved the presence of nitrogen in it, both by chemical tests, such as the production of ammonia from it, and by the spectroscope. But the nitrogen was probably a small impurity only, derived from unavoidable atmospheric contamination during the manipulation. Professor, now Sir Henry, Miers directed Ramsay's attention to this work. Ramsay was at the time engaged in a fruitless attempt to make argon enter into chemical combination, and on the chance that Hillebrand's gas might really be argon in combination with the mineral, he repeated the experiment and discovered it to be helium.

So was literally run to earth an element which, as its name implies, was originally discovered in the sun by the aid of the spectroscope. Sir Norman Lockyer in 1868 had observed in the spectrum of the solar chromosphere a very characteristic yellow line, known as D<sub>3</sub>, very near to the well-known doublet D<sub>1</sub> and D<sub>2</sub> due to sodium, and on the green side of it about twice as far from D<sub>2</sub> as D<sub>2</sub> is from D<sub>1</sub>. No terrestrial element gave such a line, and it was ascribed to a new hypothetical solar element christened helium. After being discovered in the gas given off by the uranium minerals, helium proved to be one of the most interesting elements. It has a brilliant bright line spectrum, the D<sub>3</sub> line being visually the most prominent. It is the second lightest gas known, being only twice as dense as hydrogen. Like argon it possesses no power whatever of forming chemical compounds, so that the molecules for all the gases of this zero group are monatomic, that is, they consist of single atoms, whereas most of the common elementary gases like oxygen, hydrogen and nitrogen have two atoms combined together to form the molecule. As density is proportional to the molecular weight, the single atom of helium weighs twice as much as the single molecule, that is two atoms, of hydrogen, so that the atomic weight of helium is approximately four times that of hydrogen. On the oxygen standard (O=16) the atomic weight of helium is almost exactly 4.

**Properties of Helium.**—After its discovery in the uranium minerals helium was found to exist, along with the remaining members of this family subsequently discovered, neon, krypton and xenon, in the atmosphere, though only to the extent of 4 parts in a million. Owing to its complete non-inflammability and lightness, as is everywhere now recognised after the tragic fate of the airship R 101, it is the ideal gas for balloons and airships. But it is one of the rarest of gases. It was, however, found in 1907 to be present in fair quantity in many of the natural gas sources of the United States, particularly in Kansas and Texas, some of the richest of these containing up to nearly 2 per cent. During the War, technical processes were worked out for its extraction from these gases, and it was produced by the million cubic feet for

military airships. Now these processes have been so perfected that there are some prospects that it will become cheap and plentiful enough for commercial aircraft in lieu of hydrogen. A source containing no less than 7 per cent. of helium has been found in Colorado, and a plant installed which, it is estimated, should yield an annual production of twelve million cubic feet of helium. The gas has proved to be of the utmost scientific interest and importance because it is, of all gases, the most difficult to liquefy by cold and pressure. This was successfully accomplished by Kammerlingh Onnes of Leyden University in 1908. Since then a new and almost incredible world has opened up. By the use of liquefied helium, temperatures within a single degree of the absolute zero of temperature have been reached, that is below  $-272^{\circ}$  C. At this extreme cold some metals, such as lead, seem to lose their electric resistance practically completely. An electric current once induced in a ring of such a metal at this temperature may continue for hours at undiminished strength and may require a year before the energy is dissipated. Some substances, the diamond being the most notable, at these lowest temperatures, have no appreciable specific heat. Paradoxically enough, it requires no appreciable heat to heat the diamond from the temperature of absolute zero to a temperature  $20^{\circ}$  above it! This is one of the main facts which the new theory of energy quanta has explained (see Chapter XIII).

**Helium and Radioactivity.**—Ramsay, seeking for helium in other minerals, found it only in those that contain uranium or thorium, and in 1902 the very matter-of-fact question as to how the gas comes to exist in such minerals remained unanswered. It forms no compounds, it is the most non-condensable of gases, and, once liberated from the mineral by heat or solution, it cannot be got back again. A mixed uranium-thorium mineral discovered about this time in Ceylon, and called thorianite, contains helium to the extent of no less than seventy times the volume of the mineral, measured after liberation at ordinary temperature and pressure. If the mineral was not there and occupied none of the volume, the pressure exerted by the gas would be 70

atmospheres, and actually it must be very much greater than this.

The disintegration theory of radioactivity at once suggested what proved to be the correct answer to this enigma, namely that helium is one of the ultimate stable elements produced in the break-up of uranium and thorium. It also was possible to make a shrewd guess, which was later substantiated, that the  $\alpha$ -particle expelled from the radioactive substances is a helium atom with two positive charges, *i.e.*  $\text{He}^{++}$ . Hitherto the sole method of detecting the new transmutational changes of radioactivity had depended upon the energy involved. Whereas the task of looking for the ultimate products is, as already indicated, analogous to hunting for a meteor after having observed it flash through the heavens.

Now the radioactive minerals are usually very complex. In pitchblende, for example, more than one-half of the known elements exist, naturally for the most part in minute quantity. But the occurrence of helium therein is so remarkable that the only reasonable explanation seemed to be that, during the course of ages, it had been *produced* in the mineral *in situ*, and, because of its glassy nature, had been unable at least completely to escape. It was possible to suspect one other element, namely lead, as such an ultimate product, especially after the question had been more closely examined. For clear evidence was obtained for the uranium minerals by Boltwood that the older the geological horizon from which they are obtained the greater the proportion of lead to uranium. But for thorium, owing to its rate of change being some five times slower than that of uranium, and its efficacy as a lead producer in geological time being correspondingly less, the evidence was quite equivocal until the problem was neatly solved by the discovery of the Displacement Law. This is one of the detailed advances following that discovery which has still to be dealt with.

In 1903 Rutherford had already made sufficient progress in his attempts to deviate the  $\alpha$ -rays to have shown that these consisted of positively charged particles of the same *order* of mass as the hydrogen atom. Actually these methods determine not the mass but the ratio of the mass to the charge of the particle, and this *ratio* for the  $\alpha$ -particle was twice as

great as for the hydrogen ion  $H^+$ . But if, as was subsequently proved to be the case, the charge carried by the  $\alpha$ -particle is double that carried by the hydrogen ion, its mass would be four times that of hydrogen, in agreement with that of helium.

In 1903 pure radium compounds were being put on the market by Dr. Giesel of the Chinin Fabrik, Brunswick, and with such it appeared quite feasible to try whether helium in sufficient quantity to be detected by the spectroscope was being continuously generated. The minute quantities of radium available, some 30 milligrams of the hydrated bromide, represent the concentrated radioactivity of a millionfold greater quantity of mineral. So that, slow as the change of radium is—only 4 per cent. per century—it was calculated that the spectroscope would detect the helium generated by a few milligrams of a pure radium compound in the course of a few days.

**The Production of Helium from Radium.**—The author was then working with Sir William Ramsay in his laboratory in the University College, London, in order to obtain his adhesion to the view that the radioactive emanations are argon gases. That being accomplished, it was natural to see if radon, by the aid of the micro-methods of gas-manipulation which he had devised in his work on xenon, existed in quantity sufficient to show its spectrum, and further whether the helium that it, as well as radium, might be expected to give off as  $\alpha$ -particles could be detected by these methods.

From 10 to 15 milligrams of radium (element) in the form of hydrated bromide was used for the work. Giesel had made the interesting discovery that the water of crystallisation of the salt, under the intense bombardment to which it is subjected by its own rays, is rapidly decomposed into its constituent gases, hydrogen and oxygen. The same, naturally, occurs when the radium is kept in aqueous solution. The apparatus, used in the first experiment in which the production of helium from radium was established, is shown in Fig. 12. The radium bromide was put into the little bulb, A, which was then sealed to the bulb with two taps, B, exhausted of air, and the tap between A and B closed. Water was put

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into B and the whole sealed at N to the rest of the apparatus. This comprised an ordinary gas burette, G, containing oxygen, for freeing the apparatus from air prior to exhaustion; a tube, C, containing an oxidised copper spiral, which could be maintained at a red heat by a battery; a tube, D, containing phosphorus pentoxide to remove moisture; a U-tube of capillary

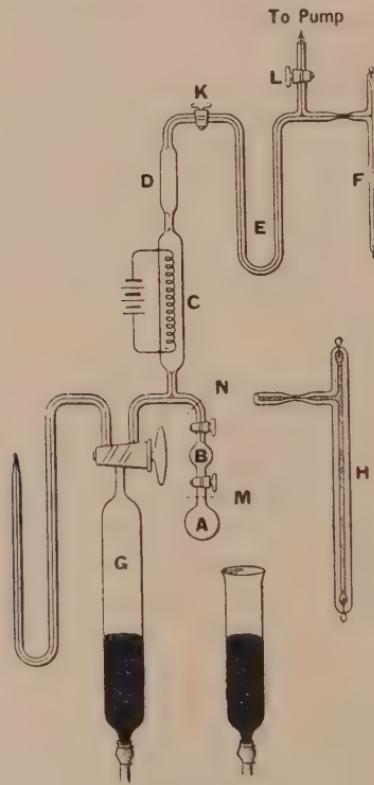


FIG. 12.

bore, E, which could be cooled by liquid air; and lastly the tiny spectrum tube, F, shown separately at H, made entirely of capillary tubing. The spectrum tube was made of the least possible volume in order that the very smallest possible quantity of helium might have the best chance of showing its spectrum. The apparatus having been "washed out" with oxygen from G and exhausted by a mercury pump through L, the tap between A and B was opened, that at K being shut.

The radium bromide dissolved with effervescence, and the gases evolved were submitted to the action of the hot copper spiral in C, whereby the hydrogen and oxygen were converted into water, which was absorbed in D. This accomplished, the tube C was cooled, and the tap L to the pump was shut and K opened, E being in liquid air. This condensed carbon compounds and radon, and the gas surviving passed into the spectrum tube F, mercury being admitted from the burette till all the gas was got into E and F. The tube F was sealed off and its spectrum cautiously examined by sending a feeble discharge through it from an induction coil, and observing the glow with a suitable spectroscope.

A photograph of the actual spectrum tube used is shown in Fig. 13 (facing p. 60). In the very first experiment, although the helium present could have only been a small part of that produced by the radium since it was made, being only that part which was occluded or stored up in the solid compound kept in an open capsule, sufficient was present to show the well known D<sub>3</sub> line of helium beyond any doubt.

**Production of Helium from Radon.**—The next experiment was even more crucial. The procedure here was different. Instead of collecting the gases generated by radium and examining these for helium, radium solution was left until the radon was in equilibrium amount, and then the gases generated were pumped off and freed from every other gas but radon, including helium, by condensing the radon in liquid air and exhausting with the pump. The pure radon then was got into a spectrum tube similar to that illustrated and sealed off. Any initial helium naturally would be removed, as helium is not condensable at liquid air temperature. It was hoped that the pure radon would be present in sufficient quantity to show its spectrum. A fleeting glimpse of a new spectrum was observed many times with the freshly prepared spectrum tube, but the real spectrum of radon was not properly established till some years later, by experiments with some twenty times as much radium as in this experiment. After the fleeting glimpse, the spectrum became simply that of hydrogen and carbon compounds, which always form the residual spectrum of a tube containing so

little gas that it will hardly pass the discharge, and which are given out by the electrodes and walls of the tube itself under the intense electric strain.

The spectrum given by the tube containing radon was examined from day to day, as the radon changed by its natural disintegration. In four days, when about one-half of the radon present had disintegrated, the well-known  $D_3$  line of helium made its appearance. On the following day it was accompanied by other well-known helium lines, and the tube soon showed the characteristic complete helium spectrum. Thus for the first time the actual birth of one element from another was observed by methods well known to science before the discovery of radioactivity. As the radon in the tube decayed, the radium from which it was derived produced a fresh crop of radon, and the same experiment was repeated again and again, proving the continuous production of the element helium from the element radium. Later, with the very much larger quantities of radium that became available, the work was repeated by many observers.

Fig. 14 is an actual photograph of the spectrum of the gas from radium by Dr. Giesel. The two middle strips represent long and short exposures, the upper being the spectrum of helium and the lower the spectrum of hydrogen, photographed in juxtaposition for comparison. In the photographs the blue and violet lines of helium appear far more intense than the visually most brilliant yellow line  $D_3$ . Some hydrogen lines are also present, but these are almost always observed in spectra taken under these extreme conditions, as already stated.

**Spectrum of Radon.**—The spectrum of radon itself was not satisfactorily determined till 1908, and for this purpose at least 100 milligrams of radium (element) are required. The gas, as the last member of the zero family of inert gases, exhibits pre-eminently the phenomenon, already well marked with xenon, of being rapidly absorbed by the walls of the tube under discharge, so that the latter soon fails to conduct the current at all. When it is considered that the maximum quantity of radon available from 100 milligrams of radium is only one-sixteenth of a cubic millimetre, or about four mil-



FIG. 13.—THE ORIGINAL SPECTRUM TUBE USED TO PROVE THE FORMATION OF HELIUM FROM RADIUM.

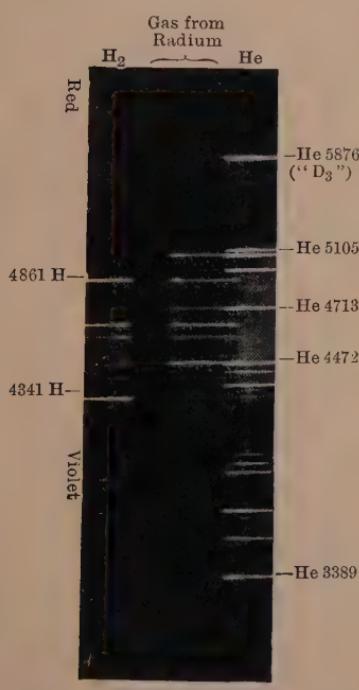


FIG. 14.—DR. GIESEL'S PHOTOGRAPH OF THE SPECTRUM OF HELIUM PRODUCED FROM RADIUM, III FOR FIVE AND II FOR TWENTY MINUTES EXPOSURE.

I is the spectrum of helium and IV that of hydrogen for comparison.

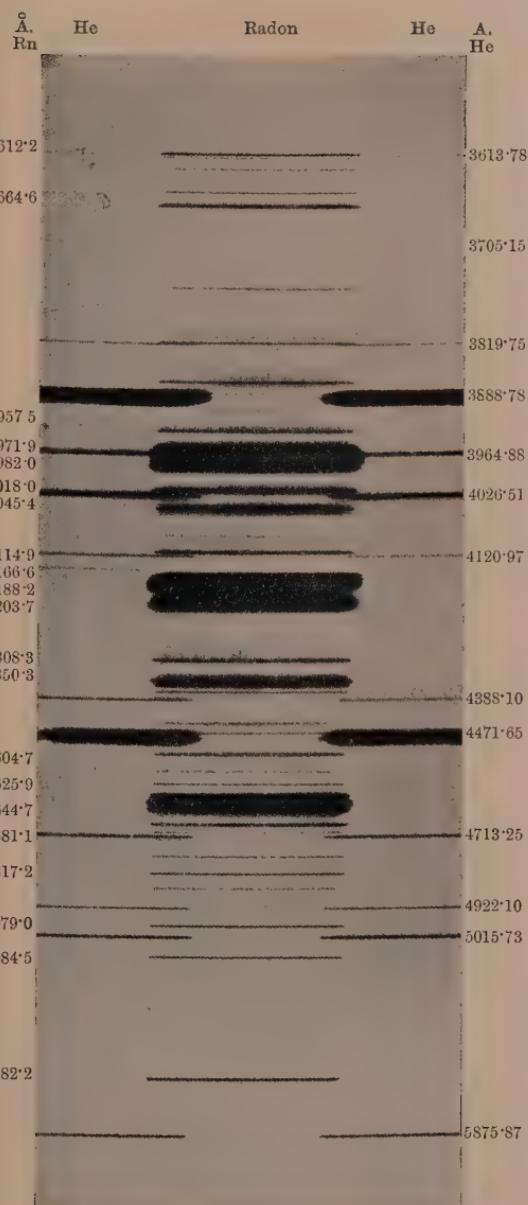


FIG. 15.—SPECTRUM OF RADON. BY RUTHERFORD AND ROYDS.



lionths of a cubic inch by volume, it will be appreciated that to photograph the spectrum satisfactorily is an arduous and difficult task, whereas helium is one of the most favourable gases to detect by the spectroscope in infinitesimal quantity. Hence Fig. 15, which shows a beautiful photograph of the spectrum of radon, with the helium spectrum on either side of it, and which was ultimately obtained in 1908 by Rutherford and Royds, may justly be regarded as a triumph of experimental manipulation and skill.

**Rate of Production of Helium and Radon.**—The same type of experiment, in which the volume of the helium generated in a known time by a known quantity of radium, or the volume of radon in equilibrium with a known quantity of radium, is exactly determined, enables the rate of change of radium to be experimentally found. The results by both methods, and many others less direct, are fairly consistent among themselves. The period of half-change of radium is known to an accuracy of 1 or 2 per cent. to be 1,600 years, and the period of average life (see p. 68) to be 2,300 years. The reciprocal of the latter gives the fraction breaking up in the year. This is so small that as yet no direct measurement appears to have been done, although for the radium preparations first made the decay of the radioactivity should now be just within the limits of measurement. As already stated, it is about 4 per cent. per century.

**Production of Helium from Other Radio-Elements.**—In due course, the production of helium from other radioactive elements which emit  $\alpha$ -radiation was experimentally observed, for actinium, polonium and ionium, by their respective discoverers, Debierne, Mme. Curie and Boltwood. The production of helium has also been observed, in the infinitesimal amounts expected from theory, for the primary radio-elements, uranium and thorium by the author, and for some natural uranium and thorium minerals by the present Lord Rayleigh, then the Hon. R. J. Strutt, the son of the discoverer of argon.

As such experiments well represent the almost incredible delicacy of the spectroscopic methods for detecting helium,

some description of the technique may be of interest. The actual quantity of helium to be detected is only a few parts per million million of uranium or thorium after a year, and it was found possible to get unequivocal evidence of

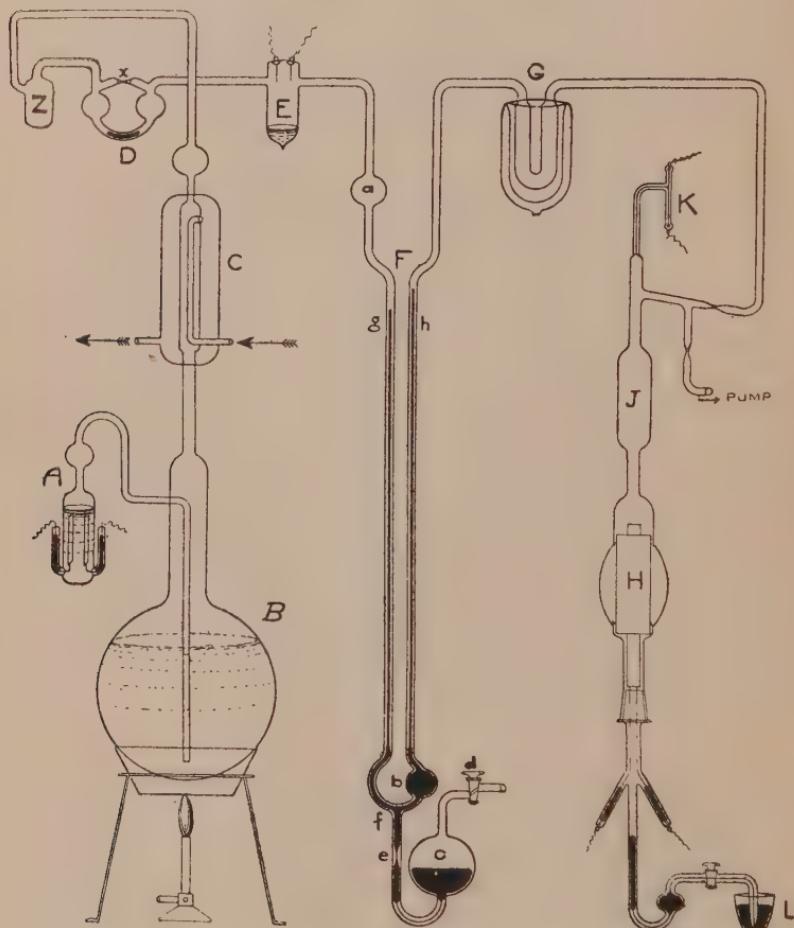


FIG. 17.

the production of helium from both these elements after a minimum of one month. The chief difficulty centres in the complete removal of air from the apparatus and from the large volumes of fluids used, as, with the methods employed, the argon in a pin's head volume of air would be sufficient completely to mask the helium spectrum. As the dissolved

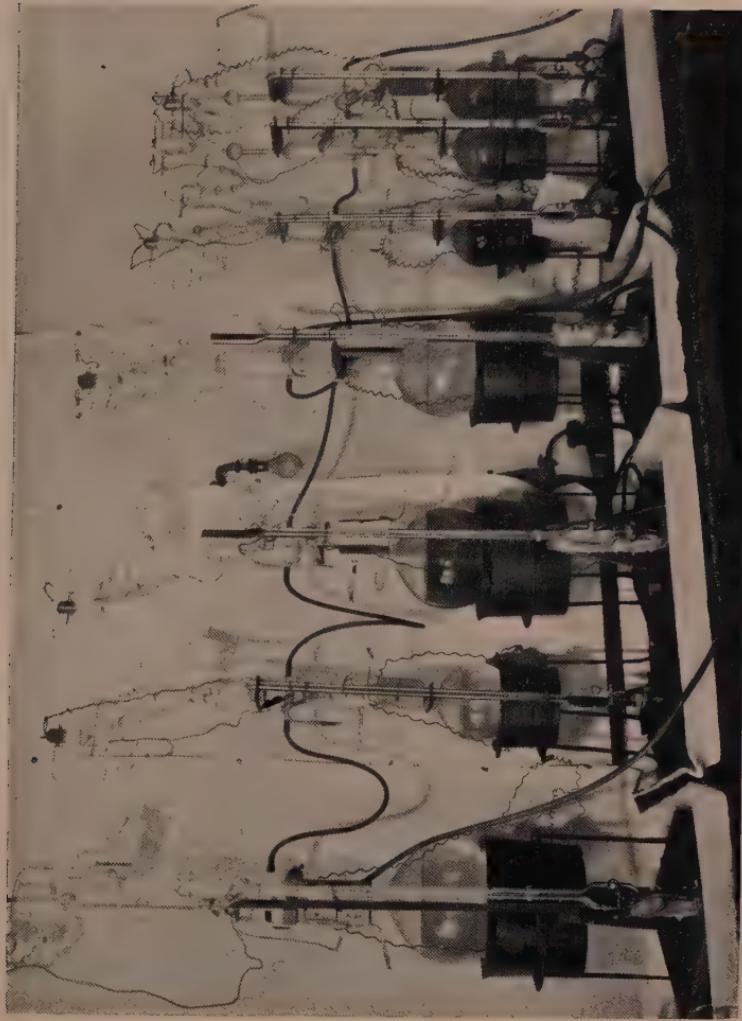


FIG. 16.—PHOTOGRAPH OF THE APPARATUS SET UP IN THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF GLASGOW TO DETECT THE PRODUCTION OF HELIUM FROM URANIUM AND THORIUM.



FIG. 22.—THE LARGEST URANIUM PREPARATION, USED TO PROVE THE GROWTH OF RADIUM FROM URANIUM.



gases are removed from the liquids by ebullition *in vacuo*, boiling becomes dangerously percussive, and to avoid this, a steady stream of hydrogen and oxygen, generated from a voltameter attached, was passed through the boiling liquid.

Fig. 16 shows a photograph of seven flasks set up in the Physical Chemistry Laboratory, University of Glasgow, and used in this work. Fig. 17 is a diagram of one of the arrangements, in which *A* is the voltameter in which water is electrolysed, the gases produced bubbling through the boiling liquid in the flask *B*. This is used both for sweeping out all the initial air, and, later, any helium that may have formed after leaving the substance to itself for a definite time. Steam is for the most part condensed in the condenser *C*. The gases arrive at the chamber *E*, where the hydrogen and oxygen are reunited to water by a hot wire or by passing a spark between the electrodes. *F* is a peculiar form of tap, which cannot leak, being a barometer column, and which is "opened" as required by attaching a pump to *d* and sucking down the barometer column below *f*.

The part of the diagram to the right of the tap *F* refers to the arrangements used to purify and test the gases accumulating. The metal calcium, which was first commercially prepared in the beginning of the present century, has the valuable property of absorbing every known gas, except the chemically inert argon gases, if volatilised at a red heat *in vacuo*. This is accomplished in the electric furnace shown at *H*, completely enclosed in the glass tube, the walls of which are protected from melting by an inner porcelain shield. *G* is a U-tube immersed in liquid air to freeze out water vapour. The whole of the right-hand side is freed from every trace of air by exhausting and "washing out" with pure oxygen, the connection with the pump is sealed off, the accumulated gases are boiled out and admitted by opening the tap, and the connection between the furnace and the apparatus is sealed off. The calcium is heated, and when the furnace is quite cold again, mercury is admitted from the vessel *L* at the bottom, and the total contents of the apparatus finally compressed into the tiny spectrum tube *K*. Accurate separate calibration experiments showed that one-millionth of a cubic centimetre of helium gas can be detected by the

spectroscope by these methods, and helium was observed to be produced at the expected rates from both uranium and thorium, when solutions of compounds of these elements were contained in the flasks *B*.

**Identity of the  $\alpha$ -Particle and the Helium Atom.**—Lastly, in 1909, there followed a direct proof of the identity of the  $\alpha$ -particle and the atom of helium by Rutherford and Royds. The former had satisfactorily proved that the mass of the  $\alpha$ -particle was four times that of the hydrogen atom and that it carried two unit or atomic charges of + electricity. This was done by directly counting a given number of  $\alpha$ -particles expelled from radium and measuring the total charge they carried, when it transpired, as had been foreshadowed, that each particle carries a double charge. The velocity at which the  $\alpha$ -particles are expelled varies for the different cases from  $1/15$ th to  $1/20$ th of the velocity of light, that is to say from 20 to 15 thousand kilometres a second. This is very much higher than for any other material projectile or particle known, and it confers on the  $\alpha$ -particle its unique properties. Owing to its relatively large mass it has nothing like the same penetrating power as the  $\beta$ -particle, which is an electron and not an atom of matter at all. But nevertheless the  $\alpha$ -particle does go clean through the atoms of matter in its path, almost as though they were not there. It has a definite penetration power, depending on the density of the material penetrated, and which, for a substance like glass, is of the order of one-thousanth of an inch. Glass tubes of capillary bore can be drawn so excessively thin in the wall that they will let the  $\alpha$ -particle go through. In most cases the thickness of the walls was less than  $1/2,500$ th of an inch. If such capillary tubes are filled with radon and held near to a screen of zinc sulphide, the  $\alpha$ -particles passing through the walls will cause it to fluoresce brilliantly, and this furnishes a simple test of the thickness of the walls. The definite "range" of the  $\alpha$ -particles, discussed more nearly in Chapter VII., can be well shown with such a tube, by varying the distance from the screen. Just within the range it will be brilliantly luminous, whilst when only a fraction of a millimetre further away there will be practically no luminosity at all.

The apparatus used in the experiment to show that the  $\alpha$ -particle is an atom of helium, by direct spectrum identification, is shown in Fig. 18. The fine capillary containing radon, A, joined to an ordinary thermometer tube, B, is fitted

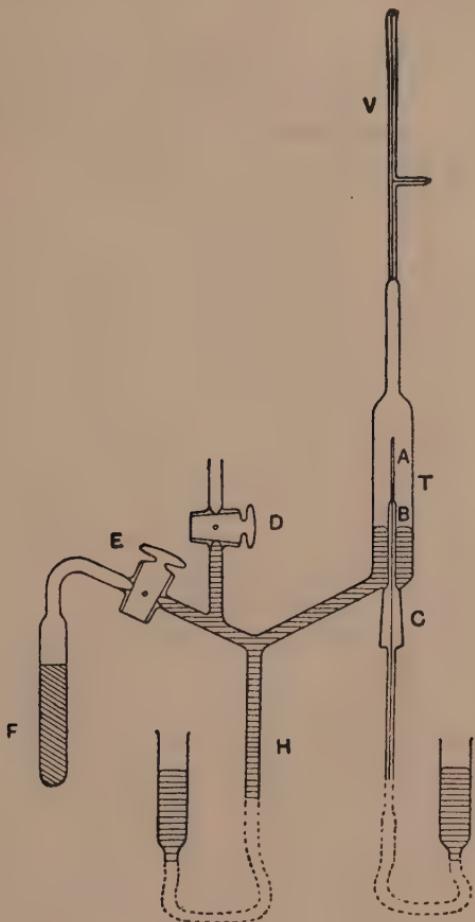


FIG. 18.

into the larger vessel, T, by a ground joint, C. The outer vessel, including the capillary spectrum tube, V, is very highly exhausted by the pump and by charcoal, in the bulb, F, cooled in liquid air, and then mercury is admitted from H to the level shown, and the apparatus left for some days for the radon in A to change. More mercury is then admitted

to compress the whole contents of T into the spectrum tube, V, and the spectrum is examined.

It was shown first by "blank experiments," in which A is filled with helium, that the walls are perfectly gas tight and that no helium leaks through into T. But when A is filled with radon and left some days, helium passes through into the outer vessel, T, and can be detected easily by the spectroscope after the contents have been compressed into V. This final experiment clinched directly the proof of the identity of the  $\alpha$ -particle with the helium atom.

## CHAPTER V

### THE URANIUM DISINTEGRATION SERIES. INITIAL PART

**The Amplification of the Uranium Series.**—In Chapter III. we saw how the completion of the thorium disintegration series (as far as thoron), by the discovery of mesothorium and radiothorium, led up to the recognition of isotopes. A somewhat similar amplification occurred in the first part of the uranium series, which is the subject of the present chapter. Although at first the uranium series looked simpler than that of thorium, it has in fact proved far longer and more complicated, both as regards the initial and the final parts. With regard to the initial part even yet some points of importance are inferred, rather than directly proved.

Looking backward over the course of its gradual unfolding, a very straightforward piece of work by Boltwood (1908) stands out as having thrown the greatest amount of new light on the problem. Boltwood separated all the known radioactive constituents which give  $\alpha$ -rays, by means of chemical analysis, from representative uranium minerals and directly determined for each constituent what proportion of the total  $\alpha$ -radiation of the mineral it contributed. This work may be considered as a further development of the type of researches already undertaken by the same investigator upon uranium minerals: firstly, the determination of the ratio between uranium and radium in minerals which established the constancy of proportionality between these elements, and secondly, the discovery of ionium, the direct parent of radium referred to on p. 36. They elucidate many essential points in the theory of radioactivity.

**Radioactive Equilibrium.**—The radioactive minerals as they occur in Nature are necessarily in the state of radioactive equilibrium to which reference has already been made (p. 28). Apart from the primary radio-element, uranium or

thorium, which is undergoing an exceedingly slow diminution in quantity in the course of geological time negligible for ordinary periods, each of the subsequent members of the series is maintained in existence by the disintegration of the preceding member of the series. Each is itself disintegrating, but, in the state of radioactive equilibrium, for each member of the series except the first, just as much is supplied as disappears, and the quantities of all remain constant, save for the exceedingly slow diminution over geological epochs, which affects all alike. In this condition the relative quantities of the various members of the series become proportional to their respective rates of change. Thus, when it was found that in all uranium minerals there is a constant proportion between the uranium and the radium contained in them—about ten million to three—not only was it almost conclusive, though indirect, evidence that radium was produced from uranium, but, from the ratio, it could be deduced that radium must be breaking up three and a third million times faster than uranium.

Similarly, by finding the exact proportion between the quantity of radon and radium when in radioactive equilibrium, which is 1:150,000, it was deduced that the half-period of radium is 150,000 times that of radon (3.83 days) or 1,600 years. By the former relation, this makes the period of half-change of uranium five thousand million years. It may here be mentioned that two periods are in common use by radioactive workers. Besides the period of half-change, the period of average life, which is uniformly greater in the ratio 1:1.443, is used. The period of average life is, as the name implies, the sum of the actual periods of life of all the atoms divided by their number. In this period the quantity of the substance is reduced to  $1/e$  of the initial quantity (where  $e$  is the exponential constant, 2.7183), that is to 0.368. Thus the period of average life of radium is 2,300 years according to the value accepted as most probable today. The advantage of using the period of average life, instead of the period of half-change, lies in the fact that it is the reciprocal of the rate of change. Thus the statement that the period of average life of radium is 2,300 years is identical with saying that the radium is changing at the rate of 1/2,300th part per annum.

**Analysis of the  $\alpha$ -Radiation of Uranium Minerals.**—Another consequence of the condition of radioactive equilibrium in minerals is that, if the disintegration series is straightforward —*i.e.* not branched or multiple—the same number of atoms of each of the members breaks up in the same time. It follows that in such a series, if each of the  $\alpha$ -ray-giving members expels one  $\alpha$ -particle per atom disintegrating, each, altogether regardless of its actual quantity, will contribute the *same* proportion to the total  $\alpha$ -radiation of the mineral. The greater activity, or rate of change, of the shorter-lived members is exactly compensated for by their proportionately smaller quantity.

Boltwood found this to be the case for the various radio-elements present in equilibrium in a pure uranium mineral, with two exceptions. The ionium, radium and polonium separated from the same amount of uranium mineral each gives the same number of  $\alpha$ -particles per second, but uranium itself is exceptional in that it gives twice this number. The other exception was the complete actinium disintegration series. In the course of this, five  $\alpha$ -ray changes occur, but, even taken all together, they make only a relatively unimportant contribution to the total  $\alpha$ -activity. This raised at once the whole question of the origin of the actinium series and its relation to that of the uranium-radium-polonium series, and this “Actinium problem” is still a hardy perennial that has not yet been completely solved.

**“The Actinium Problem.”**—There seems no doubt that actinium and all its products result from the disintegration of uranium. But, with the recognition of the existence of isotopes, that does not now necessarily signify, as it did before, that the radium series and the actinium series must have a common ancestor. So far actinium has only been found in uranium minerals, and actinium itself is relatively short-lived, the period of average life being only about 20 years. These two facts make it necessary to regard “uranium” as the first parent of both series.

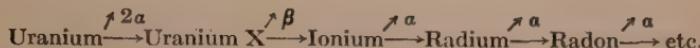
At first it was thought that, at some unknown point in the uranium series, a branch occurred, the major part of the atoms disintegrating to produce radium, etc., and a minor part

actinium. If this were so, some 97 per cent. of the atoms would have to take the radium road and only 3 per cent. the actinium road, to account for the very low proportion of  $\alpha$ -activity contributed by the latter in minerals. This was strongly supported by the subsequent discovery of actual cases of such branching in the later part of all three series among the active deposit products, that of thorium being the most notable. However, opinion today is strongly veering to the view—put forward by A. Piccard, the investigator who recently ascended ten miles in a balloon—that the actinium and the radium series are independent. On this view actinium results from an isotope of uranium, different from the main uranium isotope of atomic weight 238 which produces radium. The two isotopes, as has been proved for so many of the inactive elements, would, it is to be expected, occur together in Nature in constant proportions. This view has the advantage of making the actinium series completely independent of the main uranium series, and, from the point of view of exposition, less confusing to the reader. So that we can with a clear conscience banish the “Actinium problem” for the present, and concentrate on the main uranium series, a matter sufficiently intricate fully to monopolise a chapter.

**Uranium I and II.**—The fact that uranium gives two  $\alpha$ -particles per atom disintegrating proved to be the real beginning in the disentangling of the series. It is possible to detect experimentally the expulsion of single  $\alpha$ -particles, and several methods have been developed which enable the number of  $\alpha$ -particles emitted from a radioactive substance in a given time to be actually counted. These methods (see Chapter XVI.) had an elegant application in this question, for they were capable of deciding at once whether the two  $\alpha$ -particles from uranium are emitted simultaneously or not. In the former case, the  $\alpha$ -particles would be emitted in pairs, and, in observing single  $\alpha$ -particles from a uranium preparation, there should be a very much larger proportion of pairs of  $\alpha$ -particles than from other  $\alpha$ -ray-giving substances. But in this respect uranium proved to be no different from the other members of the series, thus proving conclusively that the two  $\alpha$ -particles must arise from two successive disintegrations of the atom.

This is now tantamount to saying that the two  $\alpha$ -particles must arise from two separate isotopes of uranium.

The Displacement Law at once cleared up this problem as it did so many others. Before it was discovered, the uranium series seemed to be represented as follows:



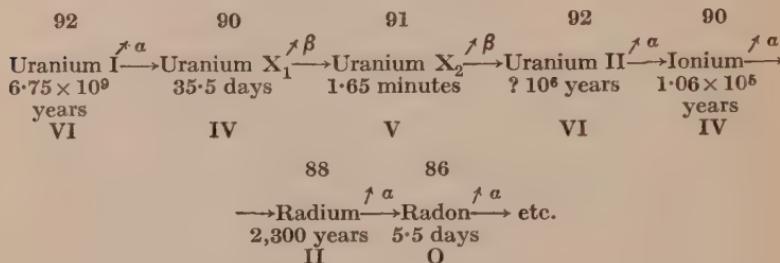
It was supposed that the two  $\alpha$ -particles were given out in successive changes, the original uranium, termed uranium I to distinguish it, emitting an  $\alpha$ -particle and changing into an isotope, uranium II, which then emitted the second  $\alpha$ -particle. But this does not conform to the rules. Neither does the representation of ionium as the direct product of uranium X do so, for both are isotopes of thorium in the IVth family (No. 90), and the product of uranium X in a  $\beta$ -ray change must be in the Vth family in the then still vacant place, No. 91, between uranium and thorium.

**The Amplified Uranium Series.**—To satisfy the rules it was necessary to suppose that uranium X, like mesothorium, really consisted of two successive substances analogous to mesothorium I and mesothorium II. Significant in this connection is the fact that uranium X gives two distinct kinds of  $\beta$ -rays—one very hard and the other very soft. Within a month, this prediction was verified experimentally by Fajans and Göhring, who separated “uranium X” by chemical methods into two substances. The first, which they termed uranium  $X_1$ , was the substance with the half-period of 24.6 days hitherto supposed to be homogeneous. But it gives only the soft or less penetrating rays. The hard  $\beta$ -rays of “uranium X,” they proved, come from the product of uranium  $X_1$ , to which they gave the name uranium  $X_2$ , or brevium. This has a half-period of only 1.15 minutes.

By the rules this body must be in the hitherto vacant place No. 91 in the Vth family, and its product must be an isotope of uranium in the VIth family in place No. 92. So that just as thorium reverts to an isotope of thorium, radiothorium, in the  $\alpha\beta\beta$  triple change, so uranium I reverts to uranium II. Since this second isotope, like the first, gives an  $\alpha$ -particle in

## 72 THE URANIUM DISINTEGRATION SERIES

disintegrating, not only do we account for the fact that each uranium atom appears to give two  $\alpha$ -particles in disintegrating, but the series now joins up correctly, the product being ionium, an isotope of thorium in the IVth family in place No. 90:



This then is the main uranium disintegration series as far as radon, and it may now be regarded as thoroughly well established. But the experimental difficulties in directly establishing each step have, owing to the enormous life-periods of the  $\alpha$ -ray-giving members between uranium I and radium, proved greater than in almost any other part of the subject.

**The Origin of Radium.**—The reason why it was supposed from the first that the element radium was a product of uranium was, simply, the association of the two elements in minerals. With rare exceptions, such as a certain deposit of pyromorphite (lead chloro-phosphate) found at Issy l'Evêque, France, in the neighbourhood of deposits of autunite (uranium calcium phosphate), radium is never found except associated with a definite proportion of uranium. The exception is of interest because it has been quite satisfactorily accounted for by the leaching action of rain washing out a part of the radium from the autunite. The radium in the water is again deposited some distance away upon *the surface* of the pyromorphite, the interior of which is quite free from radium.

The same is seen in the great areas in Colorado and Utah, U.S.A., where carnotite (uranium potassium vanadate) occurs, and which, before the War, was the chief technical source of radium. Here similar actions have transferred the radium locally from one part of the field to another, so that although variations from the normal uranium-radium ratio may occur

with any individual sample, over the whole field the normal ratio is, on the average, maintained.

It has already been mentioned that we owe to Boltwood the definite proof of the essential constancy of the ratio of uranium and radium. This showed indirectly, but quite unequivocally, that radium was actually being maintained in quantity by its being produced from uranium. But the direct proof of this proved very tedious. Since Mme. Curie had completely established, both chemically and spectroscopically, that radium is a new element, the observation of the production of radium from uranium, initially quite free from it, with the lapse of time, would constitute a direct experimental proof of the transmutation of one known chemical element into another.

If, as appeared in 1903, the change had been practically direct, it should have been possible to get direct experimental proof of it in the course of a single day's observations, so excessively delicate and unequivocal are the experimental methods for detecting radium, though only about one-seven-thousand-millionth of the uranium changes in the course of a year. Actually it took twelve weary years of waiting for the radium to arrive, and another twelve before its quantity was sufficient for the rate of production to be exactly measured. This was entirely because of the intervention of ionium in the series between uranium and radium, ionium having a life-period very much longer even than that of radium itself. The period of ionium was measured, for the first time, as a result of these experiments.

**Hydraulic Analogy for Radioactive Changes.**—One of the most helpful ways of regarding a radioactive disintegration series is by an hydraulic analogy. Instead of the succession of products, we may suppose there is a succession of reservoirs of equal area and with vertical walls, connected in series by pipes. We may suppose each reservoir has at the bottom an outlet filter, from which the water oozes or percolates out over a large area and then flows through a pipe into the top of the reservoir next in the series. Under these conditions, the rate of outflow of the water is simply proportional to the head or height of water in the reservoir, and as this has vertical

sides, to the quantity of water in the reservoir. We thus arrive easily at the fundamental law of the disintegration series, that for each member the rate at which it is supplied depends not at all on how much is already present but only on how much of its immediate parent is present, whereas the rate at which it itself is changing is proportional to the amount of it present. Each reservoir in the system is losing water at a rate proportional to the amount of water in it and is gaining water at a rate proportional to the amount of water in the reservoir preceding it in the series. In this analogy, the quantities of water in the successive reservoirs correspond with the quantities of the various successive members of a disintegration series. The relative rates of change of the successive members may be imitated by making the areas of the outflow filters of the reservoirs proportional to these rates, rapidly changing substances corresponding with reservoirs with large outlets and slowly changing ones with those with small outlets.

It is easy to understand, with such an analogy, the condition of radioactive equilibrium, such as naturally exists in a uranium mineral. The first reservoir, corresponding with the uranium, is so enormous and the outflow from it so small that it may go on for a lifetime without appreciably affecting the quantity of water in the reservoir, and we must suppose that it has actually been going on for millions of years. Under such circumstances the whole series must be in a steady state. Each of the series of subsequent reservoirs after filling up to a certain height or head will lose as much water as it gets, and after this the relative quantities of water in all the reservoirs does not change. Those with large outlets will need only a small head or quantity of water to enable them to discharge as much as they receive, and those with small outlets will need a proportionately large head or quantity of water. The outflow from all being necessarily alike and equal to that from the first reservoir, the quantities of water in the various reservoirs become inversely as the sizes of their outflows, just as the quantities of the various members of a disintegration series in equilibrium are inversely as their rates of change or simply proportional to the periods of the members.

**Uranium→Ionium→Radium.**—But now suppose that initially all the reservoirs except the first are empty, that is to say, suppose we consider a pure uranium compound instead of the old natural mineral. We need only deal with three reservoirs, calling the first uranium, the second ionium and the third radium, because the two uranisms, being isotopes, are always present in constant ratio, whether in the mineral or the pure compound, and because the life of the two uranium X members is too short, relatively to those of the others, for them to have any very important effect upon the flow.

Initially, though the water streams into the ionium reservoir at a constant speed, relatively a mere driblet escapes, because the reservoir is empty and there is no head to drive it out. Nevertheless a driblet does come through. Actually in a whole year it would amount to only about a hundred-thousandth part of the total water that has flown into the ionium reservoir. This is altogether inappreciable in diminishing the quantity of water in the ionium reservoir. So we reach the first important result that the rate of inflow being practically constant, the quantity of water in the reservoir, the head, and therefore the driblet out increase steadily, proportionally to the lapse of time. This driblet out corresponds with the rate at which radium is being produced, and the total amount that has dribbled out corresponds with the total radium that will be present with the uranium at any time subsequent to the date of purification.

Now the radium reservoir has also but a very small outlet, only sufficient to deliver  $1/2,300$ th part of the contents of the reservoir in a year. Although this is forty or fifty times greater than that from the ionium reservoir, it is still far too small to cause in a whole lifetime any appreciable diminution of the total quantity of water that has flown into it, that is of the total radium present. By what law, then, does the radium accumulate with the lapse of time? By a simple calculation it can be shown that, since the rate of supply increases steadily with the lapse of time, the total quantity accumulating will increase according to half the square of the time. This is exactly the same as the law governing the distance covered by a falling stone, where the velocity increasing continuously with the lapse of time, the distance fallen increases according

to half the square of the time—16 feet only in the first second, 64 feet in two seconds, 1,600 feet in ten seconds and in one-fifth of a minute one and a fifth *miles*.<sup>1</sup>

**Theoretical Law of Production of Radium.**—Now let us take for convenience a manageable round quantity of pure uranium element, say one kilogram or a million milligrams. After one year from the date it was purified, it will have produced 1·5 ten-thousandths of a milligram of ionium, and of this ionium only three-quarters of one-thousand-millionth of a milligram will have become radium. But after ten years, when the quantity of ionium has increased ten times, that of the radium will have increased a hundred times and will then be one-thirteenth of a millionth of a milligram. In twenty years it will be about one-third of a millionth, and so on. The first quantity is barely, if at all, detectable with certainty under the finest conditions of radioactive measurement, that is to say even if this large mass of uranium had initially absolutely no radium whatever. But the second quantity is sufficient to increase the rate of discharge of a very sensitive gold-leaf electroscope several times the “natural leak,” or irreducible minimum of the instrument when no radioactive substance is present. Whilst the last quantity, that grown by a kilogram of uranium after twenty years, is easily capable of accurate measurement to an accuracy of two or three per cent. Indeed, very much more than this could not be measured by the instrument in question so accurately or conveniently.

In this description, it has been shown how, if the rates of change of uranium and ionium are assumed, the rate of growth of radium from uranium can be calculated. Actually of course it was the other way. The rate of growth of radium was measured, and from this the rate of change or period of average life of ionium was calculated, that of uranium being known. Compared with the falling stone analogy, instead of the gravitational constant, 32 feet per second per second, we have the

<sup>1</sup> Neither law is mathematically accurate. The falling stone is checked by the viscosity of the atmosphere, and ultimately attains a steady “terminal” velocity. The growth of radium is checked by the decay of the ionium and radium that have accumulated and ultimately reached an “equilibrium” value. But over short enough times both phenomena are regulated by the law stated.



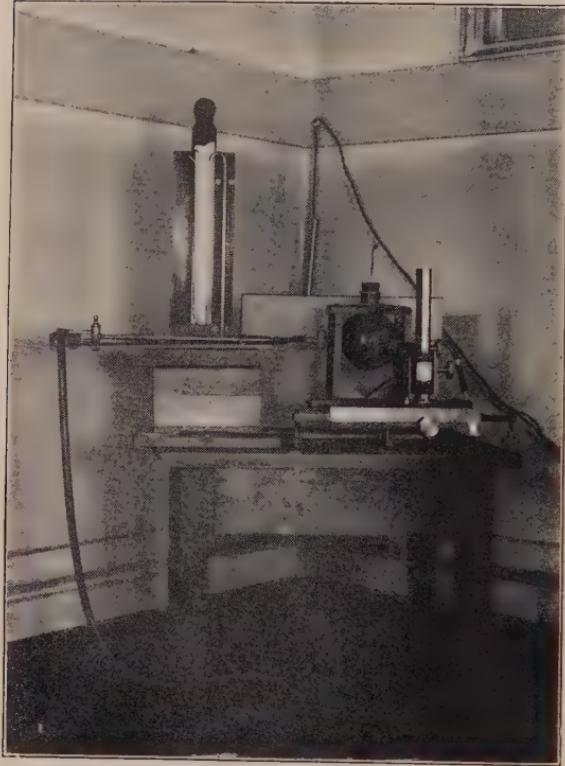


FIG. 19.—PHOTOGRAPH OF A RADON ELECTROSCOPE.



FIG. 21.—TRANSFERENCE OF RADON FROM URANIUM PREPARATION.

*To face p. 77.*

reciprocal of the product of the periods of uranium and ionium, and this product, which is what is experimentally determined, amounts to the colossal figure of 700,000,000,000,000 (years)<sup>2</sup>. Just as a stone falls 16 feet in the first second, and 16 feet for every unit in the square of the number representing the time in seconds, so, of any quantity of uranium, one part in 1,400,000,000,000 changes into radium in the first year from purification, and the same quantity in every unit in the square of the number representing the time in years. Unmeasurable as this is, with the quantity of uranium and by the methods stated, in the first few years, it would become too great to be conveniently measured by the same means before the end of a century.

**Measurement of Radium.**—Let us now consider briefly the actual experiments. They divide themselves into two parts. First, the methods used to detect and measure these absolutely infinitesimal amounts of radium; and, secondly, the initial purification of the uranium from all other radioactive constituents and its storage in a form in which the quantity of contained radium can readily be evaluated at any subsequent time.

With regard to the first, there are in general two accurate methods of measuring a quantity of radium, the first applicable to large and the second to small quantities. The first, the  $\gamma$ -ray method, is the simple comparison of the intensity of the  $\gamma$ -rays of the specimen to be measured with those of a radium standard known to contain a definite amount of radium element, by means of an electroscope or other ionisation method. It is necessary that both specimens should be in radioactive equilibrium as regards radon and the active deposit products, and for this end they must both have been contained in sealed glass tubes for at least a month. The suppression of all but the desired  $\gamma$ -rays is easily effected by screening the electroscope with a sufficient thickness of lead. The  $\gamma$ -rays being so penetrating, small differences, for example, in the quantities of the two preparations, in the thickness and shape of their glass containers and so on, and also the absorption of the rays in the air, are not of the same importance as they would be if the other rays were measured, and this

is the main reason why the  $\gamma$ -rays only are used. Besides, for any quantities of radium larger than a few hundredths of a milligram, the  $\alpha$ - and  $\beta$ -rays would produce inconveniently large ionisation, whereas the residual  $\gamma$ -rays after passing through thick metal screens give a convenient rate of discharge, which of course can be regulated by the distance of the two preparations from the electroscope.

**The Emanation Method.**—The second method depends upon the equilibrium amount of radon generated by the radium in solution in a sealed vessel, and the introduction of this radon into an airtight electroscope. It was worked out in connection with experiments of the character being de-

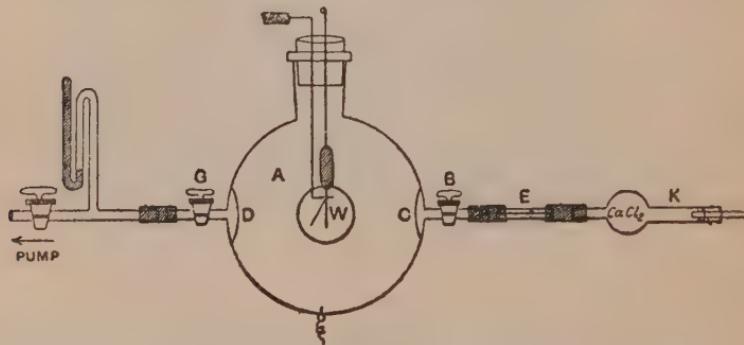


FIG. 20.

scribed, and it is extraordinarily sensitive. As already indicated, under ideal conditions as little as a thousand-millionth of a milligram of radium is, in this way, just detectable. A photograph of the instrument used in this work is shown in Fig. 19 (facing p. 77), while Fig. 20 is an explanatory diagram of it. It shows a globular glass flask of about a litre capacity, silvered internally, with a plane glass window, W, through which the gradual fall of the gold leaf of a single-leaf electroscope is observed and measured by a reading microscope. The leaf system is supported by the cork, which carries also a bent wire for charging the leaf. The leaf system is insulated from the supporting wire by a rod of sulphur. This type of system was first used by C. T. R. Wilson, and it has proved particularly suitable for radioactive work. When the electro-

scope is full of air, a good system will keep its charge for several hours in the absence of radioactive substances. The natural leak under these conditions, *i.e.* the number of divisions of the eye-piece scale of the microscope passed over per minute, is always subtracted from the leak under the conditions of measurement, to give the "corrected leak." Within certain limits, this is a measure of the intensity of the radiations, or, in this case, of the quantity of radon and therefore of the radium with which it is in equilibrium, when the measurements are made three hours after the introduction of the radon. The charge on the leaf should be positive in such measurements, to avoid disturbances due to an alteration of the distribution of the active deposit.

The instrument has first to be accurately calibrated, that is, we must know how much radium it takes to produce a corrected leak of one division a minute. For the instrument shown, this is about 20 units, the unit being the thousand-millionth of the milligram ( $10^{-12}$  gram), but of course the actual value of this "constant" depends entirely on the magnification given by the microscope employed. It is determined in two ways. Either a known weight of radium, determined by the  $\gamma$ -ray method, is, by a process of homœopathic dilutions, reduced to a known fraction of its original amount, and the equilibrium radon from this fraction measured. But a more elegant way in practice is to calibrate with a known quantity of a uranium mineral of known uranium content, such as pitchblende, making use of the known ratio, 3,800,000 to 1, between the weights of the contained uranium and radium. Actually both are used for certainty, the one value serving to check the other. In either case, the radium standards used, containing the desired number of "units" of radium, are aqueous solutions contained in sealed glass flasks, and the process of transferring the radon from them to the electroscope is identical with that used to transfer it from the uranium preparations growing radium, which also are stored in sealed flasks in an identical manner.

After these have been sealed up a month the equilibrium quantity of radon is present. The sealed outlet from the flask is connected with an exhausted vessel, the seal is broken and the solution in the flask boiled, and all the radon driven

out into the vessel by steam. The vessel is then connected to the electroscope previously exhausted, and its gaseous contents displaced into the electroscope through a calcium chloride drying tube, by filling the vessel with water. Fig. 21 (facing p. 77) is a photograph and Fig. 21A is a diagram of

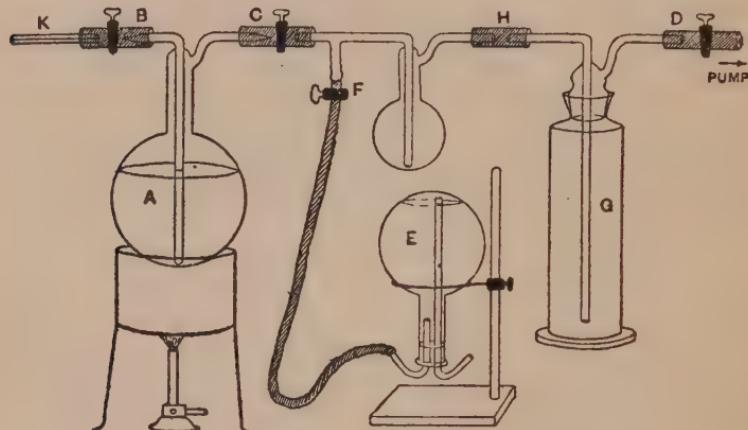


FIG. 21A.

one of the uranium preparations being boiled out so as to transfer any radon present into the glass vessel on the right.

**The Production of Radium from Uranium.**—It remains now to deal with the initial purification of the uranium preparations. At first, ionium not then being known, these were simply purified from radium only, and the results were worthless because of initially present ionium. The error corresponds with that of measuring the rate of fall of a stone not from rest but from some unknown point after it has got under weigh. In the final series, four different preparations, purified as carefully as possible from ionium as well as radium, were used. Actually the compound, uranyl nitrate, was employed, and it was purified by a variety of methods, but simple repeated recrystallisation from water is better than any. The first three contained only from a quarter to two-fifths of a kilogram of uranium, but the last, prepared after the work had been in progress without result for six years, contained three kilograms of uranium. It is seen in the photograph

in Fig. 22 (facing p. 62), immersed in a hemispherical water-bath, and carrying a self-contained condenser to condense the steam during the boiling-out processes.

The work, which was started in 1903, did not give any definitely positive results till 1915, but in that year indications were given by the two last and largest preparations which showed that the average life-period of ionium must be at least 100,000 years. By 1931 accurate records of the growth of radium had been accumulated for all four preparations

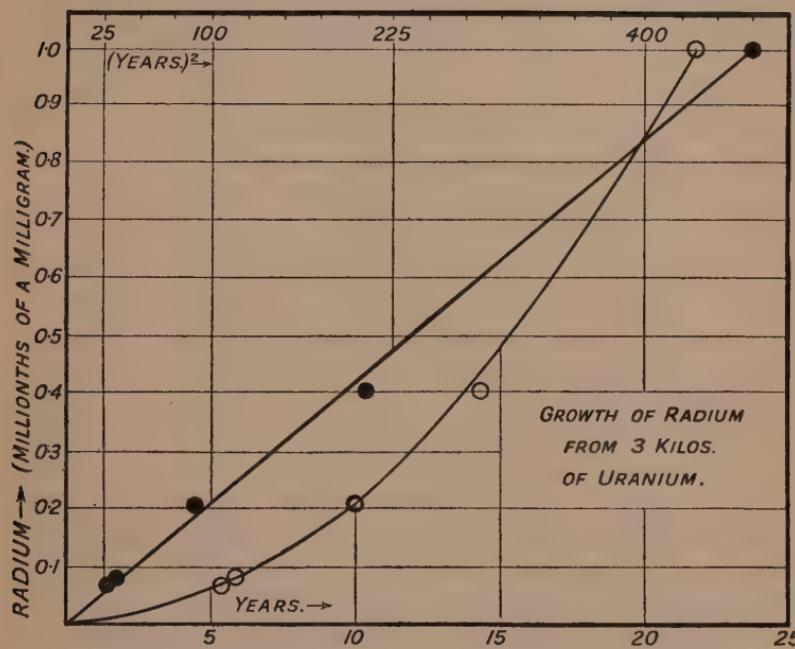


FIG. 23.

which agreed excellently among themselves and gave for the true period the value 106,000 years. Fig. 23 is a diagram showing the record of the largest preparation, in which "units" of contained radium are plotted on the vertical axis as white circles against the time in years shown at the bottom, for the curved line, and, for the straight line, as black circles against the square of the time in years shown at the top. In this way the second investigation started to demonstrate experimentally the actual spontaneous trans-

mutation of one known element into another has been recently brought to a satisfactory termination.

**The Product of Uranium X.**—There remains, however, still one point in the series to be experimentally established, and that is the nature of the product of uranium X. Experiments on this question were begun nearly a quarter of a century ago, but so far they have not given definite positive results. The method was to separate uranium X from a very large quantity (25 kilograms) of uranium and to watch, while its intense  $\beta$ -radiation decays, which it does completely in the course of a year, for the growth of a new radiation from the product into which presumably it is changing. This was done by measuring the rays in an intense magnetic field, which, by coiling up the  $\beta$ -rays into circles, prevents them entering the instrument, so leaving the way clear for the detection of any minute  $\alpha$ -radiation that grows as the other decays. At that time, it was naturally supposed that ionium was the product of uranium X, as shown in the first diagram of the series given on p. 71. Although no *growth* of  $\alpha$ -rays was observed, the preparations showed always a small *constant*  $\alpha$ -radiation. This, we know now, must have been due to ionium separated at the same time as the uranium X, for, the two being isotopes, it is impossible to prepare uranium X entirely free from ionium. The absence of any growth of  $\alpha$ -rays merely enabled the conclusion to be drawn that the product of uranium X must have a very long period. For with radioactive series the adage “A short life and a merry one” applies, and if the life is long the merriness of the product, in the sense of the intensity of the rays, is proportionately reduced. If it is very long the rays may not be experimentally detectable. That proved to be the case in this experiment.

It is probable that the life is much longer than would have been the case on the supposition that the product was ionium. We have seen how the Displacement Law showed at once that the real product must be “uranium II,” an isotope of uranium by the  $\alpha\beta\beta$  triple change, as shown in the diagram on page 72. Recent experiments by this method have been done in Oxford by C. H. Collie, using modern “valve” methods of counting  $\alpha$ -particles. He has shown that the half-life-

period of uranium II must be at least a million years. This makes the direct observation of the production of uranium II from the rapidly changing uranium X quite impracticable by the older methods, but it is possible the newer ones may ultimately prove equal to the task. As in the case of the production of radium from uranium, the possibility of getting a direct measure of the life of these long-lived  $\alpha$ -ray-giving members in the first part of the series by such experiments is now the chief justification for them. For there is now no real doubt as to the essential correctness of the sequence.

## CHAPTER VI

### RADIUM AND RADON

**Sources of Radium.**—We dealt in the first chapter with the discovery of radium by M. and Mme. Curie in 1898 in the pitchblende (uraninite) from the old State mine of St. Joachimsthal, Bohemia. Since then the demand for the element, principally in medicine and surgery, has been continuous and increasing, and the original source soon proved altogether inadequate to supply what was required. Limited quantities of pitchblende exist in Cornwall, and these sources have been from time to time worked for radium. Another limited source is the mineral autunite, originally found at and named after Autun in Eastern France, a bright yellow mineral consisting of uranyl calcium phosphate, but usually occurring as an impregnation of sandstone containing only one or two per cent. of uranium. After the French deposits were exhausted, a very low-grade ore from Guarda, Portugal, was worked up for radium for a time.

But by far the greater part of the world's radium before the War was obtained from the American sources—which cover hundreds of square miles—of carnotite, a uranyl potassium vanadate, mainly from the famous Paradox Valley deposits in West Montrose County, Colorado. The pure mineral is hardly known, and the deposits consist of impregnated sandstone, usually no richer than 1 per cent. average content of uranium. It is of a bright canary colour, and the vanadium it contains is of economic importance, in the steel industry, as well as the radium and uranium. Over 150 grams of radium were produced from this source in fifteen years from the commencement of its exploitation.

Carnotite has about twenty times as much thorium, relatively to the uranium, as Joachimsthal pitchblende, and radium prepared from it has as a maximum three parts per 2,000 of its  $\gamma$ -rays due to mesothorium. Failing the latter mineral, carnotite is easily the next best from which to make radium

standards. The newer sources all contain very much larger quantities of thorium (compare pp. 40 and 136).

**The Chinkolobwe Minerals.**—But, like pitchblende and autunite, carnotite has now ceased to furnish anything but a negligible proportion of the world's supply of radium. An unprecedented find of exceedingly rich uranium minerals, of an essentially new type, was made at Katanga in the Belgian Congo during the War, the original find being reported to contain over 200 grams of radium. Until these are exhausted any lower-grade uranium ores can no longer compete. It is essentially a species of pitchblende or uraninite, called Chinkolobwe pitchblende, from the locality where it occurs, black internally but usually presenting a brilliant canary coloured appearance externally through surface alteration. In it Schoep has recognised and named seven new uranium minerals—hydrates, silicates and phosphates of uranium and lead oxides—the average material used for the extraction of radium containing over 50 per cent. of uranium element. This material is worked up in Belgium and, since the War, has become practically the only important source of radium now technically exploited. At the time of writing, a discovery of a large and very rich uranium deposit is reported from Western Canada, but this awaits confirmation. Until the Katanga find, one would have thought such large and rich deposits of uranium ores even less likely to be discovered than a similar concentration of gold or silver, but now as they have been found in one place it seems only natural to expect that in time they may be discovered in others.

The uranium minerals furnish the source not only of radium but of actinium and ionium and of radiolead and polonium, the first pair being generated, as we have seen, before radon, and the second pair as the two penultimate products of the active deposits in the series after radon, which has still to be dealt with. The chemical separation in all cases follows the general rule. Each radio-element is concentrated with that common element most resembling it in chemical character, and is then separated from it.

**Extraction of Radium.**—The chemical properties of radium were accurately described by Mme. Curie in a sentence: “ The

salts of radium are absolutely analogous to the salts of barium." In so far as they differ, they do so in the same sense or direction as the barium salts differ from those of strontium, the preceding member of the family of alkaline-earth elements, and as those of strontium differ from those of calcium. Thus barium sulphate, before the discovery of radium, was, in water, one of the most insoluble substances known, being dissolved only to the extent of about one part in a million. Strontium sulphate is considerably more soluble, and calcium sulphate (gypsum) is sufficiently soluble to be the cause of the "permanent hardness" of natural waters. But radium sulphate is one hundred times less soluble than barium sulphate, and on this fact pivot all the methods of concentration from the mineral. The minerals are usually attacked with sulphuric acid, the uranium and some of the ionium are dissolved and there is left insoluble what is termed the "radium residues," which contain all the radium and most of the actinium, polonium and radiolead, along with silica, alumina and iron oxides and the sulphates of lead, calcium and the other alkaline-earth metals.

These radium residues are subjected to successive boilings, first with sodium hydroxide and then repeatedly with sodium carbonate, interspersed with very thorough washings of the still insoluble material, alternately first with water and then with hydrochloric acid, the object of which is first to dissolve most of the material without dissolving the radium sulphate, and, in the final stage only, to dissolve the radium as the chloride. Many tons of water have to be used in the preparation of each gram of radium.

Having been dissolved, the radium is once more precipitated as sulphate—the "raw sulphate"—reconverted into chloride, and the solution may, at this stage, be saturated with hydrochloric acid gas, when the radium and barium chlorides crystallise out pure, leaving calcium, lead, iron, aluminium and other impurities dissolved. This material, which as yet contains only something of the order of a thousandth per cent. of its weight of radium, is then fractionally crystallised from water according to a definite scheme.

Here, again, chemical analogy holds good. Calcium chloride is, of all known substances, one of the most soluble

in water, whereas barium chloride is, in cold water, only about as soluble as common salt, and radium chloride is much less soluble. So that in crystallising the mixture of radium and barium chlorides from hot water the crystals are enriched in radium, relatively to the salt left in the mother liquor, about five times. Simple repetition of this process according to a systematic plan sufficed to enable Mme. Curie to prepare ultimately pure radium compounds containing so little barium that they showed in the spectroscope only the strongest line of the latter element very faintly. But to do so, of course, enormous quantities of the radium residues from pitchblende had to be worked up.

**Low-Grade Ores.**—Each ton of uranium (element) in the original mineral is associated with only one-third of a gram of radium (element). The original rich ores may have had as much as 50 per cent. of uranium, but these were soon exhausted. As the quantity of uranium and radium in the material decreases, the quantity of "radium residues" to be worked up increases, so that for a double reason it pays to use as rich ores as possible. The treatment of such low-grade ores as the sandstones impregnated with autunite and carnotite is facilitated by the fact that the bulk of the sand may be removed in the initial stage, either by dissolving the uranium minerals out with hydrochloric acid, or, if sulphuric acid is used at the start, from the residues obtained by mechanical separation. The same is true for an ingenious process worked out for the low-grade carnotite ores occurring in large quantities at Olary in South Australia, found in association with titaniferous iron, magnetite, ilmenite, rutile, quartz and mica. This exceedingly refractory and unpromising material, after fusion with "salt-cake" (acid sodium sulphate), gives a material which, after crushing and agitation with water, can be mechanically separated into coarse sand and fine slimes, the latter in much the smaller quantity but containing practically all the radium. Mechanical methods of concentration prior to treatment, such as "oil flotation," have also been applied to low-grade pitchblendes, which for the crushed material separate the actual particles of mineral from the gangue.

**Spectrum of Radium.**—The discovery of a new element has always been one of the most coveted possible rewards of a chemical investigator, although now, thanks to the powerful aid furnished by the X-rays in the search, it is hardly likely that there will be any more such prizes. M. and Mme. Curie's discovery of radium, quite apart from the extraordinary radioactive properties of the element, was one of the most notable chemical achievements of the last century. It was very closely analogous to the discoveries of new elements that followed the development of spectroscopy. For example, Bunsen discovered the elements rubidium and cæsium in the waters of Durkheim in the Palatinate, after noticing new lines in the flame spectrum of the salts remaining after evaporating the water. These new lines served, before anything else whatever was known of the nature of the elements, to show how they behave in any chemical separation, and therefore how they could be concentrated and obtained pure and free from the common elements, potassium and sodium, with which they are associated. But to obtain them in weighable quantities very large volumes of the water had to be evaporated and the salts worked up.

For radium the radioactivity is an almost infinitely more sensitive test than the spectrum, delicate as the latter is. In the early stages of the concentration fairly active barium preparations, which, however, could not have contained more than one part in five thousand of radium, showed the first line in the new spectrum. As concentration proceeded and the activity of the material increased steadily till ultimately it became millions of times greater than that of uranium or thorium, this line increased in brilliance, and many other new lines appeared. At the same time the barium spectrum, especially towards the end of the process, became fainter, and ultimately only the very strongest line of barium was faintly visible. Demarçay, who undertook the spectroscopic investigation, classes radium as among the elements with the most sensitive spectrum reaction, yet it can be detected by its radioactivity in quantity thousands of times less than by the spectroscope. Of all the new radio-elements radium and radon are still the only ones that can be detected by the spectroscope or which have been definitely ascertained to have a spectrum of their own.

**Radioactivity of Radium.**—The radioactivity of radium, as we have already seen, is due to a number of successive changes. Strictly speaking, radium itself gives only  $\alpha$ -rays in producing radon, the radon gives only  $\alpha$ -rays in producing radium A, the latter only  $\alpha$ -rays in producing radium B. The  $\beta$ -rays originate, as regards the softer and less important part, from the transformation of radium B into radium C. The last is in reality a complex body, undergoing two successive changes which follow too rapidly to be separately distinguishable. It is in this very rapid double change that the most penetrating  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays are emitted. Now the lives of these "active deposit" members are all short and together only amount to a period of the order of one hour, whereas the period of radon is several days.

In consequence of these changes, radium freshly prepared from a solution undergoes a steady increase in its radioactivity in the first month from preparation. This is of the utmost practical importance. From the solution radon, being a gas, escapes readily, and the later products of it, if initially present, being deprived of their parent, rapidly decay. The activity then is due to the  $\alpha$ -particle, one out of a total of four, given by the radium atom in its first change. If now the radium solution is evaporated to dryness and the salt sealed up in an airtight envelope to prevent the radon from escaping, it grows in activity as the radon accumulates to the condition of radioactive equilibrium, a process that takes three weeks or a month. In this condition it gives four  $\alpha$ -particles per atom disintegrating, together with the  $\beta$ - and  $\gamma$ -rays from the C-member. About half of the total growth occurs in the first four days, half of what is still to grow, that is one quarter of the whole, in the next four days and so on, the growth getting slower and slower as the equilibrium condition is approached, until it becomes imperceptible.

Different salts differ very much in the proportion of radon they retain in the solid state when not in sealed vessels, and, in the open, lose a greater or smaller part of their radioactivity. In general, the insoluble salts, as the sulphate, retain most and the hydroxide least. So that if the radium preparation has to be used in the open, as in luminous paints and the like, the sulphate is almost always the best to employ.

**Safe Handling of Radium.**—If the compound is dissolved, the contained radon is liberated at once, the active deposit products left behind with the radium commence to decay, and in a few hours the radium in solution is back at its minimum activity, giving no  $\beta$ - and  $\gamma$ -rays and only 25 per cent. of its full equilibrium  $\alpha$ -activity. In this condition it may be handled with comparative immunity from danger, whereas fully active or "ripe" radium preparations, giving the penetrating  $\beta$ - and  $\gamma$ -rays, should not be handled except with forceps. They should be handled in fact as though they were red-hot. For although they give no immediate sensation of burning, however strong, they do burn much in the same way as a red-hot body would. The burns develop after a somewhat prolonged period, usually from ten days onwards, and, like X-ray burns, may be very serious. Some of those habitually engaged in handling radium have developed in their hands ulcers and sores of a rodent character which have resulted in loss of fingers and worse. In fact it is one of the most singular features of the action that the rays, though often successful in checking the growth of cancer and even, it is claimed in certain circumstances, effecting a "cure," nevertheless in other circumstances themselves act to start growths, which if not actually cancers, closely resemble them in their effects. It seems mainly a question of the "dose." The rays have a general destructive action exactly like a red-hot body or other cautery. But they have a selective or preferential action against certain kinds of tissues, particularly young and rapidly growing tissues, and destroy these more readily than the normal tissue of the body. The late Sir James Mackenzie Davidson, a pioneer in the medical use of X-rays and radium, who like many others suffered serious damage to his hands by exposure to X-rays, himself finally healed the X-ray burns by careful treatment with radium rays, which is an excellent illustration of the narrow dividing line in this field between cause and cure.

Radium has also been the cause of fatalities in connection with the luminous watch and allied industries, due to the operatives "pointing" with their lips the brushes used to paint the dials with luminous paint containing radium. The

radium so introduced into the system is apparently not eliminated but accumulates and sets up necrosis of the jaw and thigh bones similar to that at one time rife among the match operatives, before the introduction of the safety match. Viosterol, the action of which is analogous to that of the calcifying vitamin used for the cure of rickets, has been found effective in eliminating the radium and restoring the bone.

**Energy of Radium.**—The energy continuously evolved by pure radium compounds is sufficient to maintain them permanently a few degrees above the temperature of the surrounding air. The exact quantity of energy given out by a gram of radium (element) in an hour has been found by careful experiments and calculation to amount to 134.4 calories, the calorie being the scientific unit of heat energy, viz., the amount of heat necessary to raise the temperature of a gram of water 1° Centigrade. Of this total, 123.6 calories are due to the  $\alpha$ -rays, 4.3 calories to the  $\beta$ -rays and 6.5 calories are due to the  $\gamma$ -rays. However, the penetrating power of the last is so great that, to absorb them and convert them into heat completely, the radium would have to be surrounded by lead of several inches thickness, so the last figure is to some extent an estimate. Normally the  $\beta$ -rays appear as much more energetic than the  $\gamma$ -rays, but this is due to the small proportion of the latter used up in producing the effects. Of the 123.6 calories produced by the  $\alpha$ -rays, only 25.1 calories come from radium itself. Radon is responsible for 28.6, radium A for 30.5, and radium C for 39.4 as well as for the 10.8 due to  $\beta$ - and  $\gamma$ -rays. The numbers of  $\alpha$ -particles in the four stages are similar, but the energy increases owing to the particles being expelled at increasing velocity, as we pass from one stage to the next. This in fact is practically universally the case in all the three disintegration series for the members as far as the C-members, at which point complications occur. It is connected with the continuously decreasing periods of life of the  $\alpha$ -ray-giving members as we pass through the disintegration series, by an empirical relation known as the Geiger-Nuttall law. The shorter the life and the more rapidly the substance disintegrates, the faster and more energetic are the

rays expelled. Probably this holds for both the  $\beta$ - and the  $\alpha$ -rays, but for the latter a definite quantitative relation exists (see p. 110).

All the hypotheses that have attempted to explain the instability of the radioactive atoms are based on this connection between the period of life of the atom and the velocity of the rays expelled, but so far they have not greatly added to our knowledge of the phenomena, and, indeed, often appear merely to restate in physically unintelligible symbolism the fact they purport to explain. This criticism applies not infrequently to the theoretical physics of the second quarter of the twentieth century.

**Source of the Energy of Radium.**—In the early days, the mere magnitude of the energy evolved by radium was itself almost sufficient to rule out both the view that it could be accounted for by any change short of a veritable transmutation and the view that it might be derived from some unknown external source. But the argument became unanswerable when it was proved that by far the greater part of the energy does not, strictly speaking, come from the radium but from its products, since these are present in quantities so infinitesimal as to be almost beyond the means of detection except by the energy they are giving out.

If we assume the period of average life of radium to be 2,300 years, since  $1/2300$ th part disintegrates in a year, we may easily calculate the total amount of energy that would be given out from one gram in the course of its disintegration. It is over a million calories a year, and the total is two thousand eight hundred million calories. This is over a million times as great as can be got from a gram of any other kind of matter even in the most energetic changes known prior to the discovery of radioactivity. Thus the combustion of carbon, from which the modern world derives most of the energy by which it lives, gives out per gram of carbon about 8,000 calories. But, to burn this,  $2\frac{2}{3}$  grams of oxygen are also required, and the evolution per gram of matter is only 2,200 calories. Yet this change gives more energy, weight for weight of material employed, than any previously known change.

**Energy of Radon.**—In this calculation we have to assume that we know the rate at which the radium is changing in order to calculate the total energy evolved. But in this case of the short-lived products the whole evolution occurs in the course of a month. We have seen that the radon from radium, being a gas, is capable of detection and measurement in very minute quantity by the ordinary methods of gas manipulation, and that the actual volume from a given amount of radium has been experimentally measured. It corresponds, at normal temperature and pressure, to 0·6 cubic millimetre of radon per gram of radium, and this volume of gas—less than the size of a pin's head—weighs, it can be calculated, 1/150th of a milligram. This is quite outside the sensitiveness of the balance used by the chemist, but special balances, called micro-balances, have been constructed capable of weighing even this minute amount. Indeed, the density of radon has been experimentally determined in this way with results agreeing with the calculated value, by Ramsay and Whytlaw-Gray.

Now assuming we have the radon just liberated from a gram of pure radium (element) this 1/150th milligram of matter will give out at first 28·6 calories per hour, and after a few hours, when the active deposit products have accumulated to the equilibrium condition, it will give out 109·3 calories per hour. This is at the rate of sixteen million calories per gram per hour. If we had a kilogram of radium element, the radon from this would have a volume of 0·6 cubic centimetre and would give out more heat than an electric lamp consuming one hundred watts. If the attempt were made to store it in a glass bulb of anything like a cubic centimetre capacity it would almost instantly melt it.

As we know, the radon will disappear steadily in the course of a month, becoming at the end of each 4 days only one-half as much as it was at the beginning of that period. But the total energy it would give out can readily be summed. The period of average life being 5·5 days, or 132 hours, it is 132 times the amount evolved in the first hour after it reaches equilibrium, that is to say something like 14,500 calories from 1/150th milligram or at the rate of over two thousand million calories per gram. This is an experimental result which involves no assumptions whatever, and it is rendered possible

because of the short life of radon, relative to that of our own, making it possible to follow the process through to the end. The idea, never very probable, that radium may be acting as a transformer of energy in some unknown form traversing all space, becomes totally unable to explain the relatively much more rapid energy emission from the short-lived radioactive substances, and here, as in the case of the production of helium from radon, we can obtain direct evidence of the changes in which the energy is evolved by ordinary methods.

**Uses of Radon.**—More and more radium is being used both in laboratories and hospitals merely as a generator of radon and the active deposit products, and less and less directly. The small part of the  $\alpha$ -radiation given by the radium itself is so wasted, but this is not of great importance. The radium is kept in solution in a vessel attached usually to a mercury pump, and from time to time, when a new supply of radon is required, that accumulating in the radium solution is drawn off by the pump, and sealed up in a capillary tube or otherwise employed. The operations involved are free from danger, because, when freshly drawn off, the radon gives no penetrating rays, and the radon tubes or "seeds" can be prepared and completed before the penetrating rays become important. But after half an hour the latter begin to develop rapidly and in two or three hours reach their maximum strength. After that the whole of the rays diminish together with the period characteristic of radon, that is they fall to half the initial value every four days.

In the dark the passage of the radon through the pump and connecting tube can be followed by the faint glow the rays produce on the glass walls. If a stream of gas containing radon is sent through a glass U-tube immersed in liquid air, the radon condenses at the point where the stream enters the liquid air, and gives a bright spot usually plainly visible in an undarkened room. By the use of the usual fluorescent materials, such as willemite (zinc silicate) and various platinocyanides, brilliant fluorescent effects are produced, which, from a few milligrams of radium only, may be plainly visible in broad daylight. In honour of the discoverers of radium, the term "curie" is now employed to signify the radon in





FIG. 24.—TUBE CONTAINING WILLEMETTE USED TO SHOW RADON.

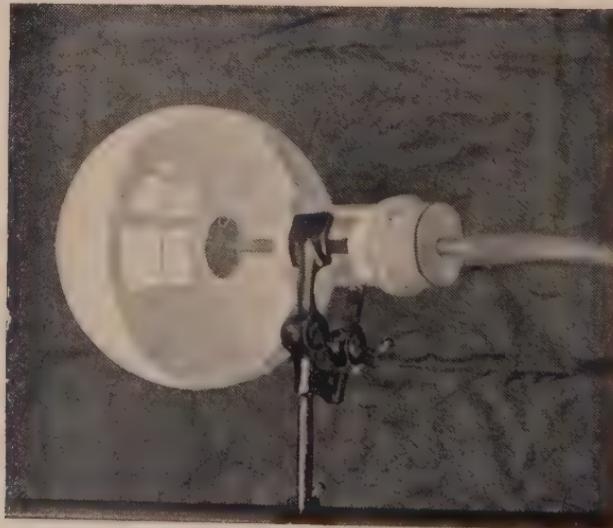


FIG. 29.—APPARATUS TO SHOW ABSORPTION OF  
 $\alpha$ -RAYS BY AIR.



FIG. 25.—THE ABOVE TUBE PHOTOGRAPHED BY ITS OWN LIGHT.

To face p. 95.

equilibrium with one gram of radium element, and the "millicurie" that in equilibrium with a milligram. Fig. 24 is a daylight photograph of a glass tube containing fragments of willemite, and Fig. 25 is a photograph of the same tube in the dark by its own phosphorescent light under the action of a few millicuries of radon. In this connection, it should perhaps be made clear that it is the *light* of the fluorescing bodies which affects the photographic plate, not the  $\alpha$ -,  $\beta$ - or  $\gamma$ -rays themselves. The latter are not refracted by the lens, and as regards the first two would not, of course, get through it at all, while the  $\gamma$ -rays would go through but, not being refracted, would merely add to the general fog of the plate. Some very amusing errors have been made, through lack of understanding such points, by spiritualists, who sometimes forget that the X-rays also are not refracted by lenses, and claim to have taken spirit photographs by the aid of the X-rays! Such spirits must have been fluorescent.

**Condensation of Radon.**—An experiment for showing the easy condensability of radon by liquid air is illustrated in

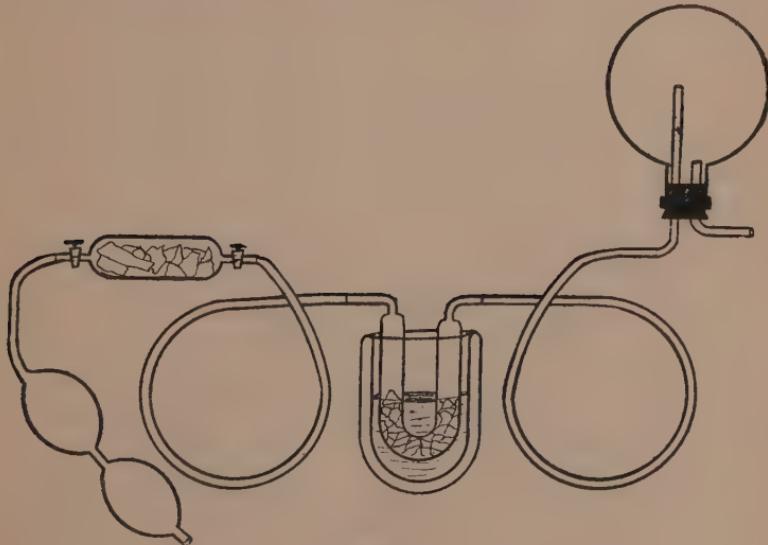


FIG. 26.

Fig. 26. The willemite tube of Fig. 24, containing a few millicuries, is connected with a rubber blowing ball and with

a length of tubing to a U-tube containing willemite cooled in liquid air, and this in turn to a flask with an internal coating of zinc sulphide. On blowing out the radon, most of it condenses instantly at the first point in the U-tube where it is cooled by the liquid air, and hardly any goes on into the flask. On removing the U-tube from the liquid air and allowing it to warm up, the radon again volatilises, and gradually the fluorescent glow spreads to the rest of the willemite in the tube. At this stage a puff of air from the bellows will displace the whole of it into the flask, which in turn glows brilliantly. But, owing to the active deposit produced, the removal of the radon does not entirely extinguish the glow of the willemite, which is the brighter and persists the longer, the longer the radon has been left in contact with it.

## CHAPTER VII

### THE RAYS FROM RADIOACTIVE SUBSTANCES.

#### $\alpha$ -RAYS

**General Properties.**—The three types of rays from the radioactive substances, though unique in the degree or intensity of the phenomena to which they are due, can all be imitated, on a lower plane of energy, by artificial means. The common effects by which the rays are recognised and studied are also shown by many other types of rays and some even by chemical reagents. The main effects, apart from the heating effects already discussed when the original energy is completely degraded by absorption in matter, are three. They are the fluorescent, photographic and ionisation effects, and probably all three are different manifestations of the ionising power of the radiations. The same effects, of course, are relied upon in the detection and study of the other new types of radiation, such as the cathode-rays, Lenard-rays, X-rays and positive rays. Ordinary light also shows all three effects provided the wave-length is sufficiently short. Thus, fluorescence and photographic action is shown even by visible light, though more strongly by the invisible ultra-violet rays. The latter have the power also of causing chemically electropositive metals, like zinc and the alkali metals, to eject electrons, which is called the photo-electric effect. But to produce true gaseous ionisation, the wave-length must be extremely short, in the region of the spectrum below 2,000 Å. known as the Schumann and Lyman rays. These ionise air and other gases strongly, and work upon them has usually to be done *in vacuo*, so great is their absorption by gases in consequence. Between these rays and the X-rays is a rapidly diminishing gap, if it has not already been bridged. For, by working in a vacuum and using suitable anti-cathodes, as also by very intense or "hot" sparks, very "soft" X-rays can be obtained of wave-length intermediate between the Schumann rays and the ordinary X-rays, which Röntgen discovered, and for which, also, the work must be done *in vacuo*. The penetrating X-rays of

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Röntgen have a wave-length of the order of only one Ångstrom unit ( $1 \text{ \AA.} = 10^{-8} \text{ cm.}$ ).

But some chemical reagents also show some of these actions. Thus the photographic plate is fogged by a number of agents like hydrogen peroxide, and the glow of phosphorus in air is accompanied by a species of electrical conductivity of the air. This accounts for some early impressions that radioactivity was really a widespread phenomenon. Also there was a tendency to regard radioactivity as a question of degree, and to imagine that, with more sensitive methods, everything would be found to be more or less radioactive, as it is, for example, more or less magnetic. But this is quite erroneous. It is true that many common materials, and most rocks and minerals, show a detectable radioactivity, but this is due to contained radio-elements in small quantities. Apart from potassium and rubidium, already referred to, the only elements that are certainly radioactive are uranium and thorium, and their numerous progeny of disintegration products. It is possible that with some of the more sensitive methods, later to be discussed, it may prove that other elements are radioactive. But, if so, we already know that their activity must be, by comparison, vanishingly minute.

**The  $\alpha$ -,  $\beta$ - and  $\gamma$ -Rays.**—A general description of the nature and properties of the three types of rays has already been given. Although all are produced uniformly throughout the mass of the radioactive substance, naturally it is only the more penetrating rays that can escape absorption, when generated beneath the surface. In the case of the very feebly penetrating  $\alpha$ -rays—and the same holds true for some of the feebly penetrating types of  $\beta$ - and  $\gamma$ -rays (distinguished in this book as ( $\beta$ )- and ( $\gamma$ )-rays)—the absorption in the material is so great that the rays emitted are practically confined to the surface. The intensity of the  $\alpha$ -rays from a given area is not increased by increasing the thickness of the layer of radioactive material above some 10 mg. per sq. cm. As the  $\beta$ - and  $\gamma$ -radiation from such very thin layers is often negligibly small, this gives an easy way of enhancing the effect of the  $\alpha$ -rays relatively to that of the others, and in studying the former practically alone. A very minute

quantity of the radioactive substance is spread over a large surface for this purpose.

The intensity of the more penetrating  $\beta$ -rays goes on increasing with the thickness of the layer up to a few grams per sq. cm., and the  $\alpha$ -rays may be suppressed by covering the surface with a screen weighing 10 mg. per sq. cm., with little absorption of the  $\beta$ -rays. Usually the  $\gamma$ -rays from a layer of 1 gram per sq. cm. are feeble, at least in the case of the feebly radioactive elements like uranium and thorium. To study these without the others much thicker layers covered by thick screens are necessary. Any radiation emerging through a screen weighing 10 grams per sq. cm. is pure  $\gamma$ -radiation.

**Chemical and Allied Actions of the Rays.**—All the rays, if sufficiently intense, have marked chemical action, of which the photographic action and the decomposition of water into hydrogen and oxygen (p. 57) are examples. The latter is mainly due to the  $\alpha$ -rays. With the  $\beta$ -rays, hydrogen peroxide ( $H_2O_2$ ) and hydrogen appear to be the main products. In general, the action of the rays may be regarded as a shattering or decomposition of the molecule, whereby the atoms are momentarily set free in the "nascent" state and then recombine among one another to form, not only the original molecule, but new molecules according to the chances of their mutual collisions. In fact, the appearance of the products may be ascribed to roundabout after-consequences of the initial act of ionisation or activation (see p. 255) of the molecules. When the rays traverse air, ozone and the various oxides of nitrogen,  $N_2O$ ,  $NO$ ,  $NO_2$ , etc., are formed, and this accounts for many of the destructive actions of the rays, on paper, linen, silk and so on in which radioactive preparations may be wrapped, the air being rendered chemically active. No doubt a quite appreciable proportion of the combined nitrogen washed down by the rain into the soil, upon which its fertility depends, and which is estimated at 10 lbs. per acre annually, is contributed by the radon in the air rather than by spasmodic lightning discharges. Carbon compounds, such as the lubricating grease of glass stopcocks, are oxidised to carbon dioxide and monoxide by radon, and such impurities have to be carefully removed when it is required to prepare the radon

in highly concentrated form, as for radon "seeds" and the like. A leakage of air into the apparatus, by the formation of nitrous oxide,  $N_2O$ , may make this difficult. The liberation of chlorine in nascent form from chlorides may cause radioactive substances in solution to attack platinum vessels, and many other examples of the rays "activating" substances which are normally inert could be cited, some of which initially led to false conclusions that the rays could effect transmutation. But it should be pointed out that, with the small quantities of radioactive substances usually available, the chemical actions are usually quite feeble compared with those produced by light, especially ultra-violet light, X-rays and cathode-rays.

**Fluorescence, Thermoluminescence and the Colouration of Minerals.**—Fluorescence is in general ascribed to the initial act of ionisation, the light emitted being, as in the present theory of spectra discussed in Chapter XIII., ascribed to the after-recombination of the ions produced. Closely related to this are the colourations produced by these rays, as also by light, X-rays and cathode-rays, upon glass, salts and certain gems and minerals, the colouration of mica and fluorspar by  $\alpha$ -rays resulting in the formation of the pleochroic haloes, discussed later in this chapter. Soft glasses containing sodium and manganese are coloured blue like amethyst, and hard glass, containing potassium and iron, usually brown. Similarly, cathode-rays produce intense colourations on transparent salts—rocksalt, for example, being coloured violet—but a great variety of colours can be obtained by adding to the substances small traces of impurities. These colours have been attributed to the ions being unable to recombine in the solid and remaining distributed through it, producing the colour much in the same way as an infinitesimal trace of gold produces the intense colour of the ruby glass used for photographic dark-room lanterns. The colour seems to be connected with the size of the gold particles uniformly distributed through the transparent medium. The colours produced by the rays are usually discharged by heating the substances, often with a brilliant evolution of light, producing the phenomenon called "thermoluminescence." Thus certain speci-

mens of fluorspar, if exposed for some hours or days to the  $\beta$ -rays of radium, will store up so much energy that on warming them up to 200° or 300° C., far below red-heat, they glow as if white-hot so brightly that the phenomenon can be seen in broad daylight. This is ascribed to the rapid recombinations of the accumulated ions.

It is possible that in some cases the colours shown by natural gems in such bewildering variety may be due to ions produced by exposure to the rays of radium in the surrounding minerals, rather than to the more permanent suspended impurities such as produce the colour in ruby glass. For the colour of such gems is often discharged by heating. Colourless gems may often be coloured by exposure to the rays of radium, the bewildering range of colour resulting depending probably upon the nature of the impurities present. Thus Sir W. Crookes was successful in colouring a large diamond to the tint of an emerald by putting it into a bottle containing a radium salt. It is significant, however, that a diamond of the first water cannot be coloured by this means, however long it is exposed to the rays. Some trace, however minute, of impurity is probably necessary both for fluorescence and for colouration.

Thus zinc sulphide, which is used to show the  $\alpha$ -rays, when absolutely pure does not exhibit fluorescence, and the best results for this purpose are got by using zinc containing one-ten-thousandth part of copper. Similarly willemite, used for the  $\beta$ - and cathode-rays, is very sensitive to the nature of the impurity present. Sir Herbert Jackson, who invented the focus tube for X-rays, manufactured a range of artificial willemites—from those, at one end, which were purely fluorescent without any trace of after-phosphorescence, to those at the other which showed a strong and persistent phosphorescence—by varying the nature of the impurity and the composition of the material.

It is significant that the colour of the light emitted is often the same as that emitted by the metal of the salt in the flame or arc spectrum. Thus lithium platinocyanide gives a deep red, sodium platinocyanide a yellow, and calcium and barium platinocyanides deep green fluorescence under the  $\beta$ - and  $\gamma$ -rays of radium and under X-rays. Curiously, magnesium

platinocyanide, which gives a brilliant rosy fluorescence with X-rays, seems hardly to respond at all to the  $\beta$ - and  $\gamma$ -rays. In general, in this subject, we have a good example of the close connection referred to on page 33, between chemical, electrical and optical phenomena, and the modern tendency to reinterpret a host of apparently disconnected and diverse phenomena in terms of the relations between the electrons and the positive ions which constitute matter.

**Ions and Rays.**—Any ion is potentially a radiant particle. If allowed to move freely or “fall” through a sufficiently powerful electric field, it will acquire sufficient velocity and energy to ionise the molecules, with which it collides, on its own account. Professor Townsend, to whom the subject owes so much, has termed this “ionisation by collision,” and he has shown how many of the salient features of the electric discharge through gases arise in this process. It is regularly employed, as discussed in Chapter XVI., to magnify the ionisation produced by  $\alpha$ - and  $\beta$ -particles to the extent that an individual particle can be electrically detected.

As Aston has well put it, the charge on an ion is a handle enabling you to get hold of it and to study it as an individual, whereas you can only deal with uncharged atoms and molecules in minimum aggregates millions of times larger than the number of people alive in the whole world. One very useful way of regarding the  $\alpha$ - and  $\beta$ -rays is to consider the strength of the electric field that would have to be employed to produce them. Thus, for the cathode-rays of the vacuum tube, the velocity and energy corresponds with a potential difference of rarely, if ever, more than a hundred thousand volts, even with the most powerful electric appliances. This gives a maximum speed not much exceeding 1/3rd that of light. Whereas speeds of 80 to 95 per cent. of light are possessed by many  $\beta$ -rays, and, to produce such rays artificially, potentials between one and two million volts would be required. Some of the  $\beta$ -rays travel with speeds almost indistinguishable from that of light, and possess energy corresponding to as much as eight million volts, but it is possible that these are exceptional and are analogous to the exceptional long-range  $\alpha$ -rays still to be discussed.

The  $\alpha$ -particles, which travel with a speed from 1/15th to 1/20th that of light, and are 7,300 times as massive as the  $\beta$ -particles, carry two positive charges and therefore would acquire in an electric field twice the kinetic energy acquired by the electron. We may suppose a stationary  $\text{He}^{++}$  ion starting at the positive pole and being attracted by the negative pole in a vacuum tube and calculate the potential difference between the poles necessary to convert the ion into the  $\alpha$ -particle. To produce artificially in this way the  $\alpha$ -particle emitted by radium C, for example, would need a potential of 3.83 million volts. In general, the energy of the various  $\alpha$ -particles corresponds with potentials between two and four million volts, while, for the exceptional long-range  $\alpha$ -particles given by radium C and thorium C, the maximum is 5.3 million volts, for the rays of range 11.5 cm. of air given by the latter.

For the positive rays, which are the nearest analogue to the  $\alpha$ -rays, the positive ions in the vacuum tube are initially moving just like the molecules of a gas, at speeds of the order of a mile a second at most. But the field "gets hold of them" and impresses upon them speeds and energy enabling them to produce fluorescence, affect the photographic plate and ionise gases. But, with the present limitations of the voltages it is possible to use, the speeds do not much exceed 1/100th of that of light.

**Artificial Transmutation.**—These considerations show very clearly one of the preliminary advances that must be made before we can hope to transmute the elements artificially. It will be necessary to be able to build transformers capable of giving many million volts before we attain sufficient intensity of electric forces to endanger the stability of the ordinary atoms of matter. The electrical engineers have begun to turn their attention to the building of such transformers and have already built them capable of giving something like a million volts. This development is being pursued in the hope that it may one day be possible to produce rays rivalling those given by the radio-elements in energy, and possibly ultimately to effect transmutations in a controllable and useful manner. There is still some distance to go in this direction, apart altogether from the difficulties that may be

expected to arise in the application of such forces to such a purpose. The artificial production of a lightning discharge several metres long in air is one thing, but the application of this potential across a single atom is another. However, there is no reason to doubt that useful and valuable results, probably wholly unanticipated, will arise from the progress of electrical engineering in this direction.

**$\alpha$ -Rays.**—The rest of the chapter is concerned with the more outstanding features of the  $\alpha$ -rays, rather than the properties of the individual  $\alpha$ -particle, which will be the main topic of Chapter XVI. The electric and magnetic deviation experiments, coupled with the determination of the number of charges carried by the individual  $\alpha$ -particle, established that it was the nucleus of a helium atom,  $\text{He}^{++}$ , that is to say a neutral helium atom that had lost its two satellite electrons, and this was directly proved as detailed at the end of Chapter IV. Since all motion is relative, even if the  $\alpha$ -particle were ejected from the radioactive atom in a neutral state, it is certain that its very first collisions with the molecules of matter in its path would ionise it, just as it itself ionises these molecules when it collides with them. It would lose one or both of its electrons on its first collision. In the early days it was of some importance to know whether the  $\alpha$ -particle was ejected from the atom initially in a charged condition or not. Experiments were performed with the very thin layer of active deposit, from which it might be reasonably supposed that most of the  $\alpha$ -particles escaped from the surface, to see if all the  $\alpha$ -particles were still deviated by a magnetic field in a practically perfect vacuum. But, even under the best conditions, when certainly a considerable proportion of the  $\alpha$ -particles could not have suffered a single collision after expulsion from the atom, they were all deviated normally by the magnetic field.

The question was decisively, if indirectly, settled by the Displacement Law, which showed that the nucleus of the atom suffers the loss of two + charges when the  $\alpha$ -particle is ejected, and that the charge on the latter therefore is intrinsic to it, and not merely a consequence of subsequent collisions. Recent researches in the Cavendish Laboratory

have shown that, during its flight, the  $\alpha$ -particle is continually gaining and losing electrons. This is not very marked except at the end of the range, where singly-charged and neutral  $\alpha$ -particles may actually predominate over the normal doubly-charged particles. This is readily shown under suitable conditions by the deviation produced by the magnetic field. In addition to the normally deflected beam due to  $\text{He}^{++}$ , there is another, deflected only half as much, due to  $\text{He}^+$ , and another, completely unaffected by the field, due to neutral atoms, He.

**Range of  $\alpha$ -Rays.**—Two characteristics especially distinguish the  $\alpha$ -rays from all other types of radiation. As regards any single change in which an  $\alpha$ -particle is expelled, all the  $\alpha$ -particles are initially expelled with the same velocity, and the rays are in this respect homogeneous.<sup>1</sup> Moreover, in general, each ray travels essentially undeflected through practically the same distance in a homogeneous absorbing medium, such as air. The consequence is that the rays have a definite distance of travel or "range." Just inside this distance they are producing their maximum effect, and just outside practically none whatever. The ionisation effects seem to increase with the time taken by the  $\alpha$ -particle to traverse the atom ionised and, as the velocity of the  $\alpha$ -particle is reduced by its collisions with matter, the rate at which it ionises increases. Hence the rate of ionisation rises to a maximum along the path and then very abruptly ceases.

This property was discovered in 1904 by Sir William Bragg. The rays from a flat surface of radium were canalised by a number of parallel slits or tubes, and passed through a very shallow ionisation chamber, only about a millimetre deep, placed parallel with the surface and at right angles to the rays. If one deals with a single  $\alpha$ -ray-giving radio-element, such as polonium or ionium, or with a freshly prepared radium preparation in which radon and active deposit products are absent, on bringing the ionisation chamber from a distance nearer the radioactive preparation, the  $\alpha$ -ray ionisation increases abruptly from zero to a maximum and then diminishes steadily as the distance decreases.

<sup>1</sup> This is the broad general rule, but certain exceptions will later have to be noticed for cases in which  $\gamma$ -rays accompany the  $\alpha$ -rays (pp. 295, 300).

**Bragg Curves.**—If the intensity of the ionisation is plotted on the horizontal axis and the distance of the source from the ionisation chamber on the vertical axis, one obtains what is known as the Bragg curve. The first examples observed are shown in Fig. 27. They were obtained for a thin film of radium salt. Curve A on the extreme left is the single Bragg curve for the  $\alpha$ -rays of radium itself, and it was obtained for the film immediately after preparation, when the radium salt had been freshly evaporated from solution and before any of

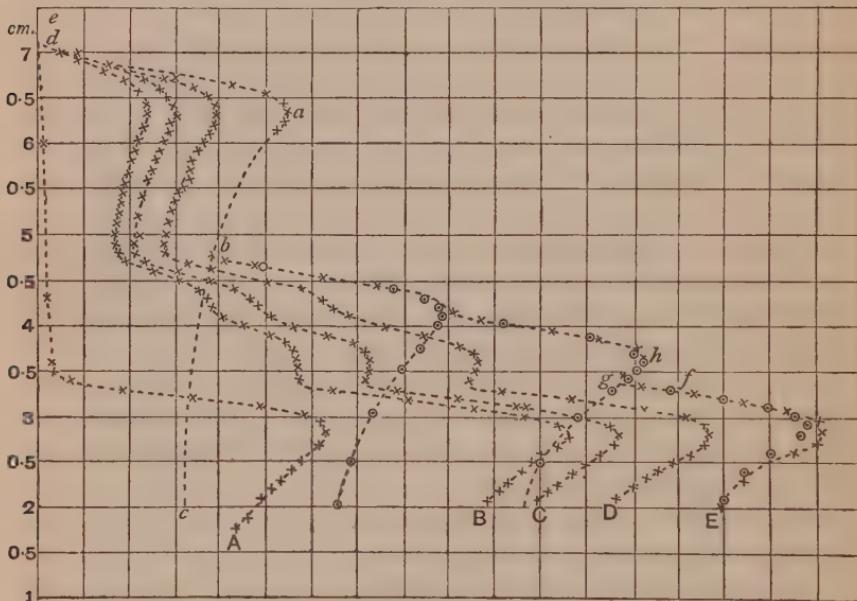


FIG. 27.

the subsequent products had grown. The curve for fully "ripe" radium is the curve E to the extreme right of the diagram, and it was obtained after one month. The curve A gradually changed with the lapse of time into curve E, and the curves B, C, D represent intermediate stages. Curve E is, of course, really composed of four separate Bragg curves for four types of  $\alpha$ -rays of different range superimposed. Proceeding from right to left, the four curves are those due respectively to the  $\alpha$ -rays of (1) radium itself, (2) radon, (3) radium A, (4) radium C, in order of increasing range. Starting from the left, the part  $d a b$  is due to RaC alone,

but at *b* the Ra-A ray comes in causing the abrupt turn to the right. The curve for pure RaC by itself would be *d a b c*, essentially similar to curve A for Ra, but of about twice the range.

A striking success by this method was obtained by Hahn in 1906. Examining the  $\alpha$ -rays of thorium C, he found them to be complex and to consist of rays of two different ranges, 4.8 and 8.6 cms., the latter being, apart from the exceptional long-range  $\alpha$ -particles already mentioned, the fastest  $\alpha$ -particle known. The curve obtained is shown in Fig. 28. As detailed more nearly in Chapter XI., in this case the two types of rays are derived from the two branches of a multiple disintegration, the rays of longer range being about twice as numerous as the other type.

A table of the ranges of all the known  $\alpha$ -rays, in centimetres of air at 15° C. and 760 mm. pressure, is printed on the chart showing the Displacement Law at the end of the volume.

The definiteness of the range of the  $\alpha$ -rays may be experimentally shown with the apparatus, of which Fig. 29 (facing p. 95) is a photograph and Fig. 30 a diagram. A shallow open tray containing a thin layer of radium, or polonium, is held centrally in a globular flask of about six inches (15 cm.) diameter which can be exhausted by a pump. The upper hemisphere of the flask is coated internally with zinc sulphide. With the flask full of air the  $\alpha$ -rays are absorbed before reaching the walls, and nothing is visible in the dark. On exhausting the flask with the pump it suddenly flashes into luminosity, and on readmitting the air it as suddenly "goes out."

**The Interpenetration of Atoms.**—The power possessed by the  $\alpha$ -particle to pass clean through the atoms of matter in its path as though they were not there is very remarkable. As Bragg expressed it, "Each  $\alpha$ -particle pursues a rectilinear course, no matter what it encounters; it passes through all the atoms it meets, suffering no deflection on account of any encounter until, at any rate, very near the end of its course. A thin metal plate may be placed in the way of the stream and so rob every particle of some of its energy, but not a

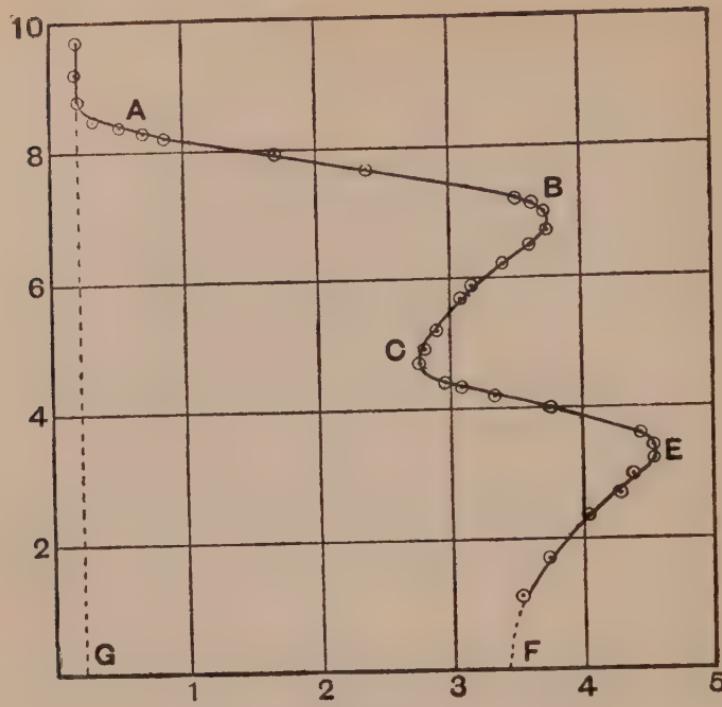


FIG. 28.

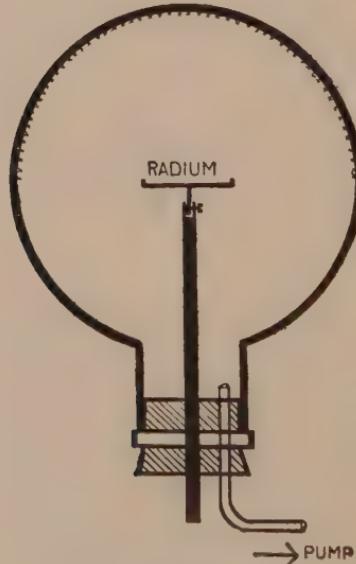


FIG. 30.

single one is brought to rest by collision with the atoms of the metal, and the number of particles in the stream remains unchanged." This vivid description is still quite true as regards the overwhelming majority of the  $\alpha$ -particles and of the collisions they suffer, though it has to be modified for a small proportion of the encounters, in which "wide-angle single scattering" occurs (Chapter XIII.).

All that happens to the atoms struck is that they are ionised, that is, one or more electrons are knocked out of them to give the positive ions which on the first opportunity recombine with other electrons to give the original atoms as though nothing had happened. But this is as eloquent of the nature of the atoms struck as it is of that of the  $\alpha$ -particle, and it is, of course, upon a closer study of this phenomena that Rutherford's nuclear theory of the atom is based.

**Range, Velocity and Stopping Power.**—One very important point is that there is no difference practically between one  $\alpha$ -particle and another if, by absorption in a homogeneous layer, the velocities and ranges of the two are made identical. The range varies as the cube of the velocity. Comparing different absorbers, Bragg found that the "stopping power" of a substance was approximately proportional to the square root of its atomic weight, if it is elementary, or to the sum of the square roots of the weights of the component atoms of the molecule, if it is a compound. This enables the range to be calculated in any substance, such, for example, as mica, from the chemical composition, and is of importance in connection with pleochroic haloes, as later discussed. A rather interesting consequence of this law of stopping power is that it gives one of the few proofs that the elements of Group O are monatomic. If hydrogen and helium had similar numbers of atoms in their molecules, helium, being twice as dense as hydrogen, would have an atom twice as heavy as that of hydrogen, which should have a stopping power  $\sqrt{2}$  times as great. Whereas, if hydrogen has two atoms of mass one and helium one atom of mass four in the molecule, the sum of the square roots of the weights of the atoms in the molecule is the same for both, and their stopping power should be equal, as in fact they nearly are.

**The Geiger-Nuttall Relation.**—As already indicated, the shorter the life of a radio-element giving  $\alpha$ -rays, the longer the range of the rays and the faster the velocity with which they

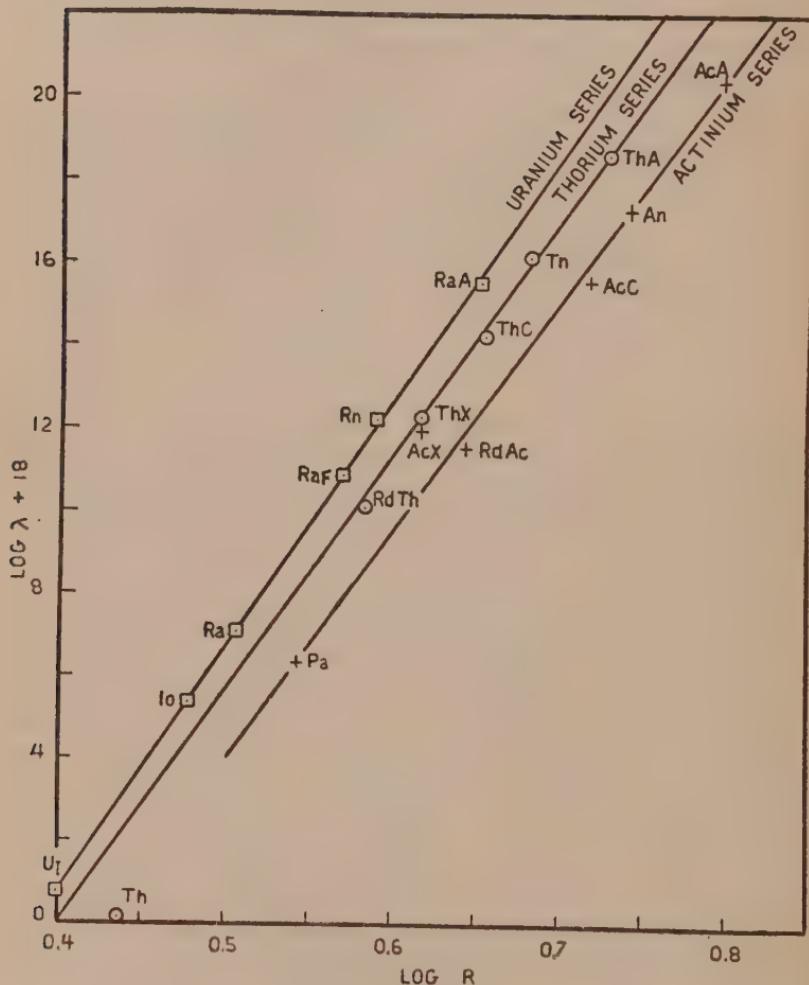


FIG. 30A.

are ejected. If the logarithm of the period of average life is plotted against the logarithm of the range or velocity, for all the radio elements giving  $\alpha$ -rays, the three series are represented by three approximately straight lines, parallel with

one another. This is the Geiger-Nuttall relation, and it clearly has some theoretical significance. It is shown in Fig. 30A, in which the logarithm of the range is shown on the horizontal axis, and the logarithm of the rate of change, or reciprocal of the period, on the vertical axis. If either the range of the  $\alpha$ -ray or the period of life is known, the other can be approximately found. Thus, long before the direct determination of the period of ionium, the range of the  $\alpha$ -ray expelled indicated correctly that it must be of the order of 100,000 years. Similarly, from the very long ranges of the  $\alpha$ -rays of radium C' and thorium C', we infer periods of the order, respectively, of a millionth and a billionth of a second. These however are not shown in Fig. 30A as they lie far outside the diagram to the right.

The generalisation holds most nearly for the uranium series and least accurately for the actinium series. Indeed, in this series radioactinium and actinium X furnish the clearest exception to the rule, for the period of the former is about twice as great as for the latter, but the range of the rays of the former is about 3 mm. the greater. This relation has been the starting-point of all attempts, beginning with one in 1915 by Professor Lindemann, to account for the break-up of the atom of the radio-elements, but the matter remains obscure. It must be remembered that the relation is neither mathematically exact nor free from exception. The most generally interesting feature of the generalisation is, perhaps, that the curves for the three series are parallel and not superimposed, as this means that each disintegration series must preserve throughout some trait of its initial character, which is different for all three series. This is one of the arguments for regarding the actinium series as genetically unconnected with the uranium series and originating in a different isotope of uranium.

Another very interesting deduction is that, if any of the common elements were emitting  $\alpha$ -rays with range and velocity much less than those of the known radio-elements, their periods would be so excessively long that, to ordinary tests, they might not show a detectable radioactivity at all. There is a certain amount of evidence in connection with the topic now to be discussed that this may actually occur.

**Pleochroic Haloes.**—The unique properties of the  $\alpha$ -rays just discussed have been found to account perfectly for certain spherical microscopic haloes, occurring in mica and other minerals, which formerly were a complete puzzle to the petrologist. They are coloured spots surrounding a minute centrally placed and often invisible nucleus, usually zircon and, more rarely, apatite. Joly, in 1907, suggested that they were due to  $\alpha$ -particles emitted by the central nucleus, which must be feebly radioactive, staining the mica over a spherical region corresponding with the range of the  $\alpha$ -particles in mica, and this explanation has been fully substantiated. He measured the radius of haloes in one specimen of biotite and found it to be  $30 \mu$  ( $0.003$  cm.), which corresponds exactly with the calculated range of the  $\alpha$ -particle of radium C' in mica. Further search revealed others of radius  $38 \mu$ , which again corresponds with the range of the  $\alpha$ -particles of thorium C'. Fig. 31 is an excellent microphotograph of two good haloes, one from uranium and one from thorium, in the same piece of mica.

These haloes show very different stages of development according to different ages of the mineral. In the first stage, corresponding to the most recent haloes, only a central pupil of radius  $13 \mu$  is present, which corresponds with the group of short-range  $\alpha$ -particles from uranium, ionium and radium itself. A little later in the development, a faint outer corona develops, due to the rays of radium C, and, as time goes on, this blackens up to a fully developed halo of radius  $30 \mu$ . In rare cases, besides the halo due to radium C, a ring between the inner pupil and the outer corona, due to the rays of radium A, can be clearly distinguished. Fig. 31A is a highly magnified photomicrograph of such a halo in biotite which shows clearly the outer corona and the inner ring. In the upper photograph the lower halo is a fully developed radium halo and the upper is a thorium halo, not fully developed, but showing the faint outer corona due to the long-range  $\alpha$ -rays of thorium C'.

A certain variety of fluorspar from Wolsendorf has latterly been found to show haloes in greater abundance and variety than any other substance, and these differ in detail from those in mica. The extreme ends of the ranges are more sharply

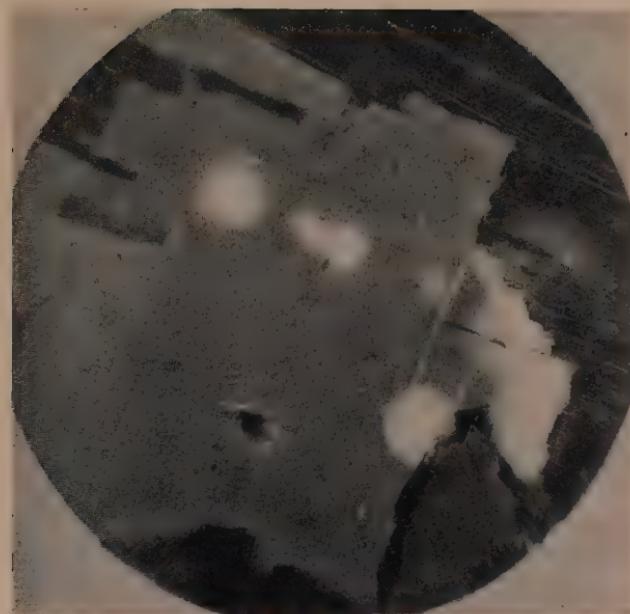


FIG. 31.—THORIUM AND URANIUM HALOES IN BIOTITE.

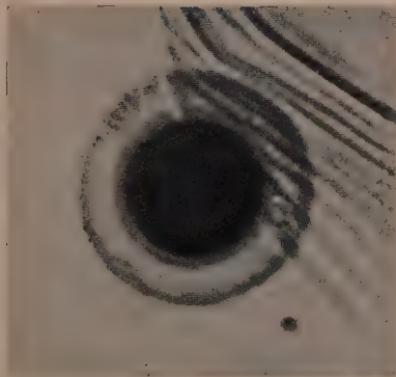


FIG. 31A.—HALO IN BIOTITE SHOWING  
RING DUE TO RADIUM A.



FIG. 32.—URANIUM HALO IN FLUORITE.

*To face p. 112.*





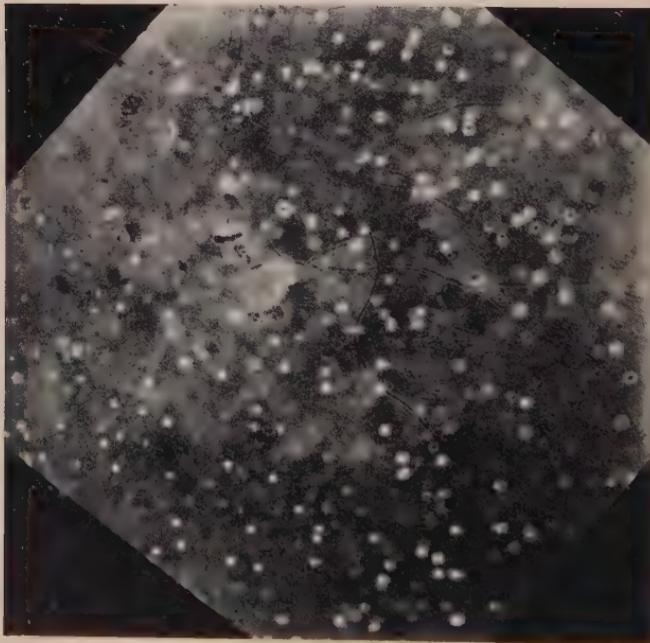


FIG. 33.—HALOES OF UNKNOWN ORIGIN IN YTTERBY MICA (ARCHÆAN).  
BY J. JOLY.

*To face p. 113.*

pronounced, so that, in some of the uranium haloes, seven out of the eight rings, due to the eight  $\alpha$ -particles in the disintegration series, have been distinguished, the innermost being of double width and presumably due to two  $\alpha$ -rays. This has enabled the range of the  $\alpha$ -particle of uranium II to be measured with more certainty than by the usual methods. A good example of a halo due to uranium in fluorite is shown in Fig. 32.

**Halo Problems and Anomalies.**—Other haloes, ascribed to radon only, have been examined. Presumably in this case the central nucleus has adsorbed and localised radon dissolved in water that has percolated through uranium minerals. But this explanation appears doubtful, particularly since haloes have now been found corresponding with  $\alpha$ -rays of very short range, from 1.5 to 2.5 cm. of air, which do not belong to any known radioactive substance. Joly, who found these, ascribed them to an unknown radio-element which he termed "Hibernium," but unfortunately all these examples were lost when his laboratory in Dublin was destroyed during the civil war in Ireland, and no more have been discovered. But Iimori has found others, similar but not identical, in a Japanese mica. Fig. 33 shows some of Joly's small haloes of unknown origin in Ytterby mica of Archæan age.

The actual radioactivity responsible for these effects must be incredibly minute and quite beyond detection by any other method. It has been estimated that some of these uranium haloes have been formed by the emission of less than 100  $\alpha$ -particles a year, continued over several hundred millions of years. The mica integrates by its discoloration these otherwise completely undetectable effects throughout the ages, leaving a permanent record, the further investigation of which is likely to add to our knowledge in spheres where no other information is available. At the same time difficulties arise in believing that the very small haloes recently discovered can be due to the excessively slow changes to which the ranges correspond, as it would seem that periods far greater than the longest estimate of the age of the earth would be required for their production.

An exceedingly curious anomaly has transpired in connec-

tion with this study. Whereas the thorium haloes are, to their minutest detail, a perfect "fit," as regards the diameters of the rings and the known ranges of the  $\alpha$ -particles of the thorium series, those of uranium are not. The inner pupil is here distinctly oversize. Joly considers this as definite experimental evidence that in past ages the period of uranium was less than it is now, that of thorium having remained constant. If this is so, it is dangerous to make use of uranium as a clock in the determination of geological age, for it has been running faster in the past, and the lead-uranium ratio, for example, will give ages for the earth and its minerals which are too long.

At first this suggestion seemed highly improbable, but now it is much less so. Indeed, it is known that what Joly suggests must have taken place, and the only doubt is as to whether the change of period is sufficient to invalidate the uranium-lead ratio as a measure of geological time. The subject is reverted to in the last chapter (Chapter XIX.).

**Radioactive Recoil.**—The atomic explosion in which the  $\alpha$ -particle is expelled obeys the ordinary law of momentum. Exactly like a gun when a shot is fired, the atom from which the  $\alpha$ -particle is ejected recoils with a momentum equal to that of the projectile. Since the mass of the atom remaining is some fifty times the mass of the  $\alpha$ -particle expelled, the velocity of recoil is only about 1/50th of that of the  $\alpha$ -particle. This is something like 200 miles a second, and while it is too small to confer on the recoiling particle the marked ionising power that characterises the  $\alpha$ -ray, it is put into evidence by the product, under suitable circumstances, being projected from the substance producing it and being deposited on the nearest available surface. The velocity of recoil corresponds for a gas molecule to a temperature of a thousand million degrees Centigrade, so that it is not surprising to find that the product of an  $\alpha$ -ray change behaves at the moment of formation as if it were volatile, although, after formation, it is not at all volatile.

The property has been of great practical use in the separation of the product from the parent in a number of cases, and a number of products have been discovered by this method.

It applies more particularly to the post-emanation members, which, as an active deposit, can be got as unweighable and invisible films on flat plates. It suffices to place over the plate another plate parallel with it and a short distance from it, to obtain on the latter the recoiling product. It is best to have the arrangement enclosed in an exhausted vessel and to make the plate on which the recoiled product is required negatively charged with respect to that containing the active deposit.

Thus, in this way radium B may be got from radium A or radium D from radium C. Owing to the small mass of the  $\beta$ -particle, there is but little recoil of the product of a  $\beta$ -ray change compared with that in an  $\alpha$ -ray change. But it is historically interesting to note that in an experiment to see whether any recoil of  $\beta$ -ray products occurred, the product, first called radium C<sub>2</sub> and now radium C'', was discovered. This, as detailed in Chapter XI. (p. 166), is a branch product of the main series in excessively small proportion. Although this method of separating it indicated that it was the product of an  $\alpha$ -change, the  $\alpha$ -rays accompanying its production have only just been put in evidence by Lord Rutherford by the differential valve method discussed on page 282.

More recent experiments have put into evidence a perceptible recoil due to  $\beta$ -rays, but it is small and uncertain. Owing to the velocity of the recoiling atom in this case being very low, it is not ionised by its collisions with the gas molecules in its path, and, in consequence, the product cannot be collected by applying an electric field.  $\beta$ -ray recoil has been used in an interesting attempt to obtain direct evidence of the very short period of radium C' (p. 111). As detailed in Chapter XI., radium C' is the product of radium C in a  $\beta$ -ray change, and itself gives  $\alpha$ -rays. Owing to its short life the two radiations normally appear to be emitted simultaneously. Under suitable conditions in a high vacuum some of the radium C' atoms may recoil from the plate containing the radium C, and emit their  $\alpha$ -particles during their flight from the plate. The velocity of the recoiling atoms can be calculated, and so it can be found how long it takes for the radium C' atom, after its production from radium C, to disintegrate. The estimates so made agree with the value of the period—about a millionth of a second—calculated from the Geiger-Nuttall relation.

## CHAPTER VIII

### $\beta$ -, $\gamma$ - AND X-RAYS

**The Modern View of  $\beta$ -Rays.**<sup>1</sup>—Although the  $\beta$ -rays were at first the only type of rays clearly recognised in the radiation of the radioactive substances, and although their general character, as electrons expelled at very high velocity, was very easily and quickly established by experiments on their deviation in electric and magnetic fields, more detailed study has shown them to be far more complicated and difficult to interpret than the  $\alpha$ -rays. Instead of a comparatively few well marked rays of definite range, one corresponding with each type of disintegrating atom, as in the latter case, the exact opposite is the case for the  $\beta$ -rays. Each type of  $\beta$ -ray disintegration gives a very complex assortment of  $\beta$ -rays, in which a variety, often a bewildering variety, of separate homogeneous types may be distinguished. But, quite unexpectedly, these definite types, which are homogeneous and possess definite initial velocity of ejection, have now been proved not to be the  $\beta$ -particles actually ejected from the disintegration in the first place. They form only a relatively small proportion of the whole, and are of the nature of secondary rays, emitted by the disintegrating atom as an after consequence of the primary disintegration. The primary disintegration electrons, as they are now called, which constitute the main part of the  $\beta$ -rays, have been now shown not to be homogeneous at all, but always to vary continuously in velocity over a wide range. So that here the indeterminateness of the state of the disintegrating atom, discussed later (p. 283), shows itself in the quite indefinite speeds with which different atoms of the same type expel the  $\beta$ -particle. But the rule, that one  $\beta$ -particle is emitted per atom disintegrating, appears to apply to the primary disintegration electrons, as it does for the  $\alpha$ -particles. This we should expect from the

<sup>1</sup> *Radiations from Radioactive Substances*, Lord Rutherford, James Chadwick and C. D. Ellis, Camb. Univ. Press, 1920.

Displacement Law, and when due allowance is made for the secondary  $\beta$ -rays, the number of  $\beta$ -rays expelled agrees with the number of atoms disintegrating.

**Photographic Action and Penetrating Power.**—The major part of the photographic action of radioactive substances, using ordinary plates, is due to the  $\beta$ -rays. This is probably because they possess the most favourable penetrating power for the purpose. The  $\alpha$ -rays can hardly penetrate sufficiently into the film, whereas the  $\gamma$ -rays go right through with very little absorption, and, therefore, with little of their total energy utilised. By the use of gelatine-less films, as with the Schumann-rays, the photographic action of  $\alpha$ -rays and positive rays may be increased, and by the use of thick or multiple films, as with X-rays, the same can be achieved for the  $\gamma$ -rays.

The photographic action of the  $\beta$ -rays of radium is well shown by Fig. 38 (facing p. 125), which was taken by writing on a photographic plate, wrapped in a light-proof envelope, with a sealed glass tube containing a radium preparation, as with a lead pencil, and then developing the plate.

The absorption of  $\beta$ -rays by matter proceeds at first exponentially, as with light through a transparent medium, the absorbing power of different substances being, to the first approximation, proportional to their density. But, after the rays have been much reduced in intensity, the proportional absorption by each additional layer increases. This is the law obeyed if the radiation is measured through a single layer of increasing thickness, or through an increasing number of sheets of metal foil piled close together on one another. Actually the  $\beta$ -rays are completely scattered even by very thin foils, so that all trace of the original direction is very soon lost. As already remarked, the  $\beta$ -rays in contradistinction to the  $\alpha$ -rays, are always heterogeneous as regards velocity, and absorption and scattering by matter reduces both the velocity and the number of the  $\beta$ -particles in the stream.

Of the various  $\beta$ -rays, the most penetrating are those of radium C', those from thorium C' and uranium X being but little inferior. These are half absorbed by each half-millimetre of aluminium in their path, and, owing to the increase

in the rate of absorption at the end, practically none escape through a layer equivalent in weight to 4 millimetres of aluminium. The next most penetrating  $\beta$ -rays are, in order, those from thorium C'' and actinium C'', the latter being only about half as penetrating as the first set. Many other less penetrating types are known, but none of them are much more penetrating than, and some not as penetrating as, the  $\alpha$ -rays.

**Magnetic Deviation.**—The salient features of the effect of a magnetic field upon the rays of radioactive substances has been already set forth in Mme. Curie's diagram (Fig. 11,

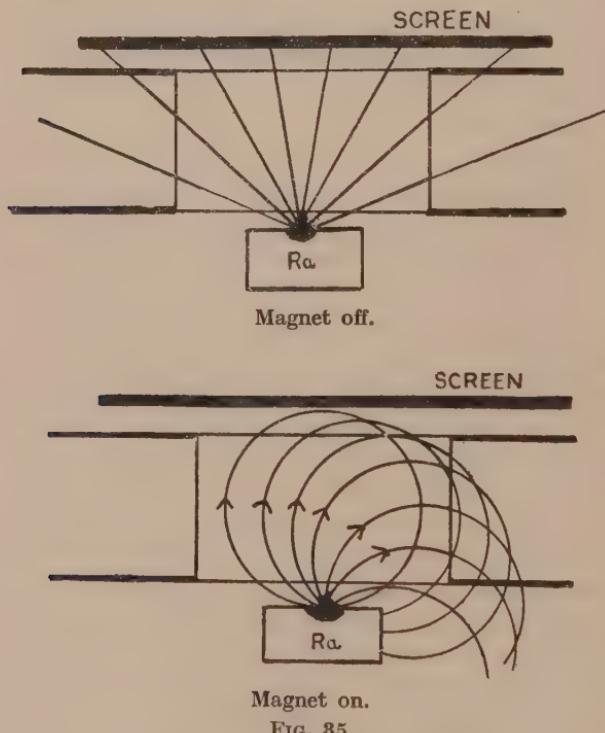


FIG. 35.

p. 21). With a preparation containing a few milligrams of radium compound the deviation of the  $\beta$ -rays may readily be shown as a lecture experiment to an audience by means of the apparatus shown in Fig. 34, with explanatory diagram Fig. 35. The first shows an ordinary electromagnet

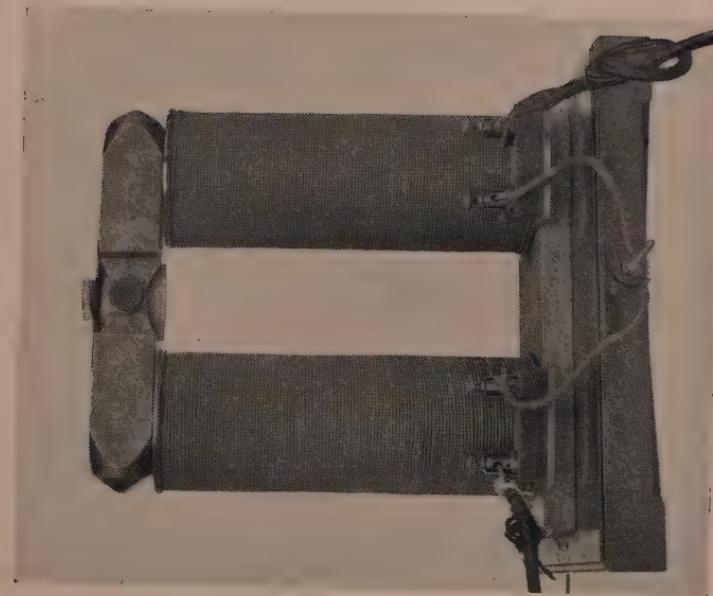


FIG. 34.—ELECTRO-MAGNET TO SHOW DEVIATION OF  
 $\beta$ -RAYS.

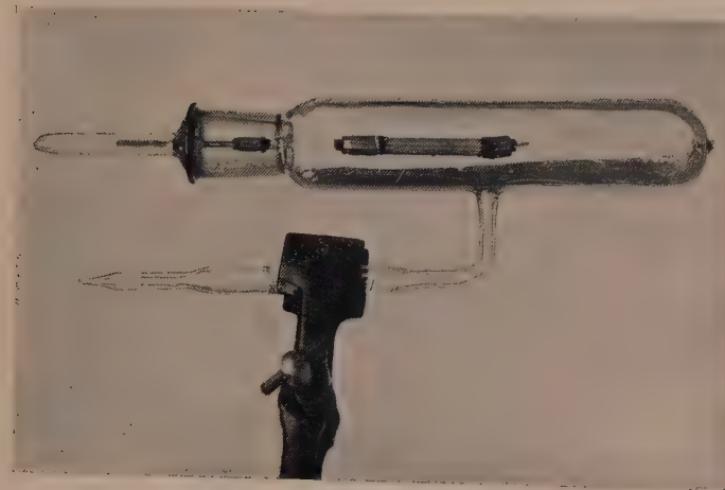


FIG. 36.—LORD RAYLEIGH'S RADIUM  
CLOCK.  
*To face p. 118.*



with flat pole-pieces close together, the gap between forming a slit through which pass the rays from the radium in a capsule fixed on the near side of the pole-pieces. On the far side, towards the audience, is fixed a piece of barium platinocyanide screen of the same kind as is used for showing X-rays. The diagram (Fig. 35) represents a plan of the arrangement as seen from above. In the upper picture, with the magnet not excited, the  $\beta$ -rays proceed in all directions of space from the radium, and some of them strike the screen and cause it to glow. When the current is turned on the rays are all deviated as shown in the lower figure, and, if the magnet is sufficiently strong, practically none of them reach the screen. The luminosity of the latter is then very faint and due to the  $\gamma$ -rays, and its intensity is now little reduced if a metal coin is inserted in front of the radium. With the coin in place, there is no difference in the glow whether the magnet is on or off.

The direction of deviation alone is sufficient to indicate to a physicist that the rays must carry a negative charge away from the radioactive substance. But this negative charge can be made manifest by receiving the rays on an insulated plate connected to an electroscope or electrometer. Conversely, if the radium is insulated and if it is contained in a sealed receptacle sufficiently thick in the walls completely to stop the  $\alpha$ -rays—and it is difficult to make a receptacle for which this is not true—the radium will acquire a positive charge through the loss of the negative  $\beta$ -rays.

Radioactivity, as the Curies first demonstrated, thus confers upon substances possessing the property the power to charge themselves up with electricity spontaneously. They recognised, moreover, that, theoretically, the potential to which the substances should be able to charge themselves must be very high. It ought to go on increasing until the positive charge left on the radioactive substance itself was sufficient to attract back to it the  $\beta$ -particles expelled from it, and for this, as we know now, theory indicates a potential of millions of volts.

**The Radium Clock.**—A very simple instrument, known as the “Radium Clock,” was devised by the Hon. R. J. Strutt,

the present Lord Rayleigh, to demonstrate this property. A photograph of the instrument is shown in Fig. 36 (facing p. 118), and a diagram explaining its construction in Fig. 37. A sealed tube of radium preparation, A, is carried on an insulating quartz or sulphur support, B, centrally in a sealed glass tube that has been exhausted to a very high vacuum. The radium tube carries at its lower end a pair of gold leaves,

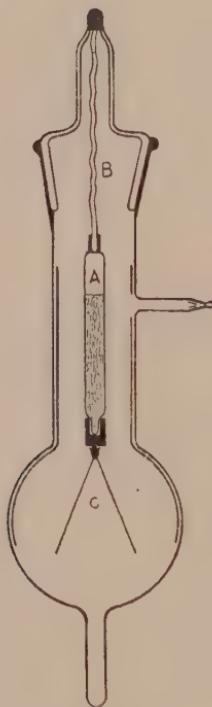


FIG. 37.

C, and to the inside walls of the tube are fixed strips of tinfoil connected by a platinum wire through the walls to the earth. The radium gradually acquires a positive charge, causing the leaves of the instrument to repel each other and open as with the gold-leaf electroscope. If the tube contained any air or other gas, the ionisation of this by the  $\beta$ -rays would discharge the instrument. In complete absence of air, the leaves diverge until they touch the sides coated with tinfoil and are dis-

charged, when the whole process begins again. With 15 milligrams of radium (element) the period is about a minute, depending on the size, or electrical capacity, of the insulated system.

The radium clock is probably the nearest approach to an actual perpetual motion machine ever yet constructed. Assuming it to be perfectly made, not with a ground-in and lubricated joint at the top as shown in the figures for ease of construction, but with the parts sealed together as in an electric lamp to prevent the possibility of air leaking in, it should go on working for thousands of years, its period growing gradually less so that at the end of every 1,600 years it would go half as fast as at the beginning. Even so, it usefully employs but a very minute proportion of the energy liberated, and it should be possible with the same quantity of radium to construct a much livelier perpetual motion machine. One day we may have enough surplus radium to spare some on scientific curiosities such as this.

Moseley, whose researches on the X-ray spectra of elements elucidated so clearly the interpretation of the Periodic Law, attempted to use the principle of the radium clock as a method of arriving at otherwise unattainable potentials. His failure is possibly indicative of some of the obstacles that must be overcome before, even if we can construct transformers to give us the necessary potentials, we can hope to do much in the way of simulating or controlling radioactive processes. He measured the maximum potential to which a perfectly insulated radium preparation would charge itself up to in a vacuum. He succeeded in reaching 150,000 volts, which may be regarded as of about the same order as can be got from a large induction coil, but further progress was always arrested by the discharge that occurred through the vacuum at this point. Probably at about this potential, under the electric stress, the ordinary solid materials of the instrument became ionised and provided carriers to transport the accumulated charge across the vacuous space. One would expect that something like this would occur long before the stress rose sufficiently to cause the atoms to break up as in radioactivity. The nuclei of the atoms are surrounded by electrons which protect them from direct electrical attack,

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and it is the nuclei, not these external electrons, which have to be got at before transmutation can be achieved.

**$\gamma$ -Rays.**—As first discovered and recognised, the term  $\gamma$ -radiation was given to indicate the most penetrating rays, more penetrating than any other known type, left unabsorbed after the passage of the radiations from radioactive substances through screens or filters thick enough completely to absorb the  $\alpha$ - and  $\beta$ -rays. They are always relatively feeble, but, on the other hand, larger quantities of the materials may be usefully employed in their study, owing to the small absorption of the rays in the substance itself. Not being deviated by magnetic or electric fields, they were generally regarded as analogous to the X-rays—and this has now been established—bearing to the  $\beta$ -rays much the same genetic relation as the X-rays bear to the cathode-rays. As with the  $\beta$ -rays, complications have ensued from their more intensive study.

By using magnetic fields to deflect away the  $\beta$ -rays, it is possible to recognise and study types of  $\gamma$ -rays very much less penetrating than when the  $\beta$ -rays have to be eliminated by absorption. In this way  $\gamma$ -rays from the various radio-elements of all degrees of penetrating power, down to and even less than that of the  $\alpha$ -rays, have been found to be present. The softer or less penetrating of these are secondary in origin and represent the characteristic X-radiation associated with the secondary  $\beta$ -rays of definite velocity ejected from the atom subsequent to the main disintegration.

The more penetrating types, it would appear, are those similarly connected with what have been termed the true disintegration electrons emitted by the atom in its  $\beta$ -ray change. But the direct causal relation between the  $\beta$ - and the  $\gamma$ -rays, which was formerly assumed, cannot be universally maintained. Only some of the  $\beta$ -ray changes give  $\gamma$ -rays also. That suffered by radium E is apparently not accompanied by any  $\gamma$ -radiation. Also,  $\gamma$ -rays, though in very small intensity and of low penetrating power, have been found to arise in some of the  $\alpha$ -ray changes.  $\alpha$ -rays, also, possess the power of exciting the characteristic X-radiation when they impinge upon atoms, though the effects are very small. Some of the  $\alpha$ -ray-producing radio-elements, for example polonium, appear, however, to emit a small quantity of

$\gamma$ -radiation of definite homogeneous type, which cannot be ascribed to this cause.<sup>1</sup> The methods of determining the wave-lengths of X-rays by crystal diffraction, described later in the chapter, have been applied successfully to these softer types of  $\gamma$ -rays. But it is still in doubt whether the strikingly penetrating varieties, originally termed  $\gamma$ -rays, come within this method of analysis at all. They may be of too short wave-length to be resolved by the crystal method. It is, however, with this type we are here chiefly concerned.

**Penetrating Power.**—The most penetrating  $\gamma$ -ray known is that emitted by thorium C, but that from radium C is very little inferior. After weeding out softer types by a thickness of about 1 cm. of lead, which also is sufficient to allow the primary rays to come into equilibrium with the softer secondary rays generated in the lead, these hard  $\gamma$ -rays are absorbed by lead according to the exponential law, without change of the absorption coefficient right up to the end of the process so far as it can be experimentally followed. This has been most accurately studied for the  $\gamma$ -rays of radium, for which it has been established beyond any reasonable possibility of doubt, not only for absorption by plates, but also for hemispheres, sliced parallel to the equatorial plane, with the radium at the centre, for which the absorption can be exactly calculated. With these, indeed, the rays appear homogeneous almost as soon as the  $\beta$ -rays have been absorbed, and there is very little other radiation but this homogeneous type.

With the proof that the  $\gamma$ -rays are of the same nature as the X-rays, the interpretation of this law of absorption is that this hard  $\gamma$ -radiation is homogeneous and of a single definite frequency or wave-length. Indeed, it was from the exponential character of the absorption of the secondary X-rays, characteristic of the elements, that Barkla deduced that they were homogeneous prior to the determination of their wave-lengths by Moseley. This conclusion as to the homogeneity of the hard  $\gamma$ -rays is not in accord with the results of later methods of examining the question, so that there is a considerable doubt as to whether the two sets of experiment are really dealing with the same phenomenon.

<sup>1</sup> For further discussion of these points see pages 298-301.

Under the above conditions the  $\gamma$ -rays of radium C are reduced to one-half their initial value by passage through each 1.4 cm. of lead. The absorption can be followed up to a thickness of a foot or more of lead. After 25 cm. the intensity of the remaining rays is about 1/250,000th of the initial intensity. For the  $\gamma$ -rays of thorium C, the thickness for half absorption is 1.5 cm. of lead. The hard  $\gamma$ -rays of mesothorium II, uranium X<sub>2</sub> and actinium C have penetrating powers, in terms of that for radium C, of about 80, 70 and between 40 and 30 per cent. respectively.

**General Properties.**—It is probable that the  $\gamma$ -rays and also the X-rays have no direct ionising action in the same sense as the  $\alpha$ - and  $\beta$ -rays. Their effects appear to be due to their "photo-electric" power of ejecting from the atoms of matter in their path high-speed electrons or secondary  $\beta$ -rays, to which their ionising power is due. This is borne out by experiments with the Wilson expansion chamber (see p. 287), which shows that the ionisation tracks produced by X-rays and  $\gamma$ -rays have no definite direction, but consist of a number of short separate tracks branching out in all directions along the path of the rays. All the types of rays generate such secondary rays on impact with matter. Those from  $\alpha$ -rays are electrons moving at speeds too low to ionise, and they are known as  $\delta$ -rays. Those from  $\beta$ -, X- and  $\gamma$ -rays consist of electrons in general less penetrating than the primary rays.

It is these soft secondary rays which, in the use of X- and radium rays in medicine, are the most dangerous and are responsible for the worst burns. This secondary radiation is set up most readily in dense metals of high atomic weight such as platinum. Relatively little is produced by the light elements such as carbon, hydrogen and oxygen. A thin layer of a substance containing only these elements, such as paper or cloth, is sufficient to absorb the undesirable secondary radiation from the metal screens surrounding the radium without itself introducing any on its own account.

If a radium tube is brought near the eye in the dark, even through a thick screen, such as a closed door, a sensation of light is experienced, which is probably due to phosphorescence





FIG. 38.—WRITTEN BY A TUBE OF RADIUM.



FIG. 55.—THE SPINTHARISCOPE OF SIR WILLIAM CROOKES.



FIG. 39.—BOX OF COMPASSES TAKEN WITH THE  $\gamma$ -RAYS OF RADIUM.

of the retina and eyeball. It is produced both by  $\beta$ - and  $\gamma$ -rays, but through the closed eyelid only the latter are operative. The blind can perceive this effect if the retina is intact, but not when it is diseased, and the test may be of use in ascertaining the cause of blindness. Those who have had much experience of counting  $\alpha$ -particles from strong sources of radon testify to the distress and fatigue produced by the  $\gamma$ -rays from sources near the eye, which it is impossible completely to suppress by absorbing screens, and to the much better results that can be obtained by the more modern methods, in which the microscopic observations are made through right-angled prisms, which allow the head to be completely screened by a block of lead.

**Photographic Action.**—The  $\beta$ - and  $\gamma$ -rays are not well suited for taking radiographs of the ordinary kind in which the bones should cast a shadow and the flesh not. The  $\beta$ -rays are not penetrating enough, so that the flesh as well as the bones cast a heavy shadow, whereas the  $\gamma$ -rays are too penetrating, the bones, even, hardly casting a shadow at all. Probably, even for surgical purposes the  $\beta$ - and  $\gamma$ -rays are not really as suitable as the hard X-rays which can be generated by the Coolidge tube, which are of an intermediate penetrating power. It is merely in the much greater ease and range of application that radium has the advantage. It is possible to introduce it, for example as radon seeds, and to confine its action, in places where it would be totally impossible to employ X-rays.

In photographs taken by the  $\gamma$ -rays, the strong secondary  $\beta$ -radiation, from the metal screens used to absorb the  $\beta$ -rays, must be suppressed as it tends to blur the picture and causes the shadows thrown to be indistinct. In the  $\gamma$ -ray photograph shown in Fig. 39 the source of radium was placed between the poles of an electromagnet, kept excited during the five days' exposure, to deflect the secondary and  $\beta$ -radiation away and prevent it fogging the plate. It represents a closed box of compasses which was placed on a table and covered with an X-ray plate, wrapped in black paper, with the film side down. The source was a few milligrams of radium bromide in a sealed tube, placed below at a

distance of two feet. It shows well the extreme penetrating power of the rays, for even the metal adjusting screws of the compasses traversed by the rays across their diameter cast only relatively light shadows.

**$\gamma$ -Ray Measurements.**—We saw (p. 77) that the properties of the  $\gamma$ -rays lend themselves particularly to accurate measurement of radioactive substances. The  $\gamma$ -ray method of estimating radium may, with proper arrangements, be applied directly to uranium minerals to give a rapid and fairly accurate measurement of their radium and, therefore, uranium content. For this purpose a large electroscope should be used, since the sensitiveness is proportional to the volume of gas ionised, and the walls may be made of thick lead to exclude the softer rays. A lump of uranium mineral weighing only a few grams, placed on or near such an electroscope, will give a measurable  $\gamma$ -ray leak. This enables one at once to settle whether or not any mineral specimen is appreciably active. By comparing the leak from the powdered mineral, in a layer of definite area, with that given by a similar weight and area of a powdered uranium mineral of known uranium content, a rapid and fairly accurate evaluation of the proportion of uranium present may be made. If the mineral contains thorium, the result is to this extent invalidated. Per unit by weight uranium is about six times as effective as thorium as a  $\gamma$ -ray producer, so that unless the percentage of thorium is high, the error is small.

**X-Rays.**—The general character of the X-rays, the fact that they are not affected by electric and magnetic fields, and particularly their velocity, which appears to be the same as that of light, had long made it appear probable that they were rays of light of very high frequency and short wave-length, far into the ultra-violet. The absence of the ordinary optical criteria, such as regular reflection, refraction, diffraction and polarisation effects, is accounted for by the shortness of the wave-length in relation to the size of molecules. But Barkla had established that the X-rays suffer a form of polarisation when they impinge upon matter, the X-rays travelling parallel with the stream of cathode-rays originating

them being less scattered by passing through matter than those travelling at right angles to the direction of this stream.

This view was established in 1912 by the work of Laue, Friedrich and Knipping of the University of Zurich. Laue conceived the idea that the regular orientation of the molecules or atoms of a crystal might act as a "grating" of the correct spacing to diffract the X-rays. The finest gratings procurable ruled by the diamond on glass with as many as 20,000 lines to the linear inch, as used in optics, are not fine enough by a thousand times for this purpose. Whereas the molecular diameter is of the order of a few Ångstrom units ( $10^{-8}$  cm.) only, and in the close packed assemblages that constitute the solid crystal the distance between the molecules must be of about this order of length.

**Diffraction by Crystals.**—This was at once established by experiment. A narrow beam of X-rays was passed through a thin crystal plate, so that the rays were normal to the surface, and, after traversing the plate, were received on a photographic plate parallel to the plane of the crystal surface. Some of the rays go through unaffected in direction, and another part is scattered uniformly in all directions, producing general and uniform fogging of the plate. But in certain definite directions, depending on the nature of the crystal used and on how it is orientated, strong pencils, or bundles, of radiation occur, which produce a geometrical pattern of black spots on the plate. Fig. 40 (facing p. 296) represents a beautiful example of this taken by Friedrich and Knipping with a zinc sulphide crystal plate, half a millimetre thick.

Sir William Bragg and his son, Professor W. L. Bragg, in this country showed that if a beam of homogeneous or "monochromatic" X-rays impinges at an angle on the face of a crystal, there are certain definite angles, depending on the nature of the crystal space-lattice and on the wave-length of the X-rays, at which the beam will be strongly and regularly reflected just like light, though, for angles only very slightly different from these, there is no regular reflection at all. They regarded the assemblage of molecules, orientated in a

definite manner, which is termed the crystal space-lattice, as like a three-dimensional wall-paper. A wall-paper has a pattern repeating itself indefinitely in two dimensions, and if we imagine the pattern repeated in the direction at right angles to the paper also, we get a good idea of the regular assemblage of molecules or atoms in a crystal, which produces its regular shape and accurately inclined faces. Sectioning such a crystal in various planes, there will be some which pass through planes very crowded with molecules, namely those that are parallel to external faces, and it is from these planes that the strongest reflections of X-rays occur.

**The Crystal Space-Lattice.**—Considering a simple cubic crystal, with the atoms or molecules arranged at the eight corners of a cube, and consisting of such cubes extending side by side in all three directions, three such planes are dis-

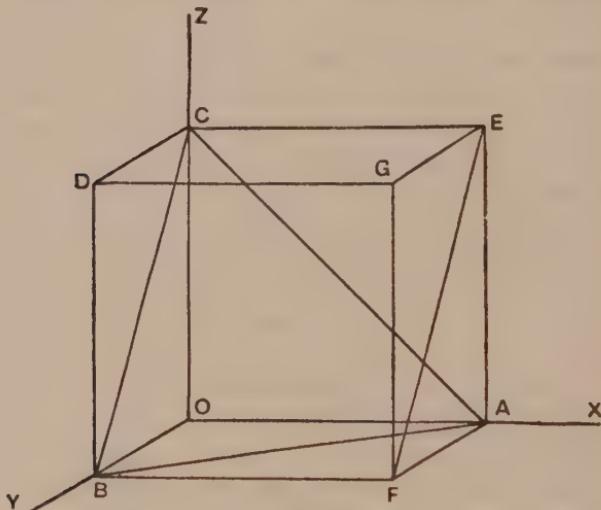


FIG. 41.

tinguished by crystallographers, illustrated in the diagram Fig. 41. There are the planes parallel to any of the six regular faces, such as one passing through the face GFAE, which is distinguished as the (100) face, one passing through the points CEBF, which is called the (110) face, and one passing through the points ABC, which is called the (111)

face. By the geometry of the system, the spacing or distance between successive parallel planes is different according as the planes pass through the three faces. If the distance for the (100) face is taken as unity, that for the (110) face is  $\sqrt{2}$  and for the (111) face is  $\sqrt{3}$ . These distances correspond with the distance between the rulings of an ordinary diffraction grating, and the same monochromatic X-ray will be reflected at different but related angles from the three different faces, the (100), the (110), and the (111) face, of a cubic crystal such as rocksalt. The so-called Bragg Equation,  $n\lambda = 2d \sin \psi$ , gives a simple relation connecting  $d$ , the distance between the reflecting planes,  $\psi$ , the angle of reflection, and  $\lambda$ , the wave-length of the X-ray,  $n$  being an integer, 1, 2, 3, according as reflection occurs in the first, second, or third orders, these terms having a significance completely analogous to their ordinary use for optical grating spectra.

With an optical grating the angles at which any given single wave-length is diffracted, in the first, second and higher orders, are those for which the paths of the rays, through the contiguous spaces between the parallel rulings, differ by one, two, or some higher *integral* number of wave-lengths. With a crystal the same is true for the paths of the rays reflected from the successive layers of atoms or molecules in the crystal space-lattice. In both cases it is the *sines* of these angles which are integrally related.

It followed from this that, if either  $d$  or  $\lambda$  is known, the other can be determined experimentally. If the spacing distance  $d$  is known for any crystal, then  $\lambda$ , the wave-length of any X-ray, may be determined in Ångstrom units by methods precisely analogous to, and not less accurately than in, ordinary spectroscopy. If, on the other hand, we deal with a monochromatic X-radiation of known  $\lambda$ , then the distance  $d$  between the planes for any of the faces of any crystal may be directly measured in Ångstrom units. Thus two quite distinct and completely new fields were opened out by this discovery. It is with the first of these we are most nearly concerned, but the second has been of incalculable service to the crystallographer. It has enabled him to check by direct measurement the various types of crystal space-lattice, which mathematical calculations had assigned

to the various types of natural crystals, and to determine the distances apart between the points of the lattices in absolute measure.

**X-Ray Spectroscopy.**—The instrument employed for this work is very similar to the ordinary spectrometer, with a crystal mounted in place of a prism or grating. The position

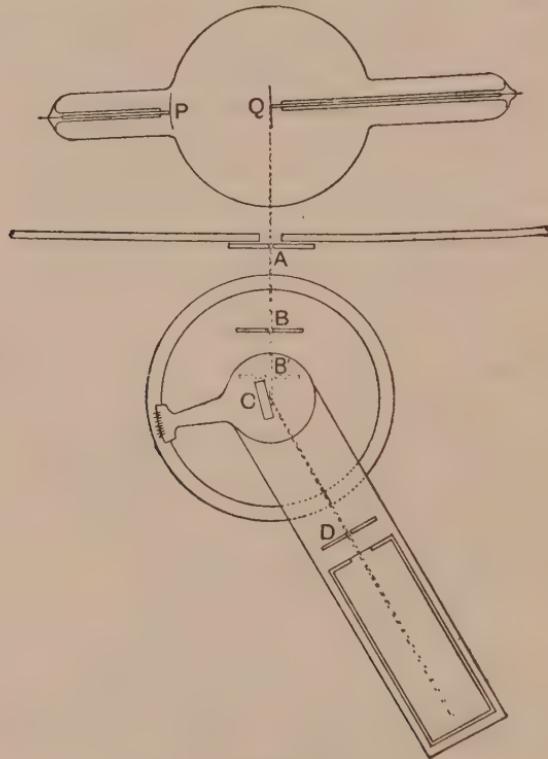


FIG. 42.

of the reflected X-ray may be determined either by photography or by ionisation methods. Fig. 42 is a diagram of one disposition employed by the Braggs. P is the cathode and Q is the anticathode of the X-ray bulb, and the pencil of X-rays used is taken from the latter at almost grazing incidence to obviate the errors introduced by the tendency of the focal spot to wander. The beam is canalised by slits A, B, and falls at a certain angle on the face of the crystal C, and

is reflected at exactly the same angle through the slit D into the ionisation chamber beyond. It is so arranged that, as the slit, D, and ionisation chamber is rotated round the centre of the crystal, the table on which the crystal is mounted shall turn through an angle half as great, in order to make the angle of incidence on the crystal face always the same as the angle of reflection from it. The experiment then consists in finding

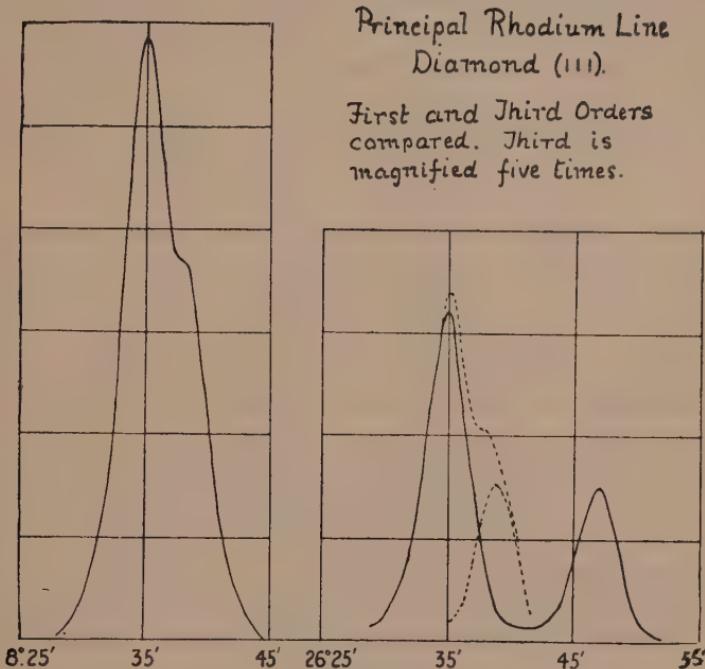


FIG. 43.

the angles at which reflection occurs and measuring them accurately.

Fig. 43 shows an example of the result obtained when the (111) face of the diamond was used as the crystal, and the anticathode of the X-ray tube was made of the light platinum element, rhodium. The diagram on the left is the first order spectrum. The height of the curve gives the intensity of the ionisation, and the horizontal axis refers to the angle of reflection. It will be seen that there is a sharp peak corresponding with the angle  $8^{\circ} 35'$ , but the curve is not symmetrical, as it has a hump on the right-hand side. The right-hand

diagram shows the same line in the third order, the ionisation being magnified five times relatively to the other. The principal line, before at  $8^\circ 35'$ , now appears at  $26^\circ 35'$  ( $\sin 26^\circ 35' = 3 \times \sin 8^\circ 35'$ ), and a second weaker component, which was the cause of the hump in the first order diagram, is now seen quite separated at  $26^\circ 47'$ . The wave-lengths of this close doublet are 0.612 and 0.616 Å. With a palladium anticathode, a similar doublet is obtained, of wave-lengths 0.584 and 0.589 Å. These are the principal lines of the "K" series of rhodium and palladium, by the measurement of which Moseley had first experimentally determined the Atomic Numbers of the elements. This topic is resumed in Chapter XIII. (p. 222).

**Rocksalt, Sylvine and Diamond.**—One very interesting and remarkable circumstance provided, almost by chance, an early clue to the interpretation of these results and greatly facilitated the progress made. Bragg examined the reflections from the various faces of the cubic crystals, rocksalt (NaCl) and sylvine (KCl), the space-lattices of which, since the two substances are very closely similar, might have been expected to be of the same type. He found that, whereas sylvine has a simple cubic lattice, rocksalt had what is termed the face-centred cubic lattice. Referring to the diagram (Fig. 44), if no regard is had to the difference between the black and white dots, it is a simple cubic lattice consisting of 8 unit cubes. If the white dots only are regarded and the black ones are supposed eliminated, it is a single face-centred cube, in which a point is placed at the centre of each of the eight faces as well as at the six corners. This is the crystal structure of the alkali halides, of which rocksalt and sylvine are typical, in which white and black dots represent respectively atoms of alkali-metal and of halogen, but it must of course be imagined indefinitely extended in all three dimensions. Then it becomes two interpenetrating face-centred cubic lattices, the black dots belonging to the one and the white dots to the other.

Now the scattering and diffracting action of an atom is mainly determined by its atomic weight. Hydrogen, the lightest atom, hardly has any effect at all and can usually

be ignored. In sylvine it happens that the two atoms of the molecule, potassium and chlorine, have almost the same atomic weight, whereas for rocksalt the chlorine atom is about half again as heavy as the sodium atom. The consequence of this is that in sylvine the two component atoms are indistinguishable to the X-rays. Thus this substance shows the simple cubic lattice, the black and white dots, corresponding to the potassium and chlorine atoms, being indistinguishable. But rocksalt shows the face-centred cubic lattice with the two separate lattices due to the sodium

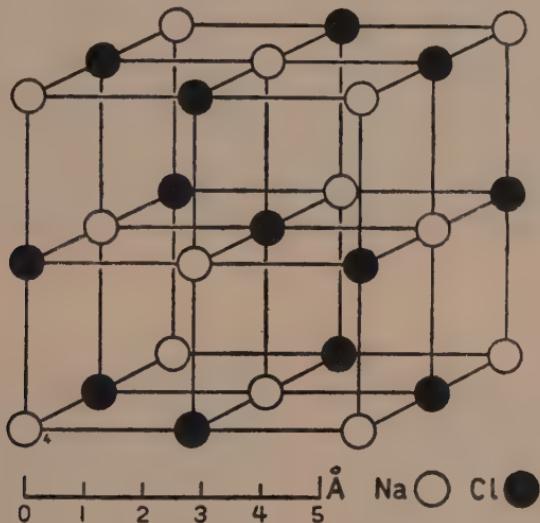


FIG. 44.

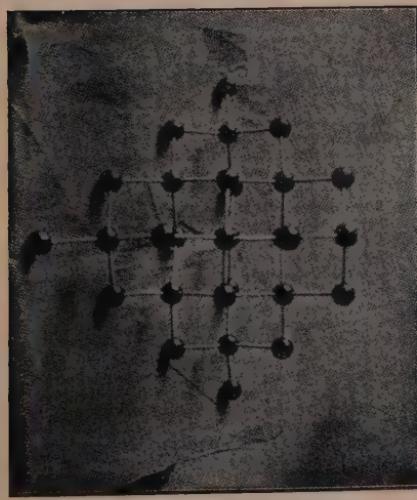
and the chlorine atoms interpenetrating. Thus this lucky chance settled many things beyond doubt. It established the real nature of the space-lattices of the crystals and also that the lattice points are composed, not of molecules of the compound, but of the two different types of atoms. This is not always the case, as in many other types of compound the lattice is built up of molecules and not atoms (see p. 265). The nature of the rocksalt and sylvine lattices being definitely established, the spacing distance,  $d$ , could be calculated for the various faces from the density of the crystal and Avogadro's number (p. 276), and the wave-lengths,  $\lambda$ , could be found in Ångstrom units.

In this way the structures of many crystalline substances have been established, and the method is being rapidly extended to substances which are not ordinarily termed crystalline, such as cellulose fibres and other organised tissues, as well as to such materials as fats and waxes, the structure of which throws a considerable light upon the peculiarities of such physical properties as fibrousness and oiliness. One of the most interesting results to the chemist was one of the first to be obtained. It refers to the diamond, which is almost pure crystalline carbon. The space-lattice unit here is a regular tetrahedron with carbon atoms at the four corners, and it is most simply constructed of the actual models of the carbon atom which chemists have, from the time of the rise of stereochemistry (p. 257), been accustomed to use to represent organic compounds ! Fig. 45 shows two views of the diamond space-lattice built up of these model carbon atoms.

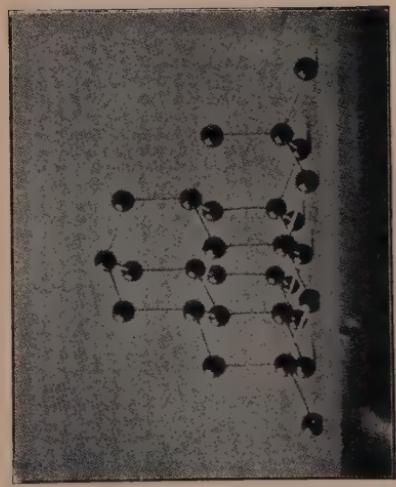


FIG. 46.—APPARATUS FOR OBTAINING THE ACTIVE  
DEPOSIT OF RADIUM.

To face p. 134.



View from above: Horizontal and vertical planes perpendicular to the paper are (110) planes



Side view: Horizontal planes perpendicular to the paper are (111) planes.

FIG. 45.—MODEL OF DIAMOND.



## CHAPTER IX

### THE THORIUM AND ACTINIUM DISINTEGRATION SERIES. INITIAL PARTS. PROTACTINIUM

**General Analogies between the Three Series.**—From an early stage in the development of the subject, interesting analogies were noticed in the general character of the course of disintegration in all three series, both as regards the succession of  $\alpha$ - and  $\beta$ -ray changes and the periods of the corresponding members. If we start in the uranium series from ionium, which corresponds in the thorium series with radio-thorium, and in the actinium series to a very similar member radioactinium (marked with a \* in the diagram below), there is a run of four successive  $\alpha$ -ray changes, getting quicker and quicker, those in the thorium series being quicker than the corresponding ones in the uranium series, and those in the

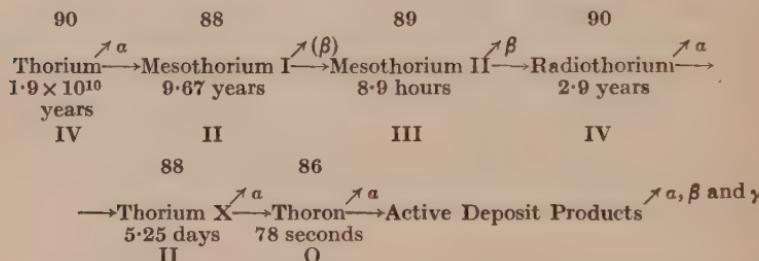
Uranium series	..	$\alpha$	$\beta$	$\beta$	$\alpha$	*	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\{\beta$	$\alpha$	$\beta$	$\beta$	$\alpha$
Thorium series	..		$\alpha$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\{\beta$	$\alpha$	$\beta$		
Actinium series	..	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	*	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\{\beta$	$\alpha$			

actinium series quicker than in the thorium, without exception. An example of this is the three emanations, the periods of average life being, radon 5.5 days, thoron 78 seconds, actinon 5.6 seconds. Then there is a  $\beta$ -ray change in all three series, the product of which, the C-member, undergoes dual transformation so that the series branches. In one branch we have a double change with the sequence  $\alpha\beta$  and in the other  $\beta\alpha$ , which terminates the thorium and actinium series. One branch of the uranium series continues, however, for three more changes,  $\beta\beta\alpha$ , before the end is reached.

Thus, except at the beginning, all three series are very alike, the thorium and actinium series being completely analogous, and the uranium series different only in continuing further.

At the beginnings we have, for the uranium, an  $\alpha\beta\beta\alpha$ , for the thorium, an  $\alpha\beta\beta$ , and, for the actinium series, an  $\alpha\beta\alpha\beta$ , sequence before reaching the starred members started from in the preceding paragraph. These analogies can be followed in detail in the Chart of the Displacement Law at the end of the volume, but for convenience are shown here. Naturally they are to be interpreted as indicating the actual sequence of the successive members in their passage through the Periodic Table.

**The Abbreviated Thorium Series.**—For convenience the chart representing the initial part of the thorium disintegration series (p. 40) is reproduced here. For many problems,



such as the initial working up of thorium minerals for the radioactive constituents, the whole thorium series essentially simplifies to Thorium  $\rightarrow$  Mesothorium  $\rightarrow$  Radiothorium, just as (p. 75) we regarded the initial stages of the uranium series as Uranium  $\rightarrow$  Ionium  $\rightarrow$  Radium. For mesothorium II is too short-lived to affect the results, and the two mesothoriums can be considered as one. Also the *whole* of the products subsequent to radiothorium may often, for the same reason, be provisionally neglected. The chemistry is thus dominated by the isotopy of thorium and radiothorium on the one hand and that of mesothorium I and radium on the other. In studying the uranium minerals we saw that it was impossible to prepare radium free from mesothorium except from minerals like Joachimsthal pitchblende, and to a lesser extent American carnotite, which are essentially free from thorium. Unfortunately no thorium minerals are known which are essentially free from uranium, so that it is

not possible to prepare mesothorium free from radium. Theoretically it should be possible to do so from pure thorium salts, which have been kept long enough—ten to twenty years—to regrow an important quantity of mesothorium, but this so far has never been done.

**Thorium Minerals.**—Thorium, from being merely a chemical curiosity, acquired quite suddenly technical importance through the discovery, in 1885, by Auer von Welsbach, of the incandescent gas mantle, which is essentially composed of thoria. Till then practically all the known thorium minerals had come from Scandinavia. They comprised chiefly the silicate,  $\text{ThSiO}_4$ , known as thorite, and the variety, orangite; monazite, a complex phosphate of the rare-earths, chiefly lanthanum and cerium, but containing varying small amounts of thoria which, however, does not seem to be an essential constituent of the mineral; and the niobium and tantalum minerals containing thorium, such as æschynite, gadolinite and samarskite. With the sudden demand for thoria in large quantity, these sources proved entirely inadequate.

Attention was directed to the working up of the deposits of monazite sand, which occur in littoral zones, chiefly in North and South Carolina and in Brazil. These are a most interesting example of the large-scale natural processes of mineral concentration effected by the waves of the sea. Monazite is, in infinitesimal quantity, a very widely distributed constituent of many igneous rocks, and so is present in the sands resulting from their denudation and detrition by water. It is much heavier than the quartz and other common minerals constituting the great bulk of these sands, and on certain coasts the waves and tides of the seas have conspired to concentrate the heavy monazite particles in certain stretches of the seashore. The monazite, together with rutile and other titaniferous minerals, have been to a large extent separated and washed free of the lighter constituents. The associated minerals can be for the most part removed from the monazite sand, before working it up for thorium, by magnetic separation. So concentrated, these sands rarely contain more than 4 per cent. of thoria. But a very interesting new source, containing as much as 10 per cent., has

been found at Travancore, Southern India, which has proved a very valuable addition to the world's available supplies of thorium.

**Ceylon Thorite and Thorianite.**—At the beginning of this century some very interesting new thorium minerals were found in Ceylon. They are collected chiefly by the gemmers in their search in the alluvial deposits of the river beds for the precious stones for which Ceylon is famed. One of these, thorianite, is a hitherto unknown mineral of Archæan period which occurs often in large almost perfect cubes, dull black in colour and of very high specific gravity (9·0). It consists essentially of a mixture, or "solid solution," of thorium and uranium oxides, the former largely predominating and sometimes constituting 70 per cent. of the mineral, the latter usually of the order of 10 per cent., but in other varieties rising to 20 and even 30 per cent. It is exceedingly curious that, whereas thoria, as artificially prepared, is, like the oxide of tin, completely insoluble in strong hydrochloric and nitric acids, and can only be dissolved by hot concentrated sulphuric acid, thorianite is readily soluble in these acids. It is one of the oldest minerals known and contains helium, from 8 to 10 c.c. per gram, more abundantly than any known mineral.

Another thorium mineral found in the same locality, in the form of brown water-worn pebbles, is Ceylon thorite,  $\text{ThSiO}_4$ , very similar to the Norwegian variety. It was from 30 kilograms of this mineral, every bit of which was selected by hand and the associated thorianite scrupulously rejected, that the author obtained enough "thorium lead" to test the prediction from the Displacement Law, that the ultimate product of thorium is, like that of uranium, an isotope of lead (p. 168). This thorite contained 55 per cent. of thorium, only 1 per cent. of uranium, and 0·4 per cent. of lead, and, at the time, was the thorium mineral with the lowest proportion of uranium known. Since then one of the Norwegian varieties, investigated by Fajans, has proved slightly superior in this respect.

**Extraction of Thorium from Minerals.**—Practically all the thorium used in the gas mantle industry, which amounts to

something of the order of a thousand tons annually, comes from one of the three sources of monazite sand referred to. It is "broken" by heating with concentrated sulphuric acid, which converts the rare-earths and thoria into sulphates, and these are then dissolved in a large quantity of water, leaving a residue of insoluble sulphates, containing the mesothorium. Thus the treatment of thorium minerals for mesothorium and radium is identical in every respect with that already described for the uranium minerals (p. 86), the active constituents being in each case separated in an otherwise technically valueless residue. Owing to the isotopy of radium and mesothorium, the further working up of these insoluble sulphate residues is necessarily identical, whether they are derived from uranium or from thorium minerals.

The thorium is separated from the solution and concentrated from the bulk of the rare-earths, which constitute the main constituent, by partial neutralisation of the sulphuric acid with magnesia, when a thorium phosphate concentrate is precipitated. The preparation of thorium compounds from this, of the very high degree of purity and freedom from didymia and other deleterious rare-earths, required for the manufacture of mantles, is a long and difficult process, still to some extent kept a secret. Both the phosphoric acid and the rare-earths have to be very perfectly eliminated to give a mantle that will remain undiscoloured and will retain to the full its luminosity in use. It is of interest that absolutely pure thoria gives hardly any luminosity when made into a gas mantle, but only a characteristic rosy glow. To produce the maximum luminosity an addition of 1 per cent. of ceria is required. This furnishes much the most exacting test of the purity of thoria that is known, for very minute traces of the rare-earths suffice to make the thoria luminous.

**Mesothorium.**—Technical mesothorium preparations, as prepared from monazite residues, owe about 75 per cent. of their  $\gamma$ -radiation to mesothorium, and 25 per cent. to radium. Since the former, owing to its relatively short period, exists only in infinitesimal relative quantity, the fractionation of the material, if proceeded with until all the barium is eliminated, results in preparations which, chemically, are essentially

pure radium compounds, but which, owing to the practically infinitesimal weight of mesothorium present, possess a  $\gamma$ -activity some four times as great as pure radium compounds. This illustrates well the much greater power of uranium than of thorium as a  $\gamma$ -ray producer, alluded to under  $\gamma$ -ray measurements (p. 126). For the actual quantity of uranium in monazite sand is very small, and, indeed, before it became of importance in this respect, it had been overlooked in the analysis of these materials.

Unfortunately this militates against the value of the thorium minerals as a source of radioactive preparations. Some 19 kilograms of thorium in a mineral are required to produce mesothorium having the  $\gamma$ -radiation of the 1 milligram of radium which is produced from 3 kilograms of uranium. Hence even the richest thorium minerals are somewhat disappointing in their yield. Practically unlimited amounts of otherwise worthless mesothorium residues being available from the important thorium industry, it was hoped at one time that mesothorium would prove a cheap substitute for radium, the lower cost compensating for the restricted period of life. Although this has to some extent been realised, and mesothorium is largely used, for example for the luminous paint of watches and the like, it appears that the cost of extraction is too great to constitute mesothorium a serious rival to radium. The two factors together, the relatively small proportion of thorium in the mineral and the relative inefficiency of thorium as a  $\gamma$ -ray producer, combine to keep up the price of mesothorium to a figure not sufficiently less than that of radium to compensate for its short life, except for certain applications.

**Effect of Age on the Radioactivity of Mesothorium.**—The variation of the activity of mesothorium after preparation is very complicated, owing to its own appreciable decay with the period of average life of 6.7 years, and to the concomitant growth of the rest of the series commencing with radiothorium, the period of which is two years. Mesothorium I shares with actinium the peculiarity of being rayless. No  $\beta$ -rays have been experimentally detected in either case, though both obey the  $\beta$ -ray rule as regards the chemical character of their

products. Mesothorium II, with the period of some nine hours, grows into equilibrium with its parent after two or three days, so that there occurs a rapid growth of the penetrating  $\beta$ - and  $\gamma$ -radiation of the latter from zero to a maximum in this period, and then, as regards this radiation considered by itself, a very slow exponential decay to zero over a very long term of years. These rays are nearly of the same penetrating power as those from radium.

The change of mesothorium II gives radiothorium, and the rest of the series quickly follows its production. In consequence, as the penetrating rays of mesothorium itself decay, there is a practically simultaneous growth of  $\alpha$ ,  $\beta$ - and  $\gamma$ -rays due to the products. The  $\beta$ - and  $\gamma$ -rays, which are emitted right at the end of the series, are among the most penetrating known, the  $\gamma$ -rays being slightly superior to those even of radium. The result is that the  $\gamma$ -rays increase to 1·62 times the initial value after three years, in ten years are much what they were at first, and continue steadily to decay to the 25 per cent. proportion, contributed by the radium present, after a further period of many years, in practice from a quarter to half a century.

**Radiothorium.**—If at any time after preparation the mesothorium is dissolved in water, and a trace of a thorium salt is added and precipitated by ammonia, the radiothorium grown in the interval can readily be separated. In spite of its somewhat short life, it is a very interesting and useful radio-element, from which by growth the whole of the rest of the products of the thorium series can be obtained in highly concentrated form, making possible many experiments, for example with the emanation and active deposit of thorium, for which thorium compounds themselves are too feebly active. This is particularly the case with the emanation, or thoron, and for these purposes radiothorium preparations are needed which emit in the solid state a large proportion of the thoron generated, that is to say are highly emanating. As Rutherford showed in 1901, the emanating power of thorium oxide is largely destroyed by strong ignition. This is due to the thoron escaping from the solid compound less freely, so that for the most part it decays in the substance before getting out.

The precipitated hydroxide of thorium containing radio-thorium, prepared as above, if dried without heat and not ignited, usually is highly emanating, whereas the ignited oxide, and insoluble compounds as the oxalate and fluoride, are usually very inferior in this respect.

From what has been said, it will be understood that the radioactivity of thorium compounds themselves is also very dependent on their age. Freshly prepared, the full equilibrium amount of radiothorium is present, but this, in the absence of its parent, commences to decay, until the decay is arrested and reversed by the regrowth of mesothorium. As regards the  $\alpha$ -rays, a minimum is reached after about two years from manufacture, followed by a slow rise continuing over many decades, until equilibrium is reached, as in the mineral. For this reason standards of  $\alpha$ -activity must not be made of thorium oxide. For feeble standards uranium oxide is suitable, and for strong ones, ionium oxide.

### THE ACTINIUM SERIES

**Actinium.**—Before considering the difficult question of the origin of actinium, already alluded to (p. 69), a brief description of the radio-element itself, and its products as far as actinon, will be given. It was discovered by A. Debierne, working with M. and Mme. Curie, in the rare-earths separated in the course of the analysis of St. Joachimsthal pitchblende. That these rare-earths contained a new radio-element, quite distinct from radium and polonium, was very conclusively proved by the new type of very short-lived emanation which they produce. Indeed, Giesel discovered the new element independently by means of this property, and named it "emanium," before it was found to be identical with Debierne's actinium. The name "emanium" has not survived, but it emphasises the most characteristic and striking feature of the radioactivity of actinium preparations in a "ripe" or fully active state. By means of simple experiments with a zinc-sulphide screen in the dark-room, the streaming away of the emanation from an active actinium preparation and the effect of slight draughts in blowing it about may readily be made visible to the eye.

In working up radium residues, actinium is obtained from the first hydrochloric extract after the residues have been boiled with caustic soda and washed with water. It is of some chemical interest that actinium should be found in these insoluble radium residues, as from its chemistry, as analogous to a rare-earth element, one would expect it rather in the solution containing the uranium. Probably this is, in part at least, due to its almost infinitesimal quantity, it being adsorbed by the solid from the solution. Ionium, which resembles it nearly in chemical character, distributes itself more equally between the solid residue and the solution, but, being many thousand times longer-lived and being in the main instead of in the minor series, it is present in nearly a million times greater actual quantity. However, even with ionium, most is found in the insoluble residues and but little in the uranium solution. The original actinium of Debierne was a mixture of ionium and actinium, the separate existence of the former not then being known.

The above hydrochloric acid extract is treated with oxalic acid, which precipitates the ionium and actinium along with the rare-earths. The separation of these depends on differences of basicity. If the rare-earths are arranged in order of decreasing basicity, the series starts with lanthanum, which is the most basic. Lanthana, like lime, will turn a moist red litmus paper blue, in this respect simulating an alkaline-earth rather than an earth like alumina. Actinium is considerably more basic than lanthanum, and stands in this respect much nearer the alkaline-earths. Thoria, on the other hand, is much less basic than the least basic of the rare-earths, although it is no longer acidic like its homologue zirconium, and cannot form salts of the type of the zirconates. The separation of ionium from the rare-earths is the same as that of thorium already discussed.

Thorium compounds, such as the phosphate, oxalate and fluoride, are always less soluble in acids and more readily precipitated in acid solution than the rare-earths, owing to the weak basic character of thorium, which enables the separation to be effected. On a small scale, there is a large variety of good analytical separations, depending on the precipitation of thorium from the mixture by special reagents

such as hydrogen peroxide, sodium thiosulphate, sodium azide, meta-dinitrobenzoic acid and sebacic acid. Zirconium phosphate is even less soluble than thorium in acids. The separation of thorium from zirconium may be effected by precipitation with ammonium oxalate in excess, when the thorium oxalate remains in solution, zirconium only being precipitated, or by hydrofluoric acid, in excess, the zirconium fluoride being soluble and the thorium fluoride insoluble.

**Properties of Actinium.**—The separation of actinium from the rare-earths, after removal of ionium, is effected along with the lanthanum present. These two elements, being by far the most basic of the rare-earths, can readily be separated together from the others by a number of fractionation methods. After all the rare-earths, except lanthanum, have been removed, the continuation of similar methods will effect, in the more basic fraction, an enrichment of the actinium relatively to the lanthanum, as the former is considerably more basic than the latter. A convenient method is the partial decomposition of the nitrates by heat, when the part not decomposed, which can be leached out with water, is enriched in actinium. It may in this way be concentrated along with lanthanum, and, though it is easy to separate lanthanum and actinium by fractionation methods, complete separation is neither possible nor desirable, owing to the infinitesimal amount of actinium actually present.

The period of actinium was determined by Mme. Curie by the direct determination of the decay of the penetrating radiation from a preparation, in equilibrium with its products, kept in a sealed tube, and found to be about 29 years for the period of average life, or 20 years for the half-period. A later determination by Stefan Meyer makes it considerably less, namely 19.4 and 13.5 years respectively. In the most active preparations examined by the author, no lines in the spectrum other than the known lines of lanthanum are present. With so short a life-period none are to be expected, and the work was mainly of interest to ascertain if a stable isotope of element No. 89 existed in pitchblende.

**Radioactinium and Actinium X.**—As already mentioned, there is practically perfect correspondence between the thorium series, from radiothorium, and the actinium series, from radioactinium, right to the end of the series. With the exception of actinium X and the last radioactive member (the C"-member), the periods of the actinium series products are uniformly less than those of the corresponding thorium series products. The chemistry is identical, the corresponding members being all isotopic, and the nomenclature for both is now the same. Hence, apart from differences introduced by the differences of the period, the actinium products call for little separate description.

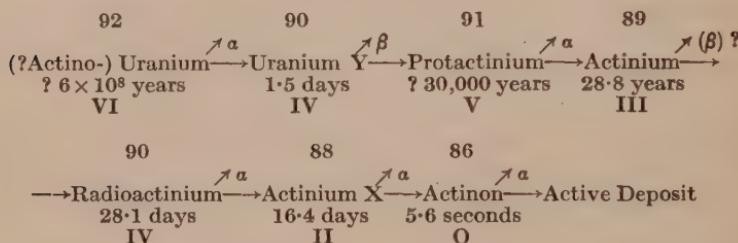
The most important point is that, actinium itself being rayless, and radioactinium and actinium X both being of moderately long and not very different period of average life, 19 and 11·2 days respectively, it is some weeks before preparations of actinium develop their activity, and, in chemical work with them, they are apt to be thrown away in consequence. The separation of radioactinium from actinium is essentially the same as the separation of the latter from thorium, of which radioactinium is an isotope, and it is effected by any of the numerous reagents (p. 144) that serve to separate thorium from the rare-earth elements.

Actinium X, as an isotope of radium, is left in solution when actinium and radioactinium are precipitated by ammonia, this being the reaction by which thorium X was first separated from thorium and recognised as a disintegration product (p. 27). Except for special purposes, since actinium can be got to any desired degree of concentration, the separation of radiothorium and actinium X from actinium is often less necessary than for the corresponding case of thorium, especially if only sources of actinon and the active deposit are needed.

Both radioactinium and actinium X give only  $\alpha$ -rays, the penetrating rays coming from the last changes in the series. Immediately after preparation in a pure state, the  $\alpha$ -rays of radioactinium increase, and attain a maximum, more than twice the initial value, after a fortnight. They then decay gradually and nearly exponentially to zero, reaching the original value after about seven weeks and becoming very

small after three to six months. The rise and fall of the  $\beta$ -rays is similar except that it starts from zero. This is due to the growth of actinium X and its products, followed by their decay as the parent radioactinium diminishes. After six months to a year there is practically no activity left.

**The Actinium Series.**—It is convenient to set forth the actinium disintegration series as far as actinon, to include not only the results so far discussed, but also those still to be considered in connection with the beginning of the series, now to be dealt with.



The most important data that remain unknown for the whole series concern the atomic weight of all the members. Opinion—it is as yet little more—is inclining to the belief that the atomic weight of the hypothetical actino-uranium is 235, which makes that of protactinium 231 and of actinium 227.

Radioactinium and actinium X furnish, as has already been stated (p. 111), the most definite exception to the Geiger-Nuttall relation, and it is perhaps significant in this respect that actinium X is also very exceptional in having a longer period than the corresponding thorium member, thorium X. Although the above scheme of disintegration is apparently well established, it is quite possible that it is seriously in error. A small host of unfavourable circumstances conspire to make the actinium series difficult to unravel.

**The Parent of Actinium.**—The short life of actinium makes it obvious that there must be a parent element in the mineral maintaining its quantity through geological time. The Displacement Law narrowed down the possible parents to two.

If actinium is produced in a  $\beta$ -ray change, its parent must be an isotope of radium. If it is produced in an  $\alpha$ -ray change, its parent must be element No. 91, between uranium and thorium, in a place in the Periodic Table then vacant, and therefore a chemically new element. It will be related to its nearest homologue, tantalum, in the same way as uranium is to tungsten. The immediate homologue of thorium was then unknown, but the next is zirconium. The missing element in the IVth Family, between thorium and zirconium, has now been discovered and is termed Hafnium, after the ancient name of Copenhagen, and this has to be reckoned as another of the triumphs of the Displacement Law (p. 245).

The first possibility that the parent of actinium was an isotope of radium was at once disproved by the author. For, if so, this isotope must be separated with and be present in radium, and actinium should grow in radium preparations with the lapse of time. An examination of some milligrams of radium which had not been interfered with in any way since it was prepared by Giesel, twelve years earlier, showed not the least trace of radioactinium, though the radiothorium produced by the infinitesimal quantity of mesothorium necessarily present was easily detected. It was practically certain, therefore, that the parent of actinium must be the missing element No. 91, the homologue of tantalum. This was shown to be correct by two independent pieces of work, in this country by J. A. Cranston and the author and in Germany by O. Hahn and Fräulein Lise Meitner.

**The Search for Element No. 91.**—In the meantime, the first representative of the vacant place No. 91 had been discovered by Fajans, as Uranium  $X_2$  or brevium (p. 71). This extremely short-lived body could not be the missing parent of actinium, but must be isotopic with it. A particular method was therefore first worked out and found capable of separating uranium  $X_2$  from uranium  $X_1$ . By passing the vapour of carbon tetrachloride over uranium  $X$  at a temperature just at or below red heat, it was found easy to volatilise uranium  $X_2$  away from uranium  $X_1$ . Pitchblende itself was then treated in an identical manner in the hope of volatilising the unknown but isotopic parent of actinium.

The sublimate so obtained was kept under observation over a term of years for a growth of actinium. The method was simple, the preparation being covered with a negatively charged plate to collect any active deposit resulting from actinium emanation, if and when it should arrive, the activity of the plate being carefully tested, after removal, in an electro-scope. In 1917 it was found that actinium was steadily growing in the sublimate from the pitchblende, although none was present initially, its identity being established beyond all doubt by the decay curve of the active deposit produced. The name "Eka-Tantalum" was proposed for the new element, in conformity with the procedure of Mendelejeff, who had given the names "eka-boron," "eka-silicon," "eka-aluminium" to the elements he predicted to exist—analogous respectively to boron, silicon and aluminium—as occupying places in his Table then vacant, and which, after discovery, were termed scandium, germanium and gallium.

The work of the German investigators went much further. They sought for and found the missing element in the last remaining residues, the so-called *Rück-rückstände*, left undissolved from the "radium residues" of pitchblende, after the exhaustive extractions used to remove the radium. They argued that, being like tantalum, one of the most refractory and insoluble of the elements, it should survive this treatment without itself being dissolved. Then they added a little tantalum to the material and separated it out in the pure state again, expecting it to carry with it its homologue, the element No. 91, if that were present. In this way, much as Mme. Curie had obtained radioactive barium and bismuth preparations from pitchblende, they found their tantalum was quite strongly radioactive. Its activity was entirely due to  $\alpha$ -rays, and these moreover had a definite range, 3.3 cm. in air, which showed them not only to be homogeneous but to be different from any known  $\alpha$ -rays. From this range they deduced that the period of the body producing the rays must be of the order of 20,000 years, and that therefore the body must exist in pitchblende to an extent by weight not entirely infinitesimal. An element having this period ought, like radium, to be capable of separation and study in the pure state in weighable amount, in contradistinction to

actinium itself, for which this, it would seem, must remain for ever impossible.

They next identified the new radio-element as the missing parent of actinium in two ways, by the gradual growth of the power to produce the actinium emanation and active deposit, as in the above-mentioned researches, and also, they looked for and observed from it a gradual growth of new  $\alpha$ -rays, beyond the range of its own intrinsic  $\alpha$ -radiation, the range of all the  $\alpha$ -rays of the actinium series being longer than 3.3 cm. To some extent, at this stage, they determined its chemical character and how it behaved towards various methods of analysis, but they were not able to separate it from the tantalum they had added to facilitate its extraction from the mineral. They christened the new element "Protactinium," and this is the name by which it is now known.

**Uranium Y.**—The rest of the series was not difficult to ascertain. If protactinium is produced in an  $\alpha$ -ray change, its parent must be in the VIIth family, a homologue of manganese, beyond uranium and the known elements altogether. If protactinium is produced in a  $\beta$ -ray change, its parent must be an isotope of thorium in the IVth family.

Now this isotope of thorium was already known and it fitted the required rôle exactly. Antonoff had discovered in 1911 that there is a third body in uranium X, which he termed uranium Y, characterised by a period of average life of 1.5 days, and giving soft  $\beta$ -rays, intermediate in penetrating power between the very soft  $\beta$ -rays of uranium  $X_1$  and the hard  $\beta$ -rays of uranium  $X_2$ . The confirmation of the existence of this body gave some difficulty, because it is isotopic with uranium  $X_1$ , that is with thorium, and Antonoff's methods of separation, like Ramsay and Hahn's methods of separating radiothorium, could not be repeated. They depended for success, not upon the particular chemical methods employed, but on the lapse of suitable intervals between the separations, which should exaggerate as much as possible the proportion of uranium Y relative to that of uranium  $X_1$ , as these two are always separated together. In the present instance, if the time between successive separations of uranium X from uranium is short, say one day, which

is comparable with the period of uranium Y, the product will be predominately uranium Y. If it be long, say one month, which is comparable with the period of uranium X<sub>1</sub>, the uranium Y will be present in too small proportion to be detectable.

Now the most interesting point about uranium Y was the very small relative proportion in which it exists compared with the other members of the uranium series. This at once served to put it in the actinium series, as, like the latter, it is produced by only about 3 per cent. of the uranium atoms disintegrating, as compared with the 97 per cent. giving ionium and radium. Hence it is concluded, without reasonable doubt, though without direct proof, that an isotope of uranium, to the extent of some small proportion of the whole, emits an  $\alpha$ -ray and changes into uranium Y, which emits a  $\beta$ -ray and changes into protactinium. The sequence is  $\alpha\beta\alpha\beta$  instead of  $\alpha\beta\beta\alpha$ , and this unprecedented order is one of the chief points of interest about the actinium series.

**Protactinium.**—The subsequent developments in connection with this element show that it is destined to become one of the most interesting and important of the new radio-elements. Although Hahn failed to separate it from tantalum, one of his pupils, Aristid von Grosse, claims to have been completely successful. If confirmed, his work will rank as one of the most elegant and most difficult accomplishments in analytical chemistry. For, from its position in the Periodic Table, protactinium is surrounded by elements, like tantalum, tungsten, hafnium, zirconium, and thorium, some of which have most indefinite behaviour, and all of which are outside the range of routine analysis and beyond the capacity of any but highly skilled analysts. Yet the work was put through with unerring chemical instinct and without the least uncertainty or indefiniteness. It followed, with appropriate variations, the well-trodden path of first separating the element with and then from the element most nearly resembling it.

The interest and importance of the work is that it deals with a new radio-element, not in impossibly minute quantity, but, like radium, in quantity sufficient to make its separation and characterisation possible. The quantity of the final

residues from the radium extraction, which formed the raw material, was 200 kilograms, and this contains protactinium to the extent of nearly 4 milligrams by weight. It was worked up in the factory by processes designed to extract the tantalum present, and thereby an enrichment of the protactinium content to the extent of some thirty-five times was effected. In the laboratory systematic purification from other radio-elements then reduced the amount to less than 100 grams, without serious loss of protactinium. Then the step was taken which had hitherto been found impossible, the separation of the protactinium from tantalum.

**Separation from Tantalum.**—Up to this, the chief analytical feature depended on in the separation was the ready solubility of the fluorides of the elements of the Vth family, niobium, tantalum and protactinium, hydrofluoric acid acting as a solvent where all other acids fail. But there is another method of putting these highly insoluble compounds into solution, which consists in fusion with alkalis. The *known* elements of this group are sufficiently acidic to form salts, the niobates and tantalates of potassium and sodium, which are soluble in water. If we compare the behaviour of the members of the IVth family, zirconium, hafnium (p. 245) and thorium, and of the VIth family, molybdenum, tungsten and uranium, with regard to this reaction, we shall find that the increasing basicity of the elements in passing down the families in the Periodic Table in a vertical direction (p. 231) operates against the success of the method. Whereas zirconium, molybdenum and tungsten can so be dissolved, as the zirconates, molybdates and tungstates, thorium and uranium cannot. The first is not sufficiently acidic to form a salt at all, whilst the second forms salts, the uranates, which are completely insoluble in water. This was the idea underlying von Grosse's successful separation of protactinium from tantalum.

On fusing the material with potassium carbonate, and treating the melt with water, it was found that, whereas the niobium and the tantalum went into solution, the protactinium remained undissolved in the residue. The radioactivity naturally enabled the manner in which protactinium,

the only radio-element present, distributed itself after any treatment, to be exactly ascertained, just as in Mme. Curie's pioneering researches with radium. The material so obtained still contained only a trace of the new element, along with a number of others including zirconium (hafnium), and phosphoric acid. Then a new treatment was followed, designed to concentrate the protactinium along *with* the constituents mentioned *from* all the other substances present. That is, it was now found possible to separate the protactinium with the zirconium phosphate and to eliminate all other foreign substances.

**The Final Steps.**—This being accomplished, the next step was the enrichment of protactinium from the zirconium. This was effected by fractional crystallisation of the oxy-chlorides. Actually the material passed through a regularly repeated sequence of processes by which the desired object was gradually effected, and the concentration of the protactinium in the ever diminishing quantities of material was continuously increased. When the original 200 kilograms had been reduced to less than 30 milligrams, still mainly zirconia, the protactinium was separated from the zirconium by adding thorium, separating the latter *with* the protactinium *from* the zirconium by well-known methods, and lastly separating the thorium *from* the protactinium by hydro-fluoric acid (see p. 143). Thorium fluoride is one of the most insoluble of fluorides, whereas, as we have seen, that of protactinium is easily soluble in water.

In this way about 2 milligrams of what was considered to be practically pure protactinium oxide,  $\text{Pa}_2\text{O}_5$ , was finally obtained as a white powder. The  $\alpha$ -activity of the material was about 100,000 times as great as that of uranium oxide. From this very active material a very feeble  $\beta$ -activity could also be detected. It has been calculated that for every milligram of radium (element) in a uranium mineral there should be about 0.4 milligram of protactinium (element). On the one hand, the quantity is some thirty times smaller by reason of the thirty times greater number of uranium atoms producing radium as compared with those producing actinium. On the other hand, the quantity is some twelve

times greater by reason of the twelve times longer life of protactinium as compared with that of radium. The two factors combine to give the proportion stated.

The way is now open for the complete study of the chemical and physical character of this interesting new element. Besides radium, it is the only one for which this can be done. It is now mainly a question of cost. When a sufficiently large quantity of the element has been accumulated, it should be possible to determine its atomic weight—and so, those of all the other members of the actinium series—the optical and X-ray spectrum and other properties. Also, the way lies open to grow from it actinium in the pure state, uncontaminated with lanthanum, and possibly to determine its spectrum. But this would necessarily be a very tedious business, and it is to be doubted if, even from relatively large amounts of protactinium, the amount of actinium obtainable would suffice to determine much more about its chemistry than is already known.

## CHAPTER X

### THE ACTIVE DEPOSITS

**Excited and Induced Activity.**—So far our attention has been directed to the first parts only of the three disintegration series, up to the gaseous emanations which are, for various reasons, both as regards their chemistry and their radioactivity, the natural middle members of the series. In this chapter we have to consider the subsequent changes of these three emanations, the products of which are known collectively as the “active deposits.” As we have seen, they were discovered simultaneously by M. and Mme. Curie for radium and by Rutherford for thorium, but the original names given to them respectively, the “induced activity of radium” and the “excited activity of thorium,” were both misleading and are no longer used. Radioactivity cannot be induced or excited in inactive matter by the rays from the radioactive substances, and the effects obtained are due to the deposition of the products of the emanations. If the radioactive preparations are confined in airtight vessels, however thin, no active deposit whatever is produced outside the vessels.

The case differs only from the normal change, of one radioactive element into another with expulsion of rays, in that the parents at ordinary temperatures are true gases. The products are in every case non-gaseous, and they settle out, or deposit, on the nearest available surfaces. The three emanations all expel  $\alpha$ -rays, and the A-products, first formed, “recoil” through the gas with velocities of the order of 200 miles a second, so that in their collisions with the molecules of the gas they become charged, for the most part positively. Hence any surface kept negatively charged with respect to the rest of the vessel attracts to itself a large part of the active deposit, so that a ready means is available for concentrating it on the surface desired.

Fig. 46 (facing p. 134) is a photograph of a convenient apparatus for obtaining the radium active deposit, and Fig. 47 is an explanatory diagram. A small glass flask, silvered internally, with a platinum seal through to connect the silvering to the positive pole of a battery or the electric supply, is fitted with a rubber cork, carrying a short length of glass tube, open at both ends. Through this tube wires or needles, connected to the negative pole, may be inserted and withdrawn at will, the joint at the top of the tube being made air-

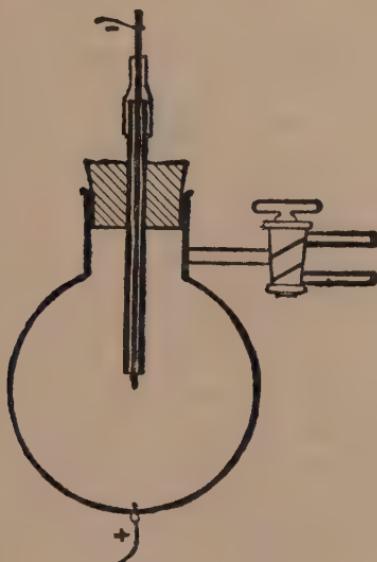


FIG. 47.

tight by a rubber cork or tube. A two-way tap serves to connect the flask either to a pump, partially to exhaust the air, or to a supply of radon mixed with air, for filling it. By simple experiments with such an apparatus, it can be shown that the products of radon are a series of bodies of various periods of life, some giving  $\alpha$ -rays only in their change, and others  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays.

**Experiments with the Active Deposit of Radium.**—To get the maximum effect the needles should be left in the emanation three or four hours. Tested in the ordinary way with a

zinc sulphide screen for the  $\alpha$ -rays, and with a platinocyanide crystal, or a piece of X-ray screen, through various thicknesses of metal, for the  $\beta$ - and  $\gamma$ -rays, the needles will be found to be emitting  $\alpha$ -rays sufficiently powerful to light up the zinc sulphide visibly even in an ordinarily lighted room, and  $\beta$ - and  $\gamma$ -rays of the same order of intensity as would be given by the radium preparation from which the radon was derived, if tested in the solid state. The  $\alpha$ -rays are extraordinarily powerful under these circumstances, because there is no absorption, as there would be from a solid radium preparation, and because of the very small area upon which the active deposit can be concentrated. If the needle merely touches any other surface, some of the active deposit is rubbed off on to that surface, and, by drawing it through emery cloth, the greater part of the active deposit may be transferred to the cloth, as can be shown by testing the latter with the fluorescent screens.

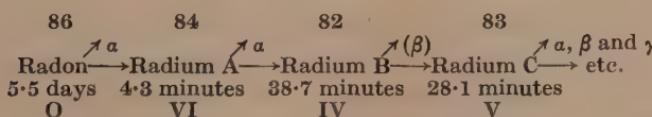
Chemical solvents, such as dilute acids, also readily dissolve off the active deposit, and, if the wire is heated to bright redness, the latter is volatilised and deposits again on the nearest cold surface. For such experiments, of course, platinum wires should be used. Yet even from a relatively large quantity of radon there is no deposit visible to the eye, and it has never been weighed, even with the microbalance. From a curie, that is the radon in equilibrium with a gram of radium (element), the active deposit, according to calculation, would only weigh one-twenty-thousandth of a milligram. Yet the  $\alpha$ -rays from a small fraction of this will produce on a zinc sulphide screen a glow which can be seen in a darkened lecture theatre by everyone in the room.

Careful study of the rate of decay of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays severally, of the active deposit produced after various periods of exposure to radon, enabled Rutherford to resolve the complex sequence of changes involved. For long exposures, after removal from the radon, there is, in the first few minutes, a considerable decay in the  $\alpha$ -rays, which quickly fall to about one-half their initial value, but no perceptible decay of the  $\beta$ - and  $\gamma$ -rays. Little further change occurs in the first half-hour or so with all three types of rays. But then they all start to decay steadily and continuously to

half-value in about half an hour. After three or four hours the decay is complete, and no activity can any longer be detected by the fluorescent screen. If, when the wire was taken out of the radon, a new one had been put in, the latter would then, after three or four hours from insertion, again have a quantity of active deposit similar to that obtained on the first wire. In three or four hours the active deposit comes into equilibrium with the parent radon, so far as concerns the first group of rapidly changing products, designated radium A, B and C.

**Analysis of the Products.**—The first of these, radium A, has a period of average life of only 4.3 minutes (half-change period 3 minutes). It is responsible for the rapid decay of the  $\alpha$ -radiation to one-half, as it furnishes one-half of the total  $\alpha$ -rays, and after 10 or 15 minutes practically none of it is left. This can be readily shown by exposing the needles only for a few minutes to the radon. Their  $\alpha$ -activity when removed is about one-half as great as the  $\alpha$ -activity from a wire exposed for 3 or 4 hours. But it decays very much further than before in the course of 10 or 15 minutes, the later products from the amount deposited in the short time being relatively feebly active. Also, it will be found that such wires, the activity of which is almost wholly due to the first product, radium A, give no  $\beta$ - or  $\gamma$ -rays to speak of. These are emitted in the last change, that of radium C.

The disintegration series runs as follows:



Radium B gives the soft and not very obvious  $\beta$ -rays, which for convenience are distinguished from the hard, characteristic  $\beta$ -rays by brackets ( $\beta$ ). At first it was thought to be rayless like actinium, but by special methods a  $\beta$ -radiation not much more penetrating than  $\alpha$ -rays was detected. This has now been intensively studied. Radium C gives, in addition to the  $\alpha$ -rays of longest range and greatest velocity in the whole series, the whole of the important  $\beta$ - and  $\gamma$ -radia-

tion of radium preparations. It is known that these result in a very complicated set of changes, the analysis of which may for the present be postponed. Till then it is to be understood that the term C member connotes here a group of successive products, rather than a single product.

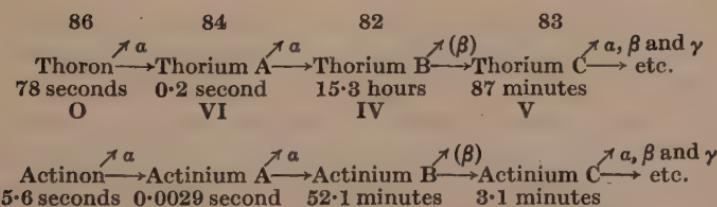
The existence of radium B, itself not giving any very obvious rays, serves to maintain the quantity of radium C, and to retard its decay after the rapid decay of radium A. For the decay of the active deposit initially in equilibrium with radon, there is a distinct delay before the decay of the  $\beta$ - and  $\gamma$ -rays due to radium C sets in. Also in activating the wire in the first instance with varying period of exposure to radon, there is a corresponding delay before the  $\beta$ - and  $\gamma$ -rays put in an appearance. The case is analogous to, but not nearly so sharply defined, as the delay in the appearance of the  $\beta$ - and  $\gamma$ -rays from a radioactinium preparation, due to the intervention of actinium X, before the actinium C member is formed. Here there is a very slow rise in the penetrating rays from zero for many days to a maximum, reached in a fortnight, and after this a regular decay with the period of radioactinium, these rays also coming entirely from actinium C (p. 145). Effects of this character, due to the delaying action of intervening members of the series, are common in radioactive changes.

**The Chemistry of the Active Deposit Products.**—This, thanks to the Displacement Law, can now be predicted at once from the sequence of the  $\alpha$ - and  $\beta$ -changes. But, actually, the gradual elucidation of the chemical nature of the successive members played a not inconsiderable part in the discovery of the Displacement Law. At first it appeared that it must be perfectly hopeless to try to ascertain the chemical character of so numerous successive products of such short life and in such infinitesimal quantity. But facts gradually accumulated which showed that they possessed an unexpected definiteness of chemical behaviour. They are, for example, readily redeposited upon the cathode from their solutions in acids by electrolysis, and often to a considerable extent by merely immersing metals like copper, bismuth and nickel in their solution. Their behaviour in this respect is

analogous to the "noble" metals, gold and silver. By carefully regulating the potential between the electrodes, fairly sharp separation of the three members could be effected by electrolysis, the A members being the easiest to deposit, then the C members and lastly the B members. Also, bismuth will deposit radium A, and nickel, radium C, from all three in solution if successively employed, enabling a fairly complete separation to be very simply effected. In this behaviour, the members of the thorium and actinium active deposits are identical with that of the radium active deposit, the A, B and C members respectively in the three series now being known to be isotopic.

Also the rather surprising discovery was made that the volatilisation of the active deposit products by heating is much affected by the nature of the atmosphere in which the volatilisation occurs. Thus, in air, the volatilisation temperatures of the three members are as follows: A, 900°; B, 600°; C, 1,100° C. But in hydrogen, all the members are completely volatilised at 650° C., and the radium C commences to volatilise at 360°, the boiling-point of mercury. This is reminiscent of the usual behaviour of the metals, which are much more volatile when in the free state than as oxides, the latter volatilising only by thermal decomposition into oxygen and the free metal.

The thorium and actinium series, as far as the C members, are given below. The successive products are completely analogous with those of the radium series just given:



Fleck's researches, upon which the Displacement Law was mainly founded, then established that radium A could be separated with but not from polonium, the B members with but not from lead, and the C members with but not from bismuth. A glance at the diagram of the series just given,

or reference to the two Charts at the end of the volume, will show that the A members, being formed from the emanations in place No. 88 in the zero family of inert gases, must be in place No. 86, in the VI<sup>th</sup> family occupied by polonium; the B members by an  $\alpha$ -ray change from the A members must be in place No. 84, occupied by the common element lead; and the C members from the B members in a  $\beta$ -ray change must be in place No. 85 occupied by the common element bismuth. But Fleck's results were purely experimental and not biased by any theoretical preconception.

**The Active Deposits of Thorium and Actinium.**—The short life of the emanations in these cases necessitates methods to be employed to obtain the active deposits of thorium and actinium entirely different from those described for the active deposit of radium. A continuous stream of gas is sent through a highly emanating preparation of thorium or actinium into a cylinder, along the axis of which is placed a wire negatively charged with respect to the cylinder. To obtain the maximum or equilibrium amount of active deposit on the wire, 2 days' exposure is required in the case of thorium, and for actinium, 4 or 5 hours. These active deposits differ in many respects from that of radium. They represent less of the total  $\alpha$ -activity, though, as with radium, the whole of the penetrating radiation of the preparation. The initial complications of the decay and recovery curves, due to the A member in the case of radium, are entirely absent in the other cases.

The reason for this is very interesting. Thorium A, and also actinium A, are bodies of such vanishingly short period that, at first, they were not separately distinguished from thoron and actinon, with the result that the emanations seemed to emit a much greater part of the total  $\alpha$ -radiation, and the active deposits a much smaller part than with radium, for which the A member had from the first been recognised by Rutherford as a separate product. As normally obtained, the active deposits of actinium and thorium consist only of the B members, which, like radium B, give only ( $\beta$ )-rays, and of the C members which, like radium C, give, in addition to the longest range  $\alpha$ -rays in the series, all the penetrating

$\beta$ - and  $\gamma$ -rays. These also are given out in what is a very complex change, the analysis of which can be postponed, the term C member being meantime used, inaccurately but conveniently, to designate the group of members at the end of the series.

As with the radium active deposit, the B member is the longest lived, but in the thorium and actinium active deposit groups, the life of the B member is so much greater than that of the others that it dominates essentially the course of the decay and regeneration curves. Thus the period of average life of thorium B is 15·3 hours, as compared with 87 minutes for that of the first change of the thorium C group. It is for this reason that equilibrium of the active deposit and emanation is not reached till after 2 or 3 days. The period of actinium B is 52 minutes, which is but little more than that of radium B, but the period of the first change of the C group is only 3 minutes, that of the longest in the group being only 6·8 minutes. Hence the actinium active deposit behaves much as that of radium with the initial effects due to radium A absent.

**Actinium A.**—This is the shortest-lived radio-element that can be put into evidence by direct experimental methods, the period of average life being only 0·003 second. Long before it was recognised as such, its existence had really been indicated by an experiment of Giesel with his active "emanium" preparations, to which reference has already been made (p. 142). He discovered what he naturally concluded was an entirely new type of ray from these preparations, apparently attracted by the electric field. If a zinc sulphide screen is brought opposite the open end of a tube containing an active actinium preparation at a little distance from it, there is a diffuse luminosity produced by the emanation escaping from the tube. Now, if the screen is connected with the negative pole of an electrical machine, *instantly* there flashes out on the screen a sharply defined spot of the same geometrical form as the opening of the tube. On disconnecting the screen this spot as instantly vanishes again. He called the supposed new radiation the "E-ray," in brief for "emanation-ray."

Like the other A members, actinium A, being formed in an  $\alpha$ -ray change, recoils and acquires a + charge, so that it is attracted to the negative electrode in an electric field, and emits its own  $\alpha$ -ray, as it turns into actinium B, at this electrode. But as it lasts only something at most of the order of a hundredth of a second, it decays practically instantly, so that on disconnecting the electrode the effect of the A member ceases practically simultaneously, making it appear that it is the ray producing the effect and not the short-lived product which is attracted by the field.

The existence of these very short-lived substances was next indicated by the method of counting  $\alpha$ -particles by the zinc sulphide screen. In the case of the  $\alpha$ -rays given by actinon it was found that a very large number of pairs of  $\alpha$ -particles were emitted, and a study of their range revealed that two different types were present, that due to actinon itself with a range of 5.7 cm., and another with a range of 6.5 cm., which, according to the Geiger-Nuttall relation, corresponds with a period of only a few thousandths of a second.

**Thorium A.**—The corresponding member in the thorium active deposit, thorium A, was also first put into evidence by the pairs of  $\alpha$ -particles emitted by thoron, but here a very significant difference was noticed. For this case, the period of average life is much longer, being 0.2 second, so that the appearance of the pairs is not absolutely simultaneous, as it seems with actinon, but there is, on the average, a distinct interval between the two flashes. The eye cannot resolve into individual images any that follow one another more rapidly than thirty to the second (cinematography depends entirely upon this), so that it cannot resolve the pairs in the case of actinon, but can in the case of thoron. Each flash is usually the signal for a second flash, in this case, a fraction of a second later.

Rutherford devised very ingenious methods for putting these short-lived bodies into evidence and for directly measuring their period of life. An endless insulated wire was passed axially through a cylinder containing the active radiothorium or actinium preparation, wrapped in porous paper, which

serves to supply the emanation. It was driven at a known linear speed, by passing it over suitable pulleys outside the cylinder, one of which was connected to an electric motor. The wire was made negative, and the cylinder positive, by connections to a battery, and the short-lived products were deposited on the wire. The experiment consisted in driving the wire through the cylinder at sufficient known speed and examining, at fixed distances from the point at which it leaves the cylinder, the rate at which its activity falls off with the distance. In this way, not only could the effect of the A members be studied outside the cylinder, but their periods could be accurately determined. The wire is being driven through the cylinder at high speed, but it is only the part nearest the exit that is active, because before it has travelled far from its source all the short-lived product decays. The later products do not begin to interfere, until the wire has been kept running some time through the cylinder, their effect for the short time necessary for the observations being negligible. If kept running for a sufficient time, the whole wire of course becomes active with the B and C members, uniformly along its whole length.

**Experiments with Radiothorium and Actinium Preparations.**—If sufficiently active and highly emanating preparations of radiothorium and actinium are available, many simple and striking experiments can be shown, illustrating the growth and decay of the short-lived gaseous members and their products. For this purpose, two sheets of glass mounted to form a shallow box hinged along one side, and covered on their internal opposite surfaces with zinc sulphide, form a convenient arrangement. The emanations may be blown in at one side by sending a puff of air through the emanating preparation contained in a glass tube, and the decay and regeneration of the emanation with time studied at will by the luminosity on the zinc sulphide screens.

With radon, of course, such methods would be quite inapplicable, because once the radon had been blown out into the room, many days must elapse before the new crop is grown. But, with radiothorium, minutes, and, with actinium, seconds, suffice to reproduce again the emanation, and for

what has been blown out completely to disappear. The experiments with actinon are especially striking, as the decay of the glow, after a puff of air has been sent through from the actinium preparation, takes place with unmistakable rapidity in a few seconds. In this way, the fundamental discoveries of the growth and production of new radio-elements in radioactive change can be made, as it were, visible to the eye.

Thorium A may be put into evidence by the method by which Giesel discovered the "E-ray," if a highly emanating radiothorium preparation is used. But here there is a distinct pause before the appearance and decay of the luminosity, respectively, on connecting and disconnecting the field. To show the phenomena as a lecture experiment, it suffices to coat a sphere with zinc sulphide and mount it centrally in a globular flask, at the bottom of which the emanating preparation, wrapped in porous paper, is placed. On connecting and disconnecting the sphere with the negative pole of an electric machine or high potential battery, the sudden brightening and extinction of the glow of the zinc sulphide can be made visible to an audience.

## CHAPTER XI

### THE ENDS OF THE DISINTEGRATION SERIES. POLONIUM. POTASSIUM AND RUBIDIUM

**The C Members.**—For convenience of exposition it has suited us till now to treat the C members of all three disintegration series as single. Not only does the fact that they all give out very powerful radiations of all three different types suggest that they are not single radio-elements, but the great range of the  $\alpha$ -rays, 7 cm. of air for radium C, and 8·6 cm. for thorium C, shows that the period of the substances producing these  $\alpha$ -rays must be vanishingly short. For actinium C the case is different, as the range, 5·4 cm., of its  $\alpha$ -rays accords well with its actual period of average life, 3·1 minutes, and is shorter than the range, 6·6 cm., of the  $\alpha$ -rays of actinium A, the period of which, 0·003 second, has been, as we saw in the last chapter, directly measured.

**Multiple Disintegration.**—The case of thorium C was the easier to elucidate, and it will be considered first, though it is only fair to say that Fajans, from the study of actually the far more difficult case of radium C, investigated the first clear case of a multiple disintegration.

The  $\alpha$ -rays of thorium C, the average life period of which is 87 minutes, give a Bragg ionisation-range curve which clearly shows them to consist of two different types, a long-range  $\alpha$ -ray of range 8·6 cm., and one of shorter range, 4·7 cm. (see Fig. 28, p. 108). The latter accords fairly well with what is to be expected from the period of the body, but the former corresponds to a period of far less than a millionth of a second. Now in this case, unlike every other previously examined, it was found quite impossible to separate thorium C into two separate products, each giving the one type of ray. That this was not merely due to two successive  $\alpha$ -ray changes, the period of the second being too small to enable it to be distinguished from the first, was shown by the fact that different

numbers of  $\alpha$ -rays of the two ranges are given out, there being about two of the faster type of ray for every one of the slower.

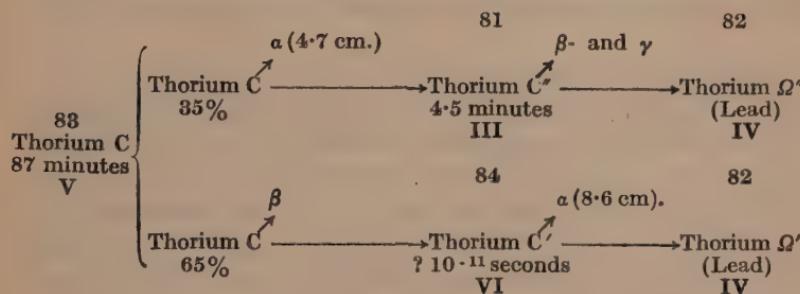
In the case of radium C, there was, until quite recently, no experimental evidence of the existence of any  $\alpha$ -rays other than the long-range type. Experiments by Fajans, however, designed to ascertain if the  $\beta$ -rays produced appreciable recoil, actually revealed the product of the  $\alpha$ -ray change by recoil methods. They showed the existence, in vanishingly small relative amount, of a new product giving  $\beta$ -rays, with an average life period of about 2 minutes. This was first named radium C<sub>2</sub>, but has been rechristened radium C'', according to a consistent scheme applicable to all the series. In this scheme the hypothetical  $\alpha$ -rayers, of vanishingly short life, are designated by the letter C'.

Similar experiments with thorium C resulted in the discovery of a new member also emitting  $\beta$ -rays, which recoils from the C member during the  $\alpha$ -ray expulsion, and so is easily obtained separately as a deposit upon a negatively charged plate placed over the preparation. This was at first named thorium D, but has been rechristened thorium C''. Its average period of life is 3·1 minutes, but, unlike radium C'', it is obtained in quantity comparable with that of the other members of the series. The interesting discovery was made that the whole of the  $\gamma$ -rays, which are the most penetrating known, appear to come from the new body, thorium C'', but only part of the  $\beta$ -rays, the  $\beta$ -rays of thorium C itself being as penetrating as those of radium C and considerably more penetrating than those from thorium C''.

**Thorium Branched Series.**—The explanation that fitted all the evidence was that the C members, in the case of thorium and radium, are really homogeneous, but that they undergo two different kinds of disintegration simultaneously and independently. In the one, a  $\beta$ -ray is emitted, followed practically instantaneously by the long-range  $\alpha$ -ray, while, in the other, the order of the two changes is reversed, the low-range  $\alpha$ -ray being first emitted, followed by a  $\beta$ -ray. For the C member of thorium the chance that the  $\beta$ -ray change occurs first is about twice as great as the chance that the  $\alpha$ -ray change occurs first, so that we get about two long-range

$\alpha$ -rays to one of short range. For the C member of radium, the chance that the  $\beta$ -ray change occurs first is about 3,000 times greater than the chance that the  $\alpha$ -ray change occurs first, so that here the long-range  $\alpha$ -rays enormously predominate, and the quantity of the recoil product of the  $\alpha$ -ray change, in which the low-range  $\alpha$ -rays are (presumably) emitted, is vanishingly small.

The case for thorium is shown in the diagram below:



As already stated, the hypothetical bodies of vanishing short life are designated by the letter C'. The diagram must not be supposed to indicate that there are two *kinds* of thorium C, but that the same type of atom is disintegrating in two ways, 35 per cent. of the total by the one and 65 per cent. by the other mode. For the upper set the order is  $\alpha\beta$ , and for the lower  $\beta\alpha$ .

This explanation received what amounted to a practical proof, so soon as the Displacement Law became known. For, as the Arabic figures indicate, the product thorium C''—resulting from thorium C in the 83rd place isotopic with bismuth, by an  $\alpha$ -ray change—ought to be in place No. 81 and therefore an isotope of *thallium*. This Fleck proved at once. Thallium, the rare element discovered by Crookes in 1861, has an interesting chemical behaviour, in some reactions behaving like lead, and in others like one of the alkali metals, such as potassium. In particular its platinichloride, like that of potassium, is insoluble in water. Fleck found that thorium C'' (thorium D as it was then known), got by recoil from the thorium active deposit, and dissolved in acids, is quantitatively precipitated from its solution with chloroplatinic acid in presence of either thallium or potassium.

This was one of the most striking and convincing of the many predictions that resulted from the Displacement Law. It is of interest to note that, had thorium C" elected to expel an  $\alpha$ -ray instead of a  $\beta$ -ray, the product—in the 79th place of the Periodic Table—would have been gold, a veritable transmutation in the sense of the old alchemists. As it is, the product of its  $\beta$ -ray change must be in the 82nd place and therefore must be lead, a *faux pas* as it would have seemed to the alchemist, but to the modern chemist just as remarkable.

**The Ultimate Products.**—With regard to the lower line, the hypothetical thorium C' must be in place No. 84 and therefore an isotope of polonium, whilst its product in an  $\alpha$ -ray change must also be in place No. 82, and therefore lead. Thus, so far as the series has been traced, both branches end in the place occupied by lead. There is no reason, at present, to believe that any further changes occur, and these products are therefore designated by the symbol  $\Omega$  to mark the end of the series. Before the Displacement Law, there was no evidence whatever to show what the ultimate product of the thorium series was. The evidence from minerals, whilst indicating clearly enough that lead was the ultimate product of uranium and radium, had been interpreted (wrongly) as against, rather than in favour of, the view that the ultimate product of thorium was also lead.

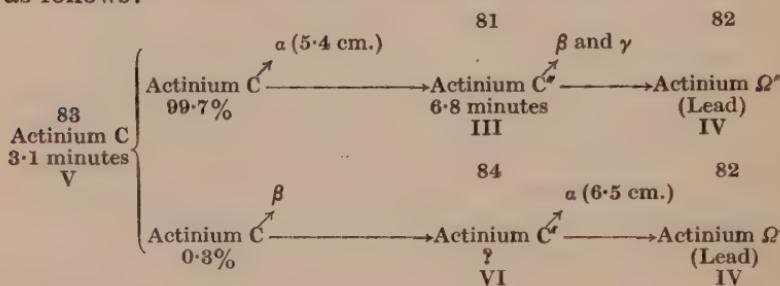
The atomic weights, to the nearest integers, of thorium and uranium are, respectively, 232 and 238. In the complete thorium series, six  $\alpha$ -particles are expelled. Since these are helium atoms of mass 4, and the mass of the  $\beta$ -particles also expelled is negligible, the atomic weight of the ultimate product of thorium should be  $232 - 24 = 208$ . In the uranium series eight  $\alpha$ -particles are expelled, and the atomic weight, therefore, of the ultimate product should in this case be  $238 - 32 = 206$ . Boltwood long ago drew attention to the almost invariable presence of lead in uranium minerals and to the increase in the lead-uranium ratio with the geologic age of the rocks in which the uranium minerals occur, and this has now been developed into one of the best methods for the determination of the age of the earth's crust (p. 323). An interesting exception is autunite (pp. 72, 84), beautifully fresh-

looking crystallised specimens of which occur in pockets in the neighbourhood of uranium mineral deposits. This often has no appreciable lead or helium, and, even to the most refined spectroscopic test, the quantities of these elements present is in some cases barely detectable. No wonder that they look as if they had just been crystallised out of the mother liquor! For this evidence can only mean that they have been so deposited in quite recent times, if not, as is more likely, that they are actually being deposited now under our eyes.

**Thorium Ω.**—With regard to the ultimate product of thorium, which the Displacement Law clearly indicated was an isotope of lead of atomic weight 208, the evidence was much less certain, owing to the rate of change of thorium being three times less than that of uranium, and to the prevalence of uranium in all thorium minerals. The question was settled by the determination of the atomic weight of the lead separated from Ceylon thorite (p. 138), for which it may be estimated, if no lead were initially present, about 95 per cent. must be due to thorium and only 5 per cent. to uranium. This was found to be 207.77 as compared with that of common lead, 207.20. The difference is here most simply shown by a difference in the densities of the two varieties of lead, prepared under identical conditions, since the volume of the two atoms is determined by the nuclear charge or by the Atomic Number, and is therefore the same for isotopes. The thorite lead was found to be about 0.25 per cent. denser than common lead. In spectra and all their chemical properties they are, of course, identical. Subsequently Fajans, working with a Norwegian thorite containing slightly less uranium, relatively to the thorium, than the Ceylon variety, obtained the value 207.9 for the atomic weight of the lead separated.

**Actinium Active Deposit.**—The actinium series in the main is the opposite of the radium series. In it the  $\alpha\beta$  mode is dominant, and the  $\beta\alpha$  mode, if it occurs at all, claims only a negligible proportion of the whole, whereas for radium the reverse is the case. Thorium resembles radium in that it is the  $\beta\alpha$  mode which is the more favoured. For this reason the

$\alpha$ -rays of very long range, which characterise thorium C and radium C, are practically non-existent with actinium C. It is true that for the latter there are a few  $\alpha$ -rays, 3·2 in a thousand, of range 6·5 cm., longer than the others, but it is difficult to be sure whether these arise in a branching of the series, or whether they are not really analogous to the exceptional very long-range  $\alpha$ -rays of radium C and thorium C, still to be considered (p. 295). Either explanation might account for them, but as they are more numerous than, and not so long in range as, these exceptional  $\alpha$ -rays, it is preferable to consider the actinium series also as branched, and to represent it as follows:



For most practical purposes the series may be considered single and consisting only of the upper line, the other being more or less inferred.

As the above shows, the Displacement Law indicates that here also an isotope of lead is the ultimate product in both branches, but there is no direct evidence of this. Aston's experiments (p. 315) on the isotopes of lead appear to indicate that one in uranium lead of mass 207 is probably derived from actinium. If so, the atomic weight of actino-uranium should be 235, and, indeed, this is the reason for this belief.

**Actinium C and Actinium C''.**—Experimentally the only other active deposit product besides and beyond actinium C is actinium C'', which, also, used to be known as actinium D. With the comparatively long period of 6·8 minutes, it was easy to show that it is isotopic with thallium. It gives both  $\beta$ - and  $\gamma$ -rays, but these are considerably less penetrating than those from the other corresponding members. Actinium C may be separated readily from the other active deposit

products by heating them for a short time to a high temperature, when it alone remains behind, the C" member being the most volatile and the B member more volatile than the C member. Under these conditions the  $\alpha$ -radiation decays with the period above given, 3·1 minutes, but the  $\beta$ - and  $\gamma$ -rays, due to the production of the C" member, rise from zero to a maximum and then decay with the longer period 6·8 minutes proper to the latter.

The new differential valve method of studying  $\alpha$ -rays, to be referred to in Chapter XVI., has recently shown that the  $\alpha$ -rays of actinium C consist of two types with different range, the main type of range 5·37 cm., and another in the proportion of 19 to 100 of the main type, of range 4·93 cm. There are several similar cases now known of the  $\alpha$ -rays from a single radio-element being complex. As indicated in the footnote on p. 105, the phenomenon is connected with the emission of  $\gamma$ -rays and is of great theoretical interest. The topic is resumed on p. 295.

**The End of the Uranium→Radium Series.**—This case, though the first to attract attention and the most important in a number of respects, has been left to the last for convenience of exposition. It differs remarkably from the other two cases. If the thorium or actinium active deposits, from sources however active, are studied with instruments however sensitive, it will be found that their decay is complete. Not a trace of activity,  $\alpha$ -,  $\beta$ -, or  $\gamma$ -, finally remains. It is true that, before recoil was recognised, a very interesting effect of it was brought to light by such studies of the active deposit of actinium. A small residual activity is sometimes left, enduring for some weeks, but ultimately it disappears completely. This was shown to be due to the recoil of actinium X from radioactinium in its  $\alpha$ -ray change.

In these two cases the series comes definitely to an end, so far as can be seen. But in the case of radium, it has been known, almost from the first, that the active deposit does not completely decay. Mme. Curie noticed that sheets of metals which have been rendered active by exposure to radium, do not, after removal, completely lose their "induced activity." After falling to a very small value, some

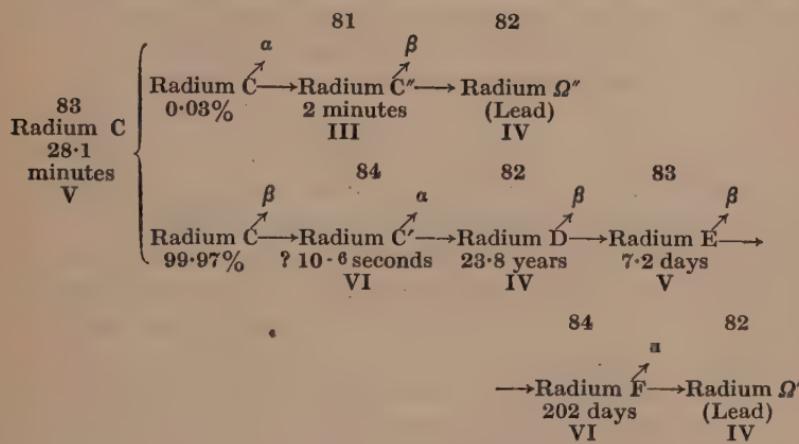
1/20,000th of the initial, the activity does not diminish further, but may even increase again with the further lapse of time. She called the residual activity the "induced activity of radium with slow dissipation." Beyond the C member, the series of changes enter upon a stage as slow as the preceding ones were rapid, and the elucidation of these later changes was one of the first investigations undertaken by Rutherford after the disintegration theory had been put forward.

**Radium D, E and F.**—Initially, the disintegration of the C member is, to an all but infinitesimal extent, the opposite to that for actinium C. The  $\beta\alpha$  mode is followed, rather than the  $\alpha\beta$  mode followed by actinium. That is to say, the radium disintegration series follows almost entirely the lower and major rather than the upper and minor of the two modes shown in the diagram for the thorium series. The upper mode in which radium C" is produced represents only one in 3,000 of the atoms disintegrating. The product of the very short-lived member that gives the long-range  $\alpha$ -rays, radium C', and which, as in the case for the corresponding member in the thorium series, must be an isotope of lead, is called radium D, or radiolead. It is not entirely stable, but has a period of average life of some 24 years. Later determinations give a higher value, 31.7 years. It gives a ( $\beta$ ) ray, so feebly penetrating that it can only be detected by special methods. But, as in so many other cases, this relatively slow  $\beta$ -ray change is followed by a much more rapid second  $\beta$ -ray change. The product of radium D is called radium E. Its average period of life is 7.2 days, and the  $\beta$ -rays it emits in disintegrating, though much more penetrating than those from radium D, are, compared with those from the C members, or from uranium X<sub>2</sub> or mesothorium II, only feebly penetrating. Radium E is remarkable in that no  $\gamma$ -rays whatever appear to accompany the  $\beta$ -rays.

The product of radium E, that is radium F, is, as Rutherford found, the first new radio-element discovered and christened by Mme. Curie, namely polonium. A little later, under the name radio-tellurium, it was rediscovered by Marckwald, to whom we owe many valuable chemical methods for effecting its concentration and purification. It has a period just long

enough to prevent the decay from being noticeable during a few months' work, but sufficiently short to ensure that practically none of it remains after five years. Its period of average life is 202 days, and its half-period 140 days. It gives  $\alpha$ -rays only. Mme. Curie's work established its chemical analogy to bismuth in place No. 83, and Marekwald showed that in many of its reactions it is analogous to tellurium (hence his name radio-tellurium).

**The Radium Branched Series.**—The end of the uranium series is shown below:



The main series is thus a very good example of the alternation, or the passage backwards and forwards of the changing element through the places in the Periodic Table. It begins, with the C member, in the bismuth place, goes one forward into that occupied by polonium, then two back into the lead place, one forward to bismuth, another forward to polonium, and lastly, two back again into the lead place. These sequences are fascinating, as they undoubtedly contain a clue to what is going on within the atomic structures, but so far it has only been possible to make vague and tentative suggestions. In this case, the isotopy of radium C'' with thallium, as also, of course, that of the C' member with polonium, is inferred rather than proved. But, in the other cases, the chemical nature has been thoroughly well established.

Radium D, or radiolead, was indeed one of the earliest

and clearest cases of isotopy among the radio-elements, for, on account of the technical advantage that would result from its separation from lead, long and persistent efforts in this direction were made by many chemists, all of which completely failed. The isotopy of all the C members and radium E with bismuth, and of all the B members and radium D with lead, threw a flood of light on the nature of these post-emancipation members. The only member that calls for fuller discussion is Radium F or polonium, which is outstanding by reason of its historical interest and of the fact that it occupies a place in the Periodic Table before vacant and is therefore a chemically new type. How often, as in this case, does discovery begin where the subsequent logical and progressive exposition of the subject ends !

**Polonium.**—Even before the Displacement Law, polonium was regarded as occupying the vacant place No. 84 in the Periodic Table, the one next after bismuth (No. 83), in the VIIth family containing sulphur, and its homologues, selenium and tellurium. But although a great deal has been learned about its chemical character by actual experiment, the short period of the element, and its consequent infinitesimal quantity, make it impossible to accumulate it and to study it in weighable quantity as was done with radium. In a quantity of uranium mineral containing a gram of radium, there is less than a quarter of a milligram of polonium. In the lengthy operations required to separate it from such a mass of mineral (over 5 tons in the most favourable case), this quarter of a milligram is rapidly becoming zero. After a year less than an eighth of that initially present remains, so that one may give up the quest in despair.

However, there is another way of proceeding. Radium D, or radiolead, has a period of some 30 years. It cannot be separated from lead, being isotopic with it, and lead is necessarily always an important constituent of uranium minerals, as we have seen. But the lead separated from uranium minerals may be used to grow polonium, just as mesothorium is used to grow radiothorium. This is now the usual procedure. The lead from the uranium mineral, containing the parent radium D, is separated in the pure

state in the form of a soluble salt, and from the solution of this at any subsequent time, the polonium that has formed in the interval may be readily separated by immersing in it a bismuth or copper plate, or by electrolysis.

**Chemical Character of Polonium.**—As already stated, polonium is separated in the ordinary analytical processes, with the Group II. metals precipitated by hydrogen sulphide from acid solution, and from them it can be separated along with bismuth. Mme. Curie, from the first, was successful in concentrating it from bismuth by a variety of methods. It is more volatile than bismuth, and more easily precipitated, as a basic salt on diluting its nitrate or chloride with water, and by hydrogen sulphide from strongly acid solution. Nevertheless to the spectroscope, even with the most intensely active preparations, only bismuth lines were seen. But in spite of this, Mme. Curie was of the opinion that polonium was really a new element and would not accept the facile explanation that it was merely bismuth that owed its activity to "induction" by the rays of the radioactive substances in the mineral.

Marckwald discovered the method of removing it from its acid solution by merely immersing in it a plate of an electro-positive metal, such as bismuth, silver or copper. He also found that reagents, such as stannous chloride, precipitate it from its solution along with a trace of tellurium that is present. If this precipitate is again got into not too acid a solution, the tellurium alone may be reprecipitated with hydrazin hydrate. The polonium left in solution can then be reprecipitated again with stannous chloride. In this way, he got, from a quantity of uranium mineral weighing 2 tons, the polonium as a preparation weighing only 4 milligrams. With no more than 1/100th of a milligram of this preparation, the glow produced on a zinc sulphide screen could be made plainly visible to a large audience in a dark lecture hall.

Many attempts have been made by these and other investigators to obtain from such preparations a definite spectrum, but without clear success, though certain lines have been recorded as possibly due to the element. Also, a laborious attempt was made to see whether the lines of

lead—which should not be visible in the freshly prepared and pure substance—would grow in the spectrum as the element decayed. This was frustrated and the results vitiated by the lead present in the paint on the walls of the laboratory, which was sufficient to contaminate everything worked up or kept there, to the extent of showing the more prominent lead lines in the spectrum.

**Radium D.**—It has been mentioned that the regular source of polonium now mostly used is not the original mineral, but the radiolead separated from it, acting as a continuous source of new polonium. But another and even more convenient source, especially in those institutions where radon is systematically used in the course of the work, is the old “radon seeds” or tubes in which the radon has decayed. These are coated internally with an unweighable and invisible deposit of pure radium D, which in the course of time affords polonium. In certain experiments, by Ramsay and Whytlaw-Gray, in which relatively large amounts of radon had been allowed to decay under pressure in exceedingly fine capillary tubes, the latter investigator subsequently observed in the tubes under the microscope a dark-coloured deposit with sub-metallic lustre. Although only of the order of 1/100th of a milligram in weight, certain microscopic chemical reactions were made with the substance. The tube was filled with chlorine gas. No action took place in the cold, but, on gently warming, the dark deposit changed to a white crystalline chloride. This was found not to be appreciably volatile *in vacuo* at 220° C., but to be sparingly soluble in water. All of this is exactly what is to be expected of metallic lead. The presence of lead in the substance was shown by a delicate microscopic reaction depending on the formation of a crystalline triple nitrite with potassium and copper. As, in this material, some of the radium D—about 15 per cent.—would have become transformed into the ultimate product, radium Ω', the experiment merely showed that one of these bodies at least is isotopic with lead. But, from the quantity of lead found, it seemed most probable that both of them are, as theory requires, identical with lead. It is along the lines of the above work that the most hopeful chance of ever

being able to prepare polonium in a pure state appears to lie. The radium D is comparatively long lived. The quantity of it will go on increasing in a radium compound for over a century before reaching equilibrium, and its removal from the radium at any time is a comparatively simple operation. From the separated radiolead the polonium will grow and nearly reach an equilibrium in a comparatively short space of a year or two, and its separation, then, from the small amount of lead should give no trouble. But long before this has been done for the oldest of the new radio-elements, it will probably have been done much more easily and satisfactorily for the newest, protactinium, the long life of which makes the problem now a straightforward one.

**Radium Ω.**—The ultimate product of the uranium series should be, for radium  $\Omega'$  in the main series, lead of atomic weight 206, and for radium  $\Omega''$  in the branch series, lead of atomic weight 210; but the latter is in too small quantity to affect the atomic weight. The lowest value found for the atomic weight of lead is 206.05, for lead from carefully selected uranium minerals, and the density of this is as much less than that of common lead as the atomic weight is less.

**Uranium Z.**—For the sake of completeness, it remains to mention one other member in the uranium series, called uranium Z, and discovered by Hahn in 1921, as a companion of uranium X. Just as uranium Y is isotopic with uranium  $X_1$  and is present in only a very small amount compared with what it would be if it were in the main uranium— $\rightarrow$ radium series, uranium Z is isotopic with uranium  $X_2$  and protactinium, and it is present in even less proportion, only 0.35 per cent. It gives ( $\beta$ )-rays, and so must produce another thorium isotope, but it has not yet been found possible to link it up with any of the known series. It appears to be in too small proportion to correspond with the actinium series. Possibly it is a small separate branch product of uranium  $X_1$ , or it may be derived from another independent isotope of uranium. Its existence as a separate member has been clearly established, and that is all that can at present be definitely stated.

**Potassium and Rubidium.**—It is convenient to refer to the radioactivity of potassium and rubidium, though here also it has not yet been possible to do much more than establish their radioactivity. This was discovered in 1907 by Campbell and Wood. It is feeble in both cases and confined to the emission of  $\beta$ -rays, those from potassium being a soft variety of the hard type, and those from rubidium definitely the soft ( $\beta$ ) type. For this reason although, to the ionisation test, the activity of the two elements is very similar, it is probable that rubidium gives out rays far more rapidly than potassium, owing to the very much greater absorption of the ( $\beta$ )-rays of the former in the substance itself. The ionisation produced by these bodies is extremely feeble, being only about one-thousandth of that produced by the  $\beta$ -rays only of uranium in similar quantity, and this is not much greater than the normal "natural leak" of an ordinary instrument. For this reason, combined with the fact that, so far, all attempts to concentrate the activity into any specific constituent or impurity have failed, very little is known about the activity. All that can be said is that it appears to be a specific property of the potassium or rubidium atom, unaffected by any external process or influence whatever, and to this extent is a true radioactivity. But there is no other evidence that these two elements are undergoing an atomic disintegration, and it is difficult to understand why they alone of all the lighter elements should possess the property. Sodium and cæsium, the homologues on either side of them in the Periodic Table, show no trace of it.

This is specially curious as this group, the alkali metals, are very strongly photo-electric—that is to say, under the influence of ordinary light, they possess in more marked degree than any other elements the power of emitting electrons of very low speed and energy (called the photo-electrons). This is the property upon which the photo-electric cell, used in television and allied processes, depends. It is shown by all metals at high temperature in the so-called thermionic phenomena, upon which the ordinary wireless valve works, but only by the chemically more electropositive metals, like zinc and magnesium, in the cold under the influence of light, and then by ultra-violet light rather than ordinary light.

The alkali metals, and particularly the liquid alloy of sodium and potassium, which has to be sealed up in a vacuum as it is spontaneously inflammable in air, show the property very strongly even with ordinary light. It would be suggestive if it were possible to link up this property with that of the radioactivity of potassium and rubidium, but the absence of radioactivity in caesium, the most electropositive element known, makes any connection improbable.

**The Radioactive Isotope of Potassium.**—Potassium consists of two isotopes, of atomic masses 39 and 41, the latter estimated to be in the proportion of only about 6·7 per cent. of the whole. It is one of the very few elements which has been partially resolved into its isotopes by a particular kind of "unidirectional" distillation in a vacuum, first worked out by Hevesy for mercury, in which all the molecules leaving the volatilising surface are condensed by a surface cooled in liquid air and do not return to the liquid. In this way the lighter molecules are, to a very slight extent, concentrated in the distillate, owing to their rather higher speed giving them an advantage over the others in leaving the surface. Hevesy, from his experiments with potassium, concluded that probably it is the heavier isotope—of mass 41 which exists in the smaller proportion—which alone is radioactive. Rubidium has also two isotopes, of mass 85 and 87, but this element has not yet been resolved, and it is impossible to say which is responsible for the activity.

If we are dealing with true cases of atomic disintegration, the product of the potassium isotope, 41, in a  $\beta$ -ray change must be an isotope of calcium of mass 41, and of rubidium an isotope of strontium. These should be formed in course of geological time, so that calcium should be a constant companion of potassium minerals. As for rubidium, no natural mineral in which it is an important constituent has been found. No isotope of calcium, 41, is known. Ordinary calcium consists of two isotopes of mass 40 and 44, and so far no evidence has been produced that the 41 isotope is a constant companion of potassium minerals, of which a large variety exist.

Again, assuming true atomic disintegration, the radio-

activity of potassium, though so feeble and confined to the  $\beta$ -ray type only, must, on account of the relatively enormous quantity of potassium in the earth's crust, be of importance comparable with that of uranium and thorium in maintaining the heat of the earth through geological time. But until this has been established more clearly as a true case of atomic disintegration, it would seem rather premature to take it into account.

PART II

THE GENERAL PROGRESS OF ATOMIC  
CHEMISTRY



## CHAPTER XII

### MATTER AND ELECTRICITY. THEORY OF RELATIVITY

**The Atomic Theory of Chemistry.**—One of the most important consequences of the discoveries in radioactivity reviewed in the first part of this book has been that it made clear to the physicist the important distinction between the atom and the molecule, which chemists, since the time of Dalton, had been striving to impart. It may be said, without much fear of serious contradiction, that until the present century, physicists, even the most eminent, used the terms almost as synonyms and without any clear understanding of the distinction. Thus we find Clerk-Maxwell in 1873 speaking to the British Association of the stars being built up of the same molecules as those we find on earth, of the vibrations due to the hydrogen molecule being the same here as in Sirius or Arcturus, and of the exact equality of each molecule giving it the essential character of a manufactured article and precluding the idea of its being eternal or self-existent. On the other hand, Sir Arthur Rücker, in his Presidential Address to the British Association on the Atomic Theory, as late as 1901 dealt with molecules rather than atoms, and it would have made little or no difference to what he said if Dalton had never existed and his atomic theory had not been propounded.

To-day, when modern physical research is to an overwhelmingly preponderating extent concentrated on the problem of the constitution of the atom, it is difficult for anyone whose scientific memory does not extend beyond the beginning of the century to realise how recently physicists have discovered the real atom. Whereas, for the best part of a century, there has been the clearest recognition among chemists between atoms and molecules, between chemical and physical changes and between either and anything of the nature of transmutation. The earlier views as to the electronic

constitution of matter made no such distinction and, in a premature and too sweeping generalisation, the electron was regarded as the primordial atom out of which the atoms of matter were built.

As it proves, it is such a sub-atomic constituent, as it is expelled from the nucleus in a  $\beta$ -ray change, which results in an atomic transformation into the next element in the sequence of elements. Even now, with our increased knowledge of atomic structure, it is difficult to understand how electrons can be constituents of the nucleus in the large numbers necessary to make the proton the other constituent. But, in all other phenomena, the electron plays a far less fundamental rôle, and its discovery has been chiefly remarkable for the interpretation it makes possible of ordinary chemical and physical processes.

**Modern Physical Theories and Speculations.**—It is, admittedly, in these days of the fundamental reconstruction of our basic ideas, not only with regard to electricity and matter, but also with regard to time and space, an exceedingly difficult task to give any consistent picture of the theoretical foundation of the physical sciences. So many of the changes of outlook demanded seem to depend upon rare, minute and relatively trivial effects, which may possibly have been misunderstood, and to leave the great mass of ascertained facts without any adequate representation at all in the schemes of interpretation put forward. Physics is suffering acutely from the bane of all philosophy that accepts its ideas from those with only a very indirect hearsay acquaintance with the facts. It is perhaps rather remarkable, considering the history of the race, that it has been able to keep on the rails as long as it has, for there are now abundant signs that it is going the way of all its predecessors.

Looking backward over the long course of history, many theories and speculations have had their day and ceased to be, and now often appear as cobwebs accumulating until they are periodically swept away. But the facts, even those discovered by primitive man before the beginning of history, are the same to-day as when first apprehended. For the one, as familiarity replaces novelty, it is accounted to it as proof

until contempt in turn replaces familiarity, but for the other the discovery once made is for all time.

Yet it is impossible not to try to give some account of the modern ideas, transcendental and metaphysical as they often appear. Many of them have justified and are justifying themselves in the winning of new knowledge, and, however ephemeral they may prove in their present form, it is impossible not to admire the mental range they exhibit, or to deny the legitimacy, in their own sphere, of the methods employed. But the description, perforce for a chemist, will be sceptical and critical—though, it is hoped, not unsympathetic—rather than that of a disciple and adherent. The emphasis will be directed to their bearing on previous ideas and knowledge rather than on the highly special, and often quite recondite, phenomena they are designed in the first place to accommodate.

**Faraday's Discoveries.**—With regard to the nature of matter and electricity, the discoveries that now stand out as the beginning of our modern views are those of the laws of electrolysis by Michael Faraday in 1834, and the even more fundamental "conversion of magnetism into electricity" in 1831, the centenary of which has just been celebrated. The first, which showed, for example, that the amount of metal deposited at the cathode by the same current, passing in series through a number of different metallic salts in solution, is proportional to the chemical equivalent of the metal, had to wait for its modern interpretation until the confusions between the chemical equivalent and the atomic weight, and between the atom and the molecule, that clouded Faraday's epoch, had been cleared up. It was in 1881 that Helmholtz, appropriately enough in a Faraday Memorial Lecture, pointed out that, just as Dalton's Law of Multiple Proportions led, without possibility of escape, to the modern atomic theory of matter, so Faraday's laws of electrolysis led to an "atomic" or discrete theory of electricity. The monovalent elements, those for which the chemical equivalent is the same as the atomic weight, all carry the same charge per atomic weight of element. The diatomic or divalent elements, for which the atomic weight is twice the chemical equivalent, carry

twice this charge per atomic weight, the triatomic or trivalent elements, three times, and so on, the charges carried by chemical equivalents being the same.

**The Faraday.**—This charge is now appropriately named the Faraday, and it is 96,500 coulombs, the coulomb being the tenth of the absolute "electromagnetic" unit.<sup>1</sup> Thus one faraday, passed through acidulated water, liberates 1 gram of hydrogen and 8 grams of oxygen, approximately, through a solution of cupric sulphate, 31.5 grams of copper, and so on, always the chemical equivalent, which is the atomic weight divided by the valency of the element in the compound electrolysed.

The step from this to the modern view of regarding, in the case of the metals, the individual charged positive ions, which transport the electricity, as the fundamental units of matter and the neutral atoms as combinations of them with one, two, three or more electrons, or atoms of negative electricity, was not taken until well on in the present century. It extends Dalton's Law of Multiple Proportions, as regulating the combination of atoms with atoms, to the combinations that occur between the positive ions and the electrons, in the case of the metals and, in general, the basic or electropositive elements, and between the neutral atoms and electrons in the case of the electronegative or acidic elements. It explains the valency of an element as the number of electrons the neutral atom can lose, in the case of a basic element, to form the positive ion, and the number it can gain to form the negative ion, in the case of the acidic element. It gives the key to the nature of chemical combination itself, in many cases, as primarily not an affair or union between the combining atoms, but rather as one between one of the atoms combining and the electrons in the other.

**The Atomic Charge  $e$ .**—What the faraday is for the equivalent weight of a monovalent ion, the atomic charge  $e$  is for the single monovalent ion. We have alluded frequently to the now classic method of determining the mass of the charged

<sup>1</sup> This unit is not to be confused with the Farad, a unit of electrical capacity, much earlier in use.

particle by the study of its deviation in both electric and magnetic fields. Applied first successfully by Sir Joseph Thomson to the electron itself in 1897, and since then, in succession, to the masses of the  $\beta$ -particle, the  $\alpha$ -particle, the H-particles generated by the latter in passage through certain elements, and, most important and far-reaching of all, by Thomson and Aston to the positive ions of the vacuum tube, it has now resulted in more exact determinations of the weights of the individual isotopes comprising an element than the chemical methods of determining the average atomic weight from the chemical equivalent and the valency. It is interesting to note that in every case the new methods do not give the weight of the charged atom or ion directly, but the weight divided by the charge carried. The quantity  $m/e$ , not  $m$ , enters into all the equations.

In chemical language we may say that the new methods, like the old, determine not the atomic weight but the chemical equivalent, or atomic weight divided by the valency, the latter being the number of atomic charges of electricity associated with the charged atom or ion. In both cases, it is a separate study to find what multiple of the equivalent has to be chosen as the atomic weight, or how many atomic charges are associated with the charged particle being deviated. The importance of this did not arise with the electron itself, or with the  $\beta$ -particle. It arose first with the  $\alpha$ -particle, which carries two positive charges, and a separate determination of the number of positive charges carried was necessary to decide  $m$  from the  $m/e$  given by the electric and magnetic deviation.<sup>1</sup> It arises in every case with the positive rays. Fortunately, here, as in chemistry, it has been possible to say what the "valency" of the ion studied is, from other considerations, and to the expert there is little danger of mistaking, for example, a particle of mass  $m$  with a single positive charge with one of twice this mass with two charges, though to the electric and magnetic field they would behave the same. But multiply charged ions are of frequent occurrence in positive-ray gas analysis, ions of mercury with as many as eight charges, for example, being known (p. 307).

<sup>1</sup> For the hydrogen ion  $e/m$  is one faraday and for the  $\alpha$ -particle only half a faraday. Since, for the latter,  $e$  is twice as great as for the hydrogen ion, the mass of the  $\alpha$ -particle must be four times that of the hydrogen atom.

**Valeancy and the Atom of Electricity.**—When it is remembered that this choice between the atomic weight and the equivalent was the most controversial question in chemistry during the first half of last century, and was correctly and satisfactorily settled before the modern atomic doctrine of electricity appeared, the *dénouement* resulting from the latter has considerable interest. Just as the controversies in chemistry concerning the existence and nature of phlogiston may fairly be regarded as an anticipation of the modern doctrine of energy, so the early controversies regarding valency, atomic weights and equivalents foreshadowed the modern atomic conception of electricity.

Before then, electricity was merely a highly mysterious fluid which flowed much as money is regarded by most people to-day, and it was considered almost an indelicacy to trespass where the experts feared to tread, and to enquire too closely as to its real physical nature. The same attitude is, of course, essential to the development of the newer transcendental conceptions of relativity, curved space, non-Euclidean geometry and wave-mechanics, but here no one, probably, yet regards these first attempts as the last words of wisdom on the matter. In any subject, ability to deal only with the recondite and the abstruse and inability to answer the simplest and most natural enquiries is, to the shrewd observer, perhaps the simplest indication that something of real interest and importance still remains to be found out.

**Electromagnetic Inertia.**—The second of Faraday's discoveries, that of electromagnetic induction, in due course was to lead to the modern electromagnetic theory of the origin of mass, but it is almost impossible to say how much of this is destined to survive the more generalised conceptions of mass and energy introduced by the theory of relativity. As first apprehended, the electromagnetic field appeared as an inevitable accompaniment of the motion of electricity. At rest, an electric charge has no magnetic properties, but when in motion, as a current of electricity, the space through which it moves acquires magnetic properties, and becomes, in Faraday's language, a field of electromagnetic force. It was recognised that in the space, in consequence, there exists a

store of energy. Hence to put electricity in motion requires work. The store of energy around the moving charge, similarly, has to disappear before the charge can come to rest again, and in doing so tends to prevent it from stopping. Hence the fluid called electricity must possess inertia. Before it can be set in motion, work has to be done on it, and before it can come to rest the energy spent in starting it has to be taken from it. It "resists" both starting and stopping, just like matter.

Inertia is the most fundamental property of matter and is the true measure of "mass." Weight is a mere accidental attribute due to the proximity of an attracting world. The constancy between mass and weight is due to the constancy of the earth's gravitational pull, and if that alters, as by passing from the Equator, where the distance from the centre is a maximum, to any latitude on either side of it, the weight of a given mass increases. But inertia is fundamental. Two railway trains colliding in mid-space, if that could be imagined, would have consequences equally disastrous to those familiar on earth. It is not the weight of the trains, but their inertia, or mass, which does the damage.

**Examples of the Inertia of Electricity.**—That electricity simulates matter in its most fundamental characteristic is the reason underlying many common electrical phenomena. If the self-induction of the circuit is large, as for example when an electromagnet is included in it, there is a distinct lag in the rise of the current when the circuit is made, and a sudden spark or arc when it is broken. The inertia effects are here increased by virtue of the fact that the current, before it can flow, has to build up its electromagnetic field of force in iron, rather than in empty space, and, the resulting electromagnetic field being much stronger in consequence, a more considerable input of energy is required before it can flow. Similarly, on breaking the circuit, the current is urged on to continue to flow by the energy in the field flowing back into the circuit, with the result that the potential across the gap rises to values far higher than that normally required to maintain the steady flow, and a powerful momentary arc or spark occurs.

Naturally these effects are most noticeable with alternating currents which rise to a maximum, sink to zero and reverse their direction rhythmically, many times a second. With frequencies of a few hundreds a second, the inertia or induction effects dominate the flow rather than the resistance, as for steady or direct currents. With the "high-frequency" currents obtained by the discharge of Leyden jars or condensers, in which the oscillations may be of the order of millions a second, many new phenomena result. Such currents can produce no appreciable electro-chemical effects and for this reason may be with impunity taken through the body. If the choice of a bent loop of thick copper bar or tube and a straight short route of high resistance is offered to such a current, it prefers the straight route to the loop, as the space that has to be magnetised and demagnetised at each half-period of oscillation in the loop route more effectively retards the flow than the high resistance. Thus with these currents one may light a straight-filament incandescent lamp, the terminals of which are short-circuited by a U bar of copper rod.

The discharge of Leyden jars was the original way of generating the electric waves used in wireless telegraphy, the wave-length of the waves generated by this means being simply the velocity of the waves, which is the same as that of light,  $3 \times 10^{10}$  cm. per second, divided by the period of oscillation. Thus for oscillations of a million a second the wave-length is 300 metres.

All these phenomena are shown in a striking degree by lightning, which is a high-frequency discharge between the clouds acting as Leyden jars. As is now well understood, but was at first extremely puzzling to electricians with experience only of direct and slowly alternating currents, lightning will always take the direct route, even through solid masonry, in preference to a thick band or rope of copper bent into a loop—if, for example, the lightning conductor is bent too suddenly round the eaves of a building.

Lord Kelvin predicted the oscillatory character of the Leyden jar discharge and was the first probably to recognise the almost perfect analogy between induction and mechanical inertia. His celebrated equations for calculating the oscillations of a circuit from the capacity, induction and resistance

can be put into a form having perfect analogy with those representing, for example, the vibration of a tuning-fork.

**Light.**—Clerk-Maxwell's electromagnetic theory of light regarded the latter as consisting of a rhythmic or wave-like disturbance of the medium transmitting the light, analogous to those that occur in a Leyden jar discharge. It predicted the possibility of generating electromagnetic waves, analogous to light, but with wave-lengths almost incomparably greater, by such means, a prediction that was verified by Hertz experimentally. These experiments formed the true starting point of wireless telegraphy. That is to say, the medium transmitting light was supposed to be the seat of a rapidly alternating electromagnetic field, reversed in direction at each half-oscillation. Such a field, on the older classical electromagnetic theory, must attend the revolution of electric charges in closed orbits. With the discovery of the electron, it was supposed that these charges were electrons in revolution in the atoms of matter, like planets round a central sun. The discoveries of Zeeman of the effect of a strong magnetic field upon the spectrum lines seemed strongly to support the hypothesis. Viewed from a suitable point outside, the direction of the electron in its orbit would be reversed at each half-revolution of the electron, and at this point the direction of the electromagnetic field attending its motion would also be reversed. The rhythmic variation in the strength of this field in the external medium was supposed to be the physical explanation of the waves of light.

The forces restraining the electron in its orbit were supposed to be the ordinary Coulomb forces of attraction between opposite charges, which, like gravitational forces, vary inversely as the square of the distance. There is thus complete mathematical parallelism between such an atom and a solar system. From that time the atom began to lose touch with reality, and to resemble, even in the case of the simplest, an exceedingly complex solar system. No mathematical distinction was, or yet is, drawn between the uniform revolution of the electron in a circular orbit, and the to-and-fro surging of an electric charge in a wireless aerial. The electron, though moving uniformly in a curved path, was

supposed to be continuously "accelerated" towards the centre by the electrostatic attraction of opposite charges, and the radiation in each case was supposed to accompany the change of direction of motion of the electric charge. On this view the period or frequency of the light is simply the periodic time of revolution of the electron in its orbit, and its wave-length in centimetres is  $3 \times 10^{10}$  divided by this frequency. This view, as we now know, is entirely at fault, and it broke down also because it entirely fails to account for the loss of energy the emission of radiation represents. The mathematicians seem to have failed to recognise any physical distinction between change of speed and change of direction, and the former appears to be essential for the production of light-waves.

**The Gamut of Radiation.**—Visible light extends only over about a single octave of frequency, from a wave-length something greater than 7,000 Å. in the red to something less than 4,000 Å. in the violet, Å. being the Ångstrom unit,  $10^{-8}$  cm. The frequency of visible light is thus of the order of  $10^{15}$  a second. But only the wave-length or frequency, not the essential nature of the phenomenon, is believed to change when we pass outside the visible region. On the one side we go through the infra-red region to radiant heat, to the short and then to the long waves used in wireless, to reach at last frequencies perhaps of 30 a second or less, generated by the alternating current dynamo, to which Faraday's discoveries directly led. On the other side we go through the ultra-violet region, the Schumann and Lyman rays to the X-rays of decreasing wave-length and increasing penetrating power, the  $\gamma$ -radiation of radioactive substances, and, lastly, in all probability to the new cosmical rays.

The total gamut of radiation embraces more than thirty octaves. Yet all the rays, so far as we know, travel at the same speed in a vacuum,  $3 \times 10^{10}$  cm. per second, or 185,000 miles a second. Indeed, it is now pretty generally assumed that the disturbances capable of being transmitted through empty space, such as gravitational attraction and the magnetic disturbances attending sun-spots, all travel at this one speed. Moreover, this speed as measured is constant

in spite of the motion of the source of light relatively to the observer, and because of this the whole of physical theory has been plunged into the deepest confusion and perplexity.

**The Origin of Mass.**—Oliver Heaviside and Sir Joseph Thomson both recognised that the mass of a charged sphere must be greater than that of the same sphere uncharged, by virtue of the inertia of the charge, but until the latter's identification of the cathode-ray particle with the free atom of negative electricity, this had merely an academic interest. The inertia is inversely proportional to the radius of the sphere over which the charge is distributed, and, for the most highly charged spheres of macroscopic dimensions, the inertia is infinitesimal. But with the discovery of the electron, the question at once came to the front. Is the very small mass of the electron due entirely to its charge ? If so, upon what size of sphere must such a charge be concentrated to have the inertia corresponding with the mass of the electron ? The answer to this is that, if the radius of the electron is  $2 \times 10^{-13}$  cm., about 1/10,000th of the average atomic diameter, the inertia due to its charge will wholly account for its apparent mass. From this time it has become customary to regard the inertia of the electron as wholly electrical, its diameter being calculated to fit this view, and the inertia of all matter as similarly due to electric charges.

**The  $\beta$ -Ray Test.**—It was thought at one time that the  $\beta$ -rays of radium offered a crucial test, because, if the inertia is of electrical origin, it should increase with the speed, when the latter approaches the velocity of light. This was predicted as an effect of the speed of the electron becoming comparable with that of the propagation of the electromagnetic field around its path. On electromagnetic theory it should never be possible to make an electron travel at the same speed as light, because, as it approaches this speed, its inertia increases, and would be infinite at this speed. This led to much careful experimentation, notably by Kaufmann and later by Bucherer, to see how the magnetic and electric deviability of the  $\beta$ -rays of radium, some of which travel with a speed

very near to that of light, compares with that for rays of lower velocity. The effect does not begin to become important until speeds exceeding one-tenth of that of light are reached, and it then increases with great suddenness, the apparent mass at one-half being about 115 per cent., at three-quarters 150 per cent., and at nine-tenths being 230 per cent. of the mass at ordinary speeds.

These experiments established in the clearest way the increase of the apparent mass of the electron with speed, the experimental value for a speed of 70 per cent. of light, for example, being 40 per cent. greater than for slow speeds. However, in the meantime, the general acceptance of the theory of relativity made it appear that this increase with speed is a perfectly general phenomenon, and therefore not indicative of the nature of the mass of the electron as first thought. According to this theory, if the symbol  $\beta$  is used to denote the speed of the body in terms of that of light as the unit, the increase of mass over that at slow speed is in the proportion given by  $1/\sqrt{1 - \beta^2}$ . This formula is rather different from those originally developed from the electromagnetic theory of inertia, and the later experiments with  $\beta$ -rays seem to conform to it somewhat more closely than to the older formulæ.

**The Principle of Relativity.**—There is a general belief, in part intuitive, and in part derived from the study of mechanics, that the absolute motion of any body, as, for example, our earth, through space cannot be experimentally determined, but only its motion relatively to some other body. This follows from classical mechanics and Euclidean geometry, if the motion is a uniform motion of translation. It does not necessarily follow either observationally or theoretically for other kinds of motion. For example, Foucault in 1850 demonstrated the rotation of the earth on its axis by his celebrated pendulum experiment. A heavy pendulum capable of maintaining its oscillations for several hours will change the plane of its oscillation relatively to the building in which it is hung. The earth in fact rotates on its axis and leaves it oscillating in its original direction. To save the face of the theory of relativity, some of its exponents no

doubt would willingly have us go back to the geocentric theory of the earth, which has been discredited by all scientific men since A.D. 1500, and to regard it as much the same whether the earth turns on its axis or whether the universe revolves round it in 24 hours, forgetting apparently that, in the latter case, everything outside the solar system must travel at speeds enormously exceeding the velocity of light.

But when it comes to uniform velocity of translation, or kinds of velocities sufficiently similar, such as the velocity of the earth in its orbit, it is certainly exceedingly difficult to get any evidence of it and all the phenomena seem to conspire to conceal it. The direction of this velocity is, of course, reversed at times six months apart. But at some times the earth must certainly have a very considerable velocity through space, if indeed it is not always careering through it. So far it has been proved impossible to put this in evidence, as Foucault did the rotational velocity of the earth on its axis.

**The Velocity of Light.**—No better example could be found than the electric charge itself. In spite of the fact that, though when at rest, it is really carried with the earth through space, it does not possess an electromagnetic field, although when it is moved relatively to the earth, as by whirling round an axis, it acquires this field. Probably this is connected with the fact that the speed of light, as measured on the earth, is independent of the direction of the light relatively to the assumed direction of the earth through space. The latter, it is true, is unknown, but all directions have been tried. In every direction and at all seasons the velocity of propagation is essentially constant, as though the earth were at rest. The well-known principle of relativity, derived from mechanical phenomena, has to be extended to include electromagnetic phenomena, and, in general, probably all the influences capable of being propagated through space with the velocity of light. Not only is motion relative to the earth essential for an electric charge to produce an electromagnetic field, but any variation of this field is propagated at a constant velocity relatively to the earth.

Of the basic fact there seems no reasonable doubt, though

it has been suggested, on the old ether-of-space theory, that the ether may be dragged along with the earth in its motion through space. The classical experiment, of course, is that performed by Michelson and Morley in 1887, and repeated by the latter in 1905, when an absolute velocity of only 2 miles a second should have been detected. The same beam of light, divided at a half-silvered mirror into two beams, is returned to the interferometer, after each half has travelled the same distance at right angles, and a change in the wave-phase looked for by an alteration of the interference fringes. But no difference whatever was found.

It is true that the constancy of the velocity of light in time is anything but well established. It has recently been pointed out by de Bray that every measurement of any accuracy ever made has uniformly given a lower velocity than the last. The difference over the observations made even in this century is not small. It is one part in 600 per century, and if this rate of diminution were maintained, the velocity would be zero by A.D. 62,000. We may leave to the fertile brain of the cosmogonist the tracing out of the consequences of such an alarming possibility. It may be connected with the recent theories that the universe is expanding at a rate continuously increasing with our distance from it, the chief experimental evidence of which is a progressive reddening of the spectra of distant nebulae, as, with more and more powerful telescopes, we explore further and further into the depths of space. This is most naturally explained as a Döppler effect due to the recession of these distant objects from us at speeds proportional to their distance. But it might be due to cosmical dust.

**The Theory of Relativity.**—It is easy for the logician or the mathematician to make the speed of light *in vacuo* constant, irrespective of the proper motion of the observer through space. The units of length and mass have merely to be altered to correspond with this requirement. This was done by the Fitzgerald transformation,<sup>1</sup> which makes the length dimension in the direction of motion of the observer decrease, and the time unit to increase, with the speed. The length of a metre rod moving in the direction of its length relatively

<sup>1</sup> Alternatively known as the Lorentz transformation.

to the observer with the velocity  $\beta$  in terms of that of light as unity, changes from 1 to  $\sqrt{1 - \beta^2}$ , while the times between the beats of a pendulum clock moving in the same way become to the observer longer in the ratio  $1/\sqrt{1 - \beta^2}$ . Clearly for the velocity of light, ( $\beta=1$ ), the length becomes zero and the time becomes infinite, whilst for still greater velocities the expressions become imaginary. This is the reason for the now well-established belief in physics that the velocity of light in a vacuum is the limiting or maximum possible velocity which cannot be exceeded. These relativity expressions were found to be in perfect accord with the experimental results of Fizeau on the velocity of light in a moving column of liquid.

The most important result, however, so far as the topics discussed in this book are concerned, arose out of the requirement that the law of conservation of energy must be obeyed by every system irrespective of its uniform motion of translation. These resulted in conclusions so nearly the same as those reached in the application of Maxwell's fundamental electromagnetic equations to the inertia of a moving electron, which predicted the increase in mass discussed in the last section, that from that time this part of the theory, the Special Theory in contradistinction to the General Theory later developed, at once gained the unanimous support of physicists. But the advance was, in reality, far more fundamental, for the relativity theory makes no distinction between one kind of inertia or mass and another. The increase of mass with speed appears to belong to the same category as the decrease of length and increase of time with speed demanded if the velocity of light is to be independent of the speed of the observer.

**Equivalence of Mass and Energy.**—Instead of the old value  $\frac{1}{2}mv^2$  for the kinetic energy, the quantity obtained, if the law of conservation is not to be affected by the changes of the units of length and time, is the extraordinary expression  $mc^2/\sqrt{1 - \beta^2}$ . This, by the Binomial Theorem of algebra, may be expressed as an infinite series, of which the first four terms are,

$$mc^2 + \frac{1}{2}mv^2 + \frac{3}{8}m(v^4/c^2) + \frac{5}{16}m(v^6/c^4) \dots$$

where  $v$  is the velocity of the body and  $c$  that of light.<sup>1</sup> The second term is the familiar expression in use. The terms to the right are of no significance at all for any ordinary speeds as they are too small to be measurable, but they express the increase of kinetic energy due to the increase of the mass at speeds comparable with that of light. But the first expression  $mc^2$  signifies that, if the velocity is zero, the kinetic energy of the body is  $9 \times 10^{20}$  ergs per gram—the erg being the kinetic energy,  $\frac{1}{2} mv^2$ , of two grams moving with the velocity of one cm. per sec.

The chemist for long has been familiar with the fact that it is impossible to determine the absolute amount of energy in substances. The most we can do is to change one substance into another, and to determine the difference of energies between the initial and final states of the substance. The best example of this, of course, is radioactive change itself. Until the changes of the radio-elements into helium and lead were known, no one had the least conception that such large amounts of energy exist in the atoms as are given out in these changes. But how much more energy there may be in the lead or helium cannot be known until they in turn change into simpler kinds of elements. In any case, the total energy must depend upon what your datum line is—*i.e.*, on what are the simplest and lowest energy-containing elements they are made of and can be resolved into. But this amazing theorem gives the answer at once. It is  $9 \times 10^{20}$  ergs per gram, if the matter is totally annihilated and transformed into energy.

**The Fusion of the Laws of Conservation of Mass and Energy.**—Coupled with the work on the inertia of the electron and its increase with speed, the twin laws of conservation came to be regarded as the two limiting expressions of a single law. Mass is conserved in all changes which involve no change of kinetic energy, and energy in all changes which involve no change of mass. But if either the energy or the mass changes, there is a concomitant change of energy at the exchange ratio already twice stated. This is the Einstein relation of equivalence between mass and energy.

<sup>1</sup> *The Theory of Relativity*, Albert Einstein, translated by R. W. Lawson, Methuen and Co., 1920.

Unfortunately, the theoretical changes of mass, relatively to the changes of energy, are far too small to be experimentally detectable even in the most energetic changes yet known. Thus we saw (p. 92) that the total energy evolved in the disintegration of a gram of radium (element) as far as and including the C member, is 2,800 million calories. From a gram of uranium, completely changing into lead and helium, the total energy may be estimated as some 4,000 million calories. This is  $1.67 \times 10^{17}$  ergs, and, dividing by  $9 \times 10^{20}$  to get the equivalent loss in mass, the result is only a fifth of a milligram or one part in 5,000. Whereas in ordinary chemical change, the next in order of energy to those of radioactivity, the proportion is over a million times smaller and quite insignificant.

It is wonderful to find how great a part familiarity plays in the evolution of modern scientific ideas. When this deduction as to the equivalence of mass and energy was put forward about a quarter of a century ago, no one probably would have been prepared to accept it without experimental proof. To-day, 1931, there is not a whit more experimental proof than when it was put forward. All that has occurred is that some *other* recondite predictions of the theory, dealing with infinitesimal astronomical and spectroscopic effects, have been brilliantly confirmed by observation. But we find one of the world's leading physicists saying, just because it suited his argument for the moment, "How dependable is this Einstein relation? I think most physicists would say that it is about as safe a guide as any theoretical equation which we now have in physics." Simple and now familiar, it is true, but if a generalisation of this order of magnitude can be considered safe until it has been experimentally tested, we shall in science soon reach the point long ago reached by the ancients, when any experiment was considered superfluous and everything was decided by such *ex cathedra* generalisations. Nevertheless it is unquestioningly accepted by the modern physicist, and all the cosmogonies referred to at the end of Chapter II. and some of the reasoning in this part of this book are based confidently upon it.

**General Theory of Relativity.**—The reader may be prepared to go a little further and bear with the author, by the nature

of his science sceptical and also quite incompetent for the task, in an attempt to portray the ideas underlying the subsequent development of this theory. The Special Theory is restricted to the one case of uniform translation, and the attempt has been made to generalise it to include accelerated motion, the chief examples of which occur in gravitational and electromagnetic phenomena. Probably the attempt could be described, not so much as one to prove the universality of the principle, as one in which the principle is accepted as true, provisionally, in order to see where it may lead. It is not valid to criticise its methods or results as physically meaningless, because its object is not to explain the unknown in terms of the known—atoms by models and light by waves—but the reverse. It seeks to find what of the greatest generality may be averred with regard to the physical world without doing violence to anything that is ascertained. And this boils down to the nature of “space.”

By further mathematical transformation of the Fitzgerald relations, due to Minkowski, in which for the time,  $t$ , an imaginary quantity,  $\sqrt{-1} ct$ , was substituted, formal identity and interchangeability between the time parameter and any of the three space parameters resulted. The expression  $ct$  is of course the distance travelled by light in the time  $t$ , but the expression  $\sqrt{-1}$  is a mathematical artifice to make a square negative. This formal identity of all four parameters has been popularly represented as constituting time as a sort of fourth dimension. The word “dimension” has at least three different common meanings: the ordinary one as signifying one of the three dimensions of space—length, breadth and depth; a scientific one in which we speak of mass, length and time as the three fundamental dimensions or quantities out of which all other physical quantities may be compounded; and a mathematical one, in which it simply refers to a parameter, or a particular magnitude of a variable, in which sense there are as many dimensions as there are variables. Simultaneous variation of pressure and temperature of a gas, for example, may be represented as a plane diagram in two-dimensional paper. If we wish to represent also the simultaneous variation of the volume we can do so by a solid diagram, as a curved surface in three dimensions. But if we

have to represent a fourth variable also graphically, it would require four dimensions and it cannot be done. But this is not the same as saying that no system can vary in more than three ways or have more than three "dimensions."

**The Nature of Space.**—It is very difficult to say in which sense the term dimension is now being used in relativity. The reason is that the formal expressions of Minkowski became immediately amenable to mathematical treatment by methods worked out previously by geometers to represent an imaginary four-dimensional space. But there was a distinct change of attitude as to the real nature of space, and the conceptions of Euclidean geometry proving inadequate and inaccurate, once the units of mass, length and time are made variables to allow the velocity of light to remain constant, attention became directed more and more to the properties of "curved space," as conceived by Riemann, originally, long previously.

In one sense the change of attitude was not new. Ever since Faraday had conceived the idea of the electromagnetic field as a state of strain in the ether, it had been necessary to separate action at a distance into two parts, first the effect of the moving charge on the space, and then the effect of the modified space upon our perception or upon the phenomenon perceived. In time gravity came to be similarly regarded. The force of gravity fell into the background, and its place was taken by a gravitational field, the nature of which was responsible for the fall of bodies to the earth. The earth, that is to say, created a special sort of space around it in which all moving matter was directly accelerated by the action of the space, and only indirectly by the earth.

At first the new views followed the old lines. Matter and electricity were supposed to cause a modification of the nature of space from that Euclid postulated into one of the newer kinds postulated by later geometers. In time, since the distinction between cause and effect in physics is always somewhat shadowy, this view was replaced by the equivalent one, that it was the nature of the space that produced not only the attraction between matter, but the matter itself. One kind of space was supposed to represent really empty

space, removed far from all matter and energy; another kind, not containing either of these but in their neighbourhood; another containing energy, as light, etc., but not matter; and another as containing matter.<sup>1</sup> The path along which matter, the electron, or light moves in space and time is called a geodesic and is regarded as an intrinsic attribute of space and time.

If we extend somewhat the original idea of modifying the units of length, mass and time, to account for any desired result, such as the constancy of the velocity of light, and modify also the units of length in the three, or any imaginary number, of space directions, so that in each dimension these vary from place to place according to any laws we please to make, one may possibly get some idea of what a mathematician understands by curved space. What does not seem yet to be possible to decide is whether these inventions of the mathematical mind can really be considered as possible forms of physical space. The question has an answer, presumably, although it is not always possible to say what the answer may really be.

**Spherical Space.**—Thus Riemann invented a kind of spherical space with remarkable properties. It is impossible to picture it except by analogy with the surface of a sphere. The mathematical criterion distinguishing such a surface is that every point on the surface bears exactly the same relation to the whole sphere as every other point. In Riemann's space every point bears the same relation to the whole space as every other point. The volume of such a space is limited just as is the surface of a sphere, though there are no boundaries. A natural unchanging path, *i.e.* a geodesic, through it will lead first to what corresponds with an antipodes and then back to the starting-point, as on the surface of the globe.

It is one thing to formulate a set of curved co-ordinates or mesh system through such a space which, when properly related, will give this or any other required result, and another to say that *our* kind of space has such a curvature, and that a ray of light if not obstructed will in time naturally return

<sup>1</sup> Compare Chapter V. of *Space, Time and Gravitation*, A. S. Eddington, Cambridge University Press, 1929, of which the above may be considered a parody rather than a description.

to its starting-point again. But towards the physical reality of such kinds of space the opinion of astronomers and mathematicians seems steadily to be tending. They are looking to see if the sun, for example, has not a "ghost" or image appearing as a faint star at the antipodes, as it should if our space is spherically curved.

**Scientific Hypothesis.**—It is not for science to quarrel with the mathematician for his methods of attempting to imitate the course of natural phenomena by appropriate juggling with the values of the physical units of measurement, though it is important they should be stripped of a certain pretentiousness they have assumed at the hands of their expositors and their real nature better understood. In a sense they represent the attitude of science towards hypothesis pushed to such extremes as almost to appear a *reductio ad absurdum*.

The scientific worker cannot proceed without a theory or hypothesis co-ordinating his knowledge and suggesting new lines of attack. In the ideal case, the theory gives a consistent generalisation, not to say explanation, of a small host of known and often apparently unconnected facts and events and will predict new phenomena as yet undiscovered. All that is asked of it is that it should not lead to error either with regard to what is already known or to what may later be found out. Whether it is a true or real explanation of natural phenomena is of less interest than that the latter are exactly as they would be were the hypothesis true. There is a natural barrier to the explanation of events and phenomena. We can do little more than account for the complex by the fewest possible number of fundamental things. With regard to these, to be asked to explain them is to assume that the simple can be explained in terms of the complex, literally that molecules may be explained in terms of men.

The mathematician is following a line of his own which appears to account for everything by varying the nature of nothingness. In effect he seems to say, all your, and for that matter my own, "common-sense" physical ideas of geometry and measurement apply perfectly so long as there is nothing to measure with or to be measured. But in dealing with anything other than absolutely empty space all the various

units of measurement change in value to give the effects we ascribe to matter, electricity, radiation and so on.<sup>1</sup> Whether this is a progress in method or a retrograde step is early to say. But it behoves the experimentalist to keep his end up and preserve a vigorous individuality. While noting and when necessary testing the conclusions of the mathematician, he must cultivate his own field and exercise his own imagination independently.

So far the kind of geometry that will account for gravitational acceleration and "explain" matter in the sense just referred to has achieved more success than similar attempts towards the understanding of the electromagnetic field. The prediction that a ray of light would be slightly but appreciably bent when passing near the sun by the gravitational field of the latter was verified during the solar eclipse of May 29th, 1919, but later eclipse observations have not confirmed the prediction in its quantitative aspect (see p. 342).

The one outstanding difficulty not only in this field, but in every theoretical view, is that so far there is absolutely no explanation of atomicity, either of electricity or matter. In this direction the electron has introduced a new difficulty that did not formerly exist, and the electronic theory of matter has made no attempt whatever to account for it. For the electron certainly, and the atomic nucleus possibly, exist, as we shall see, in spite of and in defiance of all the known laws of electricity and magnetism, which is equivalent to saying that the real laws of the latter are not yet known. In this field there are also quanta of energy to be explained, and we shall see later that an interesting beginning here has been made by the new wave-mechanics and also that the conception of energy quanta may give the clue to the nature of atomicity.

<sup>1</sup> For a very readable and suggestive extension of this neodoxy to the quantum see *The Physical Significance of the Quantum Theory*, by F. A. Lindemann, Oxford, Clarendon Press, 1932.

## CHAPTER XIII

### THE STRUCTURE AND SPECTRUM OF THE ATOM

**The Thomson Atom.**—The advances detailed, concerning the electron and the origin of its inertia, quickly led to the view that all mass was of electromagnetic origin, and, at first, that the mass of the atom was due to the constituent electrons. This view is now known to be at fault, as only a quite negligible part of the mass of the atom arises in this way. It would require about 1,840 electrons to equal in mass one hydrogen atom, whereas the actual number is now assumed to be one, instead of 1,840, for each unit of atomic weight.

In Sir Joseph Thomson's atom it was supposed that only the negative charges were discrete or atomic, and that the constituent positive charge of the atom was in the form of a sphere of uniform electrification of the same diameter as the atom, and, therefore, not contributing appreciably to the mass. Although now only of historic interest as a stepping-stone to present views, it was in one respect a remarkable anticipation of them and would have been quite accurate but for the false basis of the theory that the mass was due to the electrons.

From experiments with models and calculations as to how a collection of isolated electrons would tend to orientate themselves in such an atom, he concluded that, as electrons were added to the system one by one, they would form a ring or shell which would grow in number of electrons up to a point, and then a new ring, outside of and concentric with the first, would proceed to be built up without further alteration of the inner ring already formed. This simulates very well the periodic sequence of the chemical properties of the elements as we pass from one to the next in order of atomic weight. If the outer electrons only are of influence, and the inner completed rings of little effect, we should expect a periodic repetition of similar chemical character after passing

through a certain number of elements in the sequence of elements, that is, of places in the Periodic Table.

By 1913 evidence had accumulated that the number of electrons in this atom had been enormously overestimated, and that there was only something like one per unit of atomic weight. The Displacement Law showed that by the loss of an electron as a  $\beta$ -ray the element changes into the next place to the right, and by the loss of the  $\alpha$ -particle with two + charges into the next-but-one place to the left, showing that the difference between the successive places consisted of a single unit charge of electricity.

**The Nuclear Atom of Rutherford.**—The experiments which led to the adoption of the well-known nuclear atom that now holds the field were an extension of those first done by Bragg on the passage of  $\alpha$ -particles through matter, the remarkable character of which was described in Chapter VII. When  $\alpha$ -particles pass through matter a certain amount of general scattering occurs, but it is small. The average angle through which the paths of the rays is deflected, even at the end of their range, is only a few degrees. But in 1909 Geiger and Marsden, working with Rutherford, made the important discovery of what is termed “single scattering,” to distinguish it from the general scattering described above.

A few of the  $\alpha$ -particles are scattered through large angles by single encounters with an atom in their path. About one in 8,000 are scattered by platinum through more than a right angle and appear to be reflected from the platinum and to be returned from it in a direction more or less opposite to that in which they started. This could only be accounted for by supposing that there must be, inside the atoms deflecting the  $\alpha$ -particles, a much more intense electric field than in the models previously proposed. Rutherford supposed that the positive charge associated with the negative electrons in the atom, which keeps the atom as a whole electrically neutral, is concentrated at the centre as a minute but massive “nucleus.” The rarity of the phenomenon of single scattering showed that this nucleus can only occupy a very minute fraction of the whole volume of the atom.

Experiments to test this theory confirmed it as regards the

relative numbers of  $\alpha$ -particles scattered through various angles by various thicknesses of matter and with  $\alpha$ -particles of different velocities. For a given thickness and velocity, the relative number scattered through different angles varies as the fourth power of the cosine of half the angle of scattering. For a given angle and thickness, the number scattered varies inversely as the fourth power of the velocity of the  $\alpha$ -particle.

**The Nuclear Charge.**—But the manner in which the single scattering depends upon the nature of the scattering element was of greater interest and importance. The theory showed that it should depend on the square of the, then unknown, central or nuclear positive charge, and it enabled this charge to be roughly evaluated. The results were in general agreement with the conclusions drawn from the scattering of  $\beta$ - and cathode-rays, which had indicated that the number of electrons in the atom is of the same order, at least, as the number representing its atomic weight, in terms of that of hydrogen as the unit. The scattering of the  $\alpha$ -rays agreed with a value for the central + charge of about one-half this number.

In 1913 van der Broek pointed out that even better agreement with Rutherford's experimental numbers is obtained if the value of the central charge is taken as the number of the element in serial order in the Periodic Table. This was the first suggestion of the fundamental importance of the quantity that is now familiar as the Atomic Number. On the average, it is about half the atomic weight for the light elements up to calcium—atomic weight 40, atomic number 20—but becomes less than this for the heavier elements, being for uranium, of course,  $92/238=0.4$  approximately. This suggestion was later (1920) proved to be exact by Chadwick in special experiments for the scattering from copper, silver and platinum.

**The Instability of the Astronomical Model Atom.**—The scattering of the  $\alpha$ -particle may be said to have revealed the small massive highly charged central nucleus experimentally, and the Rutherford atom was experimentally rather than theoretically supported. For any "astronomical" model atom, in which electrons revolve in orbits like the planets of a solar

system, offended against the ordinary "classical" electromagnetic theory, as theoretically it should not be stable. The nuclear type of atom had in fact been suggested by Nagaoka in 1904, but, in absence of experimental evidence, it was not further considered as it does not satisfy the condition of stability. The instability arises from the continuous "acceleration" in mathematical language of the electrons to the centre, and on the views then prevalent, which received great support from the discovery of electromagnetic waves by Hertz, this should result in a continuous emission of radiation.

Certainly the electron is moving at one instant in one direction, and, half a revolution later, in precisely the opposite direction. But its speed is constant if it moves in a circular orbit. Whether this physical change of direction is on a par with an actual variation of speed, as it is regarded by the mathematical physicists, has always seemed to the author a point that could not be determined without reference to the facts, and these are now conclusively against this view. In the production of Hertzian waves the electrons are accelerated both as regards direction and speed, and here, apparently, the requirements of the electromagnetic theory of radiation are perfectly borne out in practice.

However, it suited the theorists, guided or misguided by the electronic theory of matter and seeing in the revolution of the electron the obvious explanation of spectra, not to be too particular about distinctions of space and time, and it was held canonically that a revolving electron must radiate continuously light of the same frequency as the frequency of the revolution of the electron in its orbit. This would result in a drain of energy from the atom. The orbits of the electrons would continually shrink, and their frequency, and that of the light emitted, must continuously increase, until the electron fell into the nucleus of the atom. Whereas ordinarily atoms neither radiate away their internal energy spontaneously, nor does the frequency of their spectrum lines change with age. They furnish in fact the standards by which the practical units of length are determined, these being expressed in terms of certain selected wave-lengths in the spectrum of cadmium, which are more easily and

exactly reproducible and determinable than any other standards of length, by means of interferometer measurements. As Clerk-Maxwell himself said in 1873, an atom of hydrogen, whether here or in Arcturus or Sirius, bears upon it the stamp of a metric system as distinctly as does the metre of the Archives of Paris, or the double royal cubit of the temple of Karnac.

**Spectrum Series.**—A definite relation may exist between the wave-lengths, or frequencies, of the lines of a spectrum, analogous to those that exist between the notes of a musical scale. The first to be discovered was that by Balmer in 1885, for the ordinary visible spectrum of hydrogen as produced, for example, in a vacuum tube, and it is known by his name. The relation is always now expressed as follows:

$$1/\lambda = R[1/2^2 - 1/n^2]$$

By giving to  $n$  the successive integral values, 3, 4, 5 . . . we get from the formula the reciprocals of the wave-length,  $\lambda$ , or wave-numbers,<sup>1</sup> for the well-known lines of the hydrogen visible spectrum.  $R$  is a constant, known as the Rydberg constant, which has the value 109,675. By making  $n$  successively, 3, 4, 5 and 6, we get the first four lines of the series. The first is the well-known red line, the wave-length of which is 6,563 Å, and the second is the green-blue line, 4,861 Å, Å. being  $10^{-8}$  cm. They were discovered first by Fraunhofer as dark lines in the solar spectrum and labelled C and F by him. The next two are 4,340 and 4,102 Å, in the blue and indigo respectively.

These series, as  $n$  is indefinitely increased, reach a limiting value or “head” of the series, the wave-length of which is got when  $n$  is made infinite, so that the second term  $1/n^2 = 0$ . The lines are widely spaced apart at the red end, but the distance between for each successive line continuously gets less, and they crowd together to the limiting or head value towards the violet, getting fainter as they approach the head.

In 1897 Pickering discovered in the spectrum of the star

<sup>1</sup> The wave-number is the number of waves per centimetre, and the frequency, as the number of waves per second, is the wave-number multiplied by the velocity of light,  $3 \times 10^{10}$  cm./sec.

$\zeta$  Puppis a similar series of lines now known by his name, in which  $n$ , instead of being successive integers, represents these same integers increased by one-half, the  $1/n^2$  being replaced by  $1/(n+\frac{1}{2})^2$ . This, naturally, was also ascribed to hydrogen, though it had not then been observed on earth. Rydberg and Ritz then showed that the spectra of many of the other elements can be expressed by similar series. The latter predicted, from general analogy, that there ought to be another series for hydrogen in which the first term within the brackets should be  $1/3^2$  instead of  $1/2^2$ , which would lie in the infra-red. When looked for, sure enough this series was found by Paschen in 1909.

It was at this stage, after Rutherford had proposed the nuclear type of atom, that Bohr evolved his theory of spectra to account for these series relationships. Before considering this, two other hydrogen series may be mentioned. The first is the Lyman series, discovered in 1915, in which the first term within the brackets is unity ( $1/1^2$ ) and  $n$  has the successive values, 2, 3, 4 . . . This lies very far into the ultra-violet in the Schumann region in which Lyman had specialised, where fluorite is the only material available for lenses and prisms; the spectra have to be taken in a vacuum because of the strong absorption of the rays by air, and the photographic plates must contain no gelatine. Clearly the wave-number of the first line is  $3/4$  R and the wave-length 1215.7 Å. Yet another infra-red series was discovered by Brackett in 1922, similar to the Paschen series, but with  $1/4^2$  as the first term instead of  $1/3^2$ .

**The Quantum Theory.**—In 1900 Max Planck in order to account for the experimental laws of the emission and absorption of radiation, in which field the classical electromagnetic theory had also been found to lead to absurdities, put forward his now famous quantum theory. Radiation is not emitted as a continuous but as a discontinuous process which can only occur by whole "quanta," not by fractions of a "quantum." If insufficient energy is available to enable a whole quantum to be emitted, then none is, and, in general, any excess of energy over that required for an integral number of quanta is left over and not transmitted. The quantum of

energy is proportional to the frequency of the radiation, and is always referred to as  $h\nu$ , where  $\nu$  is the number of vibrations per second and  $h$  is a universal constant ( $6.5 \times 10^{-27}$  ergs-sec.), known as Planck's constant of "action" (see p. 214).

At first sight this looks rather like an atomic theory of energy, and it is sometimes loosely spoken of as such, but it is nothing of the sort. Indeed, it is more nearly the opposite, difficult as the idea is to grasp. The quantum of energy is a perfectly continuous variable, being always in constant proportion to the frequency, which is a continuous variable. Thus the quantum for ultra-violet light is relatively large, and that for infra-red heat rays is relatively small. Arranged in order of magnitude of quanta, that of the cosmical rays would be the largest known, then follow in descending order, that of the  $\gamma$ -rays, X-rays, ultra-violet, visible, infra-red heat and "wireless" rays. The theory applies, in the first instance, only when vibrations or oscillations are concerned. It does not apply to a continuous motion of translation. Here, it may be said, that  $\nu$  being 0,  $h\nu$  is 0, and the transference of energy being by infinitesimal quanta is continuous. This illustrates very well the peculiar inversion of common ideas implicit in this theory. A vast number of quanta does not necessarily mean a vast quantity of energy, but quite the contrary in the more modern developments of the quantum theory. For zero frequency, an infinitesimal quantity of energy is divided into an infinite number of quanta. On the other hand, it is quite possible to imagine a frequency so high that all the energy in the universe would not suffice to make a single quantum.

**Zero Specific Heat.**—The theory has achieved great and striking successes in realms far removed from that for which originally it was proposed. In particular, it has explained the specific heats of solids at low temperature, and the velocity with which, in photo-electric phenomena, the electrons are emitted from metals by the action of light. We have already had occasion (p. 55) to consider one excellent illustration of it in the former field, namely that the specific heat of the diamond is zero below  $20^\circ$  Absolute. In solids, the particles are anchored to each other, and the heat energy which, for

gases, appears as energy of translation, here takes the form of energy of oscillation or vibration. But diamond is the hardest substance known, its atoms are locked together with great rigidity and strength, and the period, or frequency, of its heat vibration is correspondingly high. At low temperatures, its quantum is so large that it cannot take up heat from  $0^{\circ}$  to  $20^{\circ}$  Abs., because no heat passes before a single quantum is available, and very few pass until the temperature is above  $20^{\circ}$  Abs. In general, the quantum laws pass gradually into the classical laws under suitable circumstances, in this case at high enough temperature. The specific heats of solids obey classical laws at high temperatures and quantum laws at low temperatures.

**Bohr's Theory of Spectra.**—Niels Bohr, starting from our experimental knowledge of spectra series, and from Planck's theory of the quantum, modified the latter to explain the former. The main innovation he introduced was to suppose that there were in the hydrogen atom a certain number of possible orbits in which an electron can revolve indefinitely at constant speed and distance from the centre, *without* radiating. He called these the stationary states, meaning that the orbits remain stationary without shrinking through a drain of energy by radiation, not that the electrons are stationary. But outside of this particular explanation of spectra, for many purposes the electrons may be considered without serious error as stationary also, occupying positions at definite distances from the centre.

However, to satisfy the proprieties—for at that time it would probably have seemed too heretical to imagine that the electrons were held out at certain distances from the central nucleus without immediately falling into it—Bohr kept them in revolution on the strict understanding that they were not to radiate, as that would make them fall in and defeat the object for which and which alone they now had to revolve. Such are the philosophic foundations of a really successful and fruitful scientific theory in these days, and few theories have been as amazingly successful as Bohr's theory of spectra.

The electromagnetic theory depicts light as a variable

electric and magnetic field of force, propagated outwards from a charge in regular rhythmic motion. The discovery of the electron led to the electronic theory of matter, in which electrons, like planets in solar systems, ceaselessly revolve in orbits within the atoms, and by virtue of electromagnetic laws radiate light with the frequency of their revolution, so accounting for their spectra. With the advent of the nuclear atom, the electrons are left revolving, like planets obeying Kepler's laws, to keep them from falling into the nucleus on condition that they are not to do the very thing their revolution was invented to explain. The radiation, on Bohr's theory, originates in quite another way. In order that a spectrum line may be emitted, the electron must *jump* suddenly from one stationary state to another nearer the centre.

**Excitation and Ionisation.**—It is to be understood that the theory first applied only to the hydrogen atom, for which a single electron revolves round a hydrogen ion, or proton,  $H^+$ . In the normal "unexcited" condition, the electron is supposed to occupy the orbit nearest to the nucleus—No. I orbit, it may be called. Preparatory to the emission of a spectrum line, the electron is displaced to a more distant orbit, say No. N, and the emission of the line is due to its falling back into one of the orbits nearer the centre. In extreme cases, the electron may be removed altogether, that is to say the hydrogen atom is now completely rather than partially ionised, and then the radiation accompanies the recombination of the electron and the positive ion. In the equation given representing a spectrum series, the integer in the denominator of the first term represents the number of the orbit *into* which, and the integer in the denominator of the second term the number of the orbit *from* which, the electron falls. When the latter is infinite, we have the case of complete ionisation, and the radiation is then due to the actual recombination of the ion and the electron. The frequency of the radiation is then that of the "head" line of the spectrum series. But it is to be understood that this is the exceptional case. More usually the atom is "excited" rather than ionised, that is to say the electron is not completely removed from it, but only banished to a more distant orbit.

**The Quantised Orbits or Stationary States.**—The second innovation introduced by Bohr is more technical, and refers to the particular way he “quantised the orbits.”<sup>1</sup> So far we have spoken only of energy quanta, but in derivation they are somewhat different. Planck’s constant,  $h$ , has the physical dimensions of “action,” where “action” is the technical term for the product of a kinetic energy and a time interval. For a uniformly revolving body the “action” is *twice* the kinetic energy multiplied by the period of revolution. There are profound dynamical reasons for this, as the “principle of least action” and the idea of the conservation of action go back to a very much earlier period of dynamics. But for present purposes it suffices to note that the kinetic energy of the electron must be a definite integral number, not of quanta, but of *half-quanta*. Even in Planck’s original oscillators, in which, on the average, one-half of the energy is kinetic and one-half potential energy, the change of *kinetic* energy is by half-quanta.

Another purely equivalent and very useful mathematical way of regarding Bohr’s method is to say that his stationary states, or permissible orbits, are those in which the angular momentum— $mvr$ , where  $m$  is the mass,  $v$  the velocity and  $r$  the radius of revolution of the electron—is an integral multiple of  $h/2\pi$ , the integer increasing by units, from unity for No. I orbit, as we go forward from orbit to orbit. But for clearness we shall deal with quanta of radiant, but half-quanta of kinetic energy, it being understood that the bisection of the quantum, as regards the kinetic energy of the electron, arises only through the derivation and nature of the quantity, and has no ulterior implication.

Bohr’s orbits are derived from purely astronomical, as distinct from electromagnetic considerations, in the sense that, though both obey forces varying inversely as the square of the distance, the point is that in these orbits the electrons do not radiate. In fact, Kepler’s laws are applied to determine the orbits in general, and quantum laws the permissible ones. In these latter, which may be numbered from the innermost,

<sup>1</sup> For a clear and simple mathematical presentation of Bohr’s Theory of Spectra see *The Structure of Matter* (Appendix), by J. A. Cranston, Blackie and Sons, Ltd., 1924.

I, II, III . . . N, the kinetic energy of the revolving electron is 1, 2, 3 . . .  $n$  half-quanta, or  $\frac{1}{2} h\nu$ , where  $\nu$  has reference to the frequency, or the reciprocal of the periodic time of the electron in that orbit.

**The Relation between the Frequencies of the Lines and the Frequencies of the Electrons.**—The difficulties of this subject arise mainly from the fact that two separate frequencies have to be taken into account, which are only very indirectly related. There is the frequency of the emitted light, or the number of its vibrations per second, and there is the frequency of the electron in its orbit, or the number of its revolutions per second. The reader should note carefully that, in this section, the first is denoted by  $\nu_1$ , and the second by  $\nu_2$ . Consider first a fully ionised atom, and the electron “falling,” from right outside, a certain distance to the nucleus at the centre. It will acquire kinetic energy by its fall just twice that needed to keep it revolving in an orbit at that distance, without either falling further in or moving further out. To take up a specified orbit, therefore, it must radiate away one-half of its acquired kinetic energy as a single quantum of radiation  $h\nu_1$ , where  $\nu_1$  refers to the frequency of the light radiated and governs its wave-length. The retained half of the kinetic energy, which is the same as the radiated half, must be a certain number,  $n$ , of half-quanta,  $\frac{1}{2}nh\nu_2$ , of kinetic energy, where  $n$  is the same as N, the number of the orbit into which the electron falls, and  $\nu_2$  refers to the frequency of the revolving electron. Thus for orbit No. I,  $n=1$ , and  $\nu_2=2 \nu_1$ ; for orbit No. II,  $\nu_2=\nu_1$  and so on.

But these are very special cases, and do not as a rule occur in practice, as they apply to the frequency of the lines when the electron falls from right outside into the completely ionised nucleus. The frequencies,  $\nu_2$ , refer, that is, to the limiting or “head” frequencies of the various series. More usually, the electron falls from an outer orbit,  $N_1$ , to an inner,  $N_2$ . Then  $\nu_1=c/\lambda=R[1/n_2^2-1/n_1^2]$ , the intensity of the emitted lines tending to fall off progressively towards the “head” of the series. But, in every case, half the kinetic energy acquired by the fall is radiated as  $h\nu_1$ , and the half

retained, now added to what the electron had in its original orbit, makes  $\frac{1}{2}n_2 h\nu_2$  and keeps the electron in revolution in the new stationary orbit at the frequency,  $\nu_2$ , appropriate to this orbit.

The consequence is that there is now, in general, no direct relation between the frequency of the spectrum line and that of the electron in its orbit. Half the whole kinetic energy of fall may be given out as an infinite number of quanta of radiation, if the electron falls stage by stage from each orbit to the next, which quanta are infinitesimal for the distant orbits and increase in magnitude progressively up to that of the first line of the Lyman series for which  $1/\lambda = R[1/1^2 - 1/2^2]$ . But if the electron falls straight from right outside into orbit No. I, we obviously get a line emitted which is the line of greatest frequency the hydrogen atom can emit, the wave-number of which is, as we already know, though Bohr did not, the Rydberg constant  $R$ , given by  $1/\lambda = R[1/1^2 - 1/\infty^2]$ , or  $\lambda = 1/R = 917.8 \text{ \AA}$ . It is very far into the ultra-violet, the whole Lyman series being comprised between 1,216 and 918  $\text{\AA}$ . This is quite beyond the range of ordinary spectroscopic investigation and a long way on to the region occupied by the X-rays.

The quantum of energy corresponding with this ray is  $hRc$  ( $= 2.15 \times 10^{-11} \text{ erg}$ ), and this, necessarily, is also the kinetic energy of the electron revolving in No. I orbit, since the excess to be radiated is equal to the quantity retained. But also, the frequency, or reciprocal of the periodic time, of this electron, multiplied by Planck's constant, must be an integral number, in this case one, of half-quanta of kinetic energy on Bohr's theory. So we have  $hRc = \frac{1}{2}h\nu_2$ , or  $\nu_2 = 2Rc$ , where  $\nu_2$  is the frequency of the electron. From the kinetic energy, we can find the velocity of the electron, if its mass is known, and from this and the frequency, the radius of its orbit. The result is that No. I orbit is  $0.531 \times 10^{-8} \text{ cm.}$  in radius, and the electron revolves in it once in  $1.5 \times 10^{-16} \text{ second}$ . This orbital diameter has been described as the most fundamental unit of length in the universe. It is a necessary consequence of the mass and charge of the electron, the magnitude of  $h$ , the quantum of action, and the law of electrostatic attraction.

**The Rydberg Constant.**—The foregoing shows the intimate connection of the Rydberg constant,  $R$ , with the frequency of the electron and the diameter of its orbit in the normal unexcited condition. Actually Bohr's theory achieved its first triumph, before the Lyman series had been discovered, by showing that  $R$  was a complex but independently calculable quantity, namely  $(2\pi^2 m E^2 e^2)/(ch^3)$ , where  $e$  and  $m$  are the charge and mass of the electron,  $c$  the velocity of light,  $h$  Planck's constant,  $E$  the charge on the nucleus of the hydrogen atom, and  $\pi$  the ratio of the circumference of the circle to the diameter. Each of these quantities is independently known,  $E$  and  $e$  being, for the hydrogen atom, the same, and, when the experimental values were put in, the calculated value of  $R$  was almost identical with the spectroscopist's experimental value. The approximation was practically perfect when the mass of the central nucleus was allowed for. In the approximate theory it is supposed to be so large relatively to the mass of the electron that the complication it introduces can be neglected.

**The Pickering Series.**—The next great success was that, though the theory accounted perfectly for the Balmer and Paschen series, and, after they were discovered, for the Lyman and Brackett series, it would not account for the Pickering series, which is  $1/\lambda = R[1/4 - 1/(n+\frac{1}{2})^2]$ . Bohr showed that this is to be expected of an atom for which  $E=2e$ , that is to say for helium, not for hydrogen. The terms  $E^2 e^2$ , which for hydrogen become  $e^4$ , for helium are  $4e^4$ , so that the constant becomes, for helium,  $4R$ . The Pickering series is really  $1/\lambda = 4R[1/4^2 - 1/(2n+1)^2]$ . This series and two corresponding series  $1/\lambda = 4R[1/3^2 - 1/(2n)^2]$  and  $1/\lambda = 4R[1/3^2 - 1/(2n+1)^2]$  were observed for helium in the laboratory by Fowler. Such brilliant experimental confirmations naturally resulted in the immediate acceptance of this theory, and it was rapidly extended and proved to be the key to the unravelling of all spectra. It has had also an important influence in the deciphering of the Periodic Law and in explaining the existing number of elements.

**The Quantum and the Continued Co-Existence of Opposite Charges.**—At this point it is worth while to consider, a little

more generally, the precise implication of the application of the quantum idea to the electrodynamics of a revolving electron. In Bohr's theory for the orbits termed I, II, III . . . N, the electrons have respectively 1, 2, 3 . . . n half-quanta of kinetic energy. These orbits, when chosen in this way, fit the frequencies of the various lines in the different series of hydrogen spectra, the spectral term, or quantity placed in square brackets in the series formula, for an electron falling from say the N<sub>1</sub> to the N<sub>2</sub> orbit being  $(1/n_2^2 - 1/n_1^2)$ .

But so far as Kepler's laws are concerned, any orbits are possible, the limitation being introduced because, the "action" being quantised, the kinetic energy cannot be other than integral multiples of half-quanta. These laws tell us that in No. II orbit the electron moves at half the speed, at a radius four times as great, with a kinetic energy one-fourth as great and a frequency one-eighth as great as for the corresponding values for No. I orbit. In general for any orbit N, corresponding with n half-quanta of kinetic energy, the radius is  $n^2$ , the velocity  $1/n$ , the kinetic energy  $1/n^2$  and the frequency  $1/n^3$  in terms of the values for No. I orbit.

No better illustration could be had of the peculiar inversion the quantum theory brings with it. For, as the kinetic energy of the electron decreases from 1 to  $1/n^2$ , the number of half-quanta, into which it is done up, increases from 1 to n. This is because the frequency is reduced more rapidly than the kinetic energy. The smaller the energy of a revolving electron the larger the number of quanta into which it is done up. As the energy falls to  $1/n^2$  the frequency falls to  $1/n^3$  resulting ultimately in an infinitesimal quantity of energy being done up in an infinite number of quanta.

But now turn it round and look at it the other way. Let us send the electron in from the outside to the nucleus and see what happens. We pass from the 2-quantum orbit to the 1-quantum orbit with an increase in kinetic energy of four times and of frequency of eight times and arrive now at the energy and frequency appropriate to the single quantum, *and beyond this it is not possible to go*. Thus the quantum idea really of itself, and without any other assumption whatever, explains one of the most insoluble mysteries of physics,

why it is that the electron in its fall into the nucleus falls only thus far and no further! We have only to state that a kinetic energy of revolution less than a half-quantum cannot exist to say that the electron cannot approach nearer to the nucleus of a hydrogen atom than  $0.531 \times 10^{-8}$  cm. The nearer it can get to the centre the greater is its kinetic energy, and if it could reach the centre—that is, if the electron and the nucleus were really point charges—the energy acquired by the electron in its fall would be infinite. But it avails it nothing, for the infinity of energy would not make a single quantum! The energy increases inversely as the distance, but the frequency inversely as the distance raised to the power of 1.5, and the frequency is directly proportional to the magnitude of the quantum. So the quantum has it in this race between these reciprocals of infinitesimals on their way to become infinities.

Thus if we imagine an orbit  $n=\frac{1}{2}$ , in which the velocity of the electron is twice, the kinetic energy 4 times and the frequency 8 times that in No. 1, our 4 times greater energy now only amounts to half a half-quantum. In fact, at the orbit for which  $n$  would equal  $\frac{1}{2}$ , the electron would have a complete half-quantum if it had not radiated any energy, but, if it spirals in the least bit further, then its kinetic energy will not suffice to make a single half-quantum. What is it to do? It cannot continue to revolve where it is, at  $n=\frac{1}{2}$ , as it is going much too fast, and it cannot get any nearer the centre as Professor Planck has stopped it, when nothing else that was known could, so back it has to spiral under the centrifugal tendencies created by its too great speed. As in the Hertz oscillator, a component of the velocity of the electron is now really reversed, in speed as well as in direction, and it *radiates* its excess energy away on its way back to the next stable orbit. Thus, in a far wider sense than in Bohr's original theory, the conception of quanta explains not only radiation but the continued coexistence of opposite electric charges in non-radiating orbits.

It may be that, possibly with laws of force other than the inverse square of the distance law, the same idea will explain the atomicity of matter and electricity and give us the secret of the stability both of the electron and the nucleus (p. 297).

**The Static Atom.**—So far as chemistry is concerned this astronomical model atom is not very suitable or convenient. It seemed at first the obvious way of explaining the emission of spectra. But now we know that the origin of the emission of the spectrum lines is the sudden shifting about of the electrons from one position to another, and that no radiation results from their alleged continuous change of direction. It is true the physicist may have a use for revolving electrons in theories of magnetism and the like, but even these, like the electronic theory of matter and all the other attempts to explain phenomena by the revolution of electrons, seem to have reached a stage of arrested development, and to be ripe for replacement by more fertile ideas.

We may suppose that in the hydrogen atom, for example, there are a certain number of positions possible for an electron to take up, which vary in distance from the centre outward in the ratio  $1 : 4 : 9 : 16 \dots$ , at any of which the whole kinetic energy, acquired by the fall into this position, is radiated as a single quantum, and therefore at a frequency proportional to the energy radiated. It is no criticism, in these days, to dismiss such an atom as unstable. We have not the remotest idea how the single electron holds together. It ought to be one of the most explosive and unstable things in physics, yet it behaves as a permanent existence, in defiance of every known physical law. It is a small crime, in comparison, for chemists, if they want to, to regard the electrons as hung up like Mahomet's coffin round the nucleus where the properties of the atom show them for the most part to be.

If this is too physically outrageous, we may compromise with the physicist, perhaps, by allowing them to revolve so long as they do not change their position. For all the requirements of structural chemistry and for all the common properties of materials, the solar system atom is worse than useless. These indicate that the molecule has a definite structure with a shape and architecture of its own whatever its internal squirm. An interesting compromise along these lines seems to be afforded by the new wave-mechanics.

**The Dilemma of Physics.**—This theory, like those of relativity and curved space, as yet deals only with mathe-

matical symbols, the physical interpretation of which is as yet, if at all, only very imperfectly understood. It attempts to reconcile the greatest outstanding difficulty of modern physics, the two entirely different conceptions of light, according as we regard it as a spherical wave or pulse spreading in all directions, or a concentrated quantum of energy or "photon." We may quote some remarks of Sir William Bragg illustrating the difficulty. He said, "We must think in terms of the older classical theory on Mondays, Wednesdays and Fridays, and in terms of the new quantum theory on Tuesdays, Thursdays and Saturdays."

One of the most difficult phenomena to reconcile is the photo-electric action, which may be described as a reversed spectrum emission. When an electron falls into a charged atom, a quantum of radiation is emitted with a frequency corresponding with the kinetic energy acquired in the fall. But this same quantum may be absorbed by another and distant atom with the ejection of an electron from it, the kinetic energy of which accords with the frequency of the quantum, and that of the original electron that generated it. As Bragg puts it, this is as though we have two ships a great distance apart on an ocean, and, a plank being thrown overboard from a certain height from the one ship, it causes a similar plank to start up to the same height from the other ship. Incidentally, it may be mentioned that it was the photo-electric action of the X-rays, and the much greater kinetic energy of emission of the photo-electrons produced by this radiation as compared with those produced by ordinary light, which convinced physicists that the X-rays must be a light radiation of excessively high frequency, long before the experiments of Laue (p. 127).

**Quanta on the Wave Mechanics.**—The new theory attempts to meet the dilemma by supposing that a particle (electron or atom) is, or is associated with, a set of stationary waves,<sup>1</sup> something as a stone or obstruction in a flowing river may be associated with a set of stationary ripples in the stream. The group of waves tends to spread, and if we consider the case of an electron revolving in an orbit, it will

<sup>1</sup> What the waves are of or in is left to the imagination.

spread round the orbit, so that instead of a single point we have to imagine a ring of stationary waves. That is to say, if it revolves at all, it is as a ring, not as a point, without any change of position, the compromise above referred to.

But, owing to interference between the two ends of the spreading train of waves round the orbit when they join, only certain orbits will be possible, and the radii of these possible orbits, or stationary states in Bohr's theory, for the hydrogen atom follow from this theory without any special hypothesis. At intermediate radii, interference will cause the waves to cancel one another out. This, though no doubt a very crude and highly imperfect picture of this transcendental hypothesis, is the only explanation yet put forward for the existence of light and other forms of kinetic energy as definite quanta, proportional to the frequency.

**Barkla's Characteristic Homogeneous Secondary X-Radiations.**—We saw at the end of Chapter VIII. how the development of X-ray spectroscopy made it possible to determine the wave-length of any X-ray, and we considered the wave-lengths of the principal ray (a very close doublet) in the "K" series, given when a rhodium or palladium anticathode is used in the X-ray bulb. Before this development, Barkla had discovered a type of X-ray fluorescence, generated when X-rays of sufficient penetrating power are allowed to fall on matter. A secondary radiation is emitted, which absorption experiments proved to be essentially homogeneous in type, which is the more penetrating, or "harder," the higher the atomic weight of the element.

We must here anticipate the conclusions of the next chapter to the extent of saying that the structure of the electronic system round the nucleus is believed to be much what was postulated in Thomson's atom, the nucleus being supposed to be surrounded with completed concentric rings or shells of electrons, much as the shells round an onion, the distance of which from the centre, or radii, are probably quantised in much the same relation as in Bohr's hydrogen atom. In the latter case there is one electron, which may have any one of the possible orbits when in an excited state and about to emit its spectrum line. In the normal unexcited

state the electron occupies the innermost, or No. I orbit. With the succeeding elements in the Periodic Table in the normal state, for helium there are two electrons in the inner ring, which is called the K ring. Then an outer, or L ring, is built up, electron by electron, being complete by neon with 8 electrons, and then follows a similar ring of 8, the M ring, completed by argon.

Barkla's K and L series of characteristic radiations have been identified with the fall of electrons, in the first case, from an L into a K ring, and in the second case from an M into the L ring. Beginning with light elements, such as aluminium, and proceeding through the Periodic Table, the K radiation is excited by X-rays of only moderate hardness. But this K radiation rapidly increases in hardness with atomic weight, and the primary X-rays necessary to excite it must always be harder than those generated. About silver, in the Periodic Table, we have reached a position where the K radiation is getting so hard that only very hard primary rays can excite it. But at this point a new series, known as the L series, commences, and, for a few elements more, both series can be studied. The L series ray is at first extraordinarily soft, but with each successive element the radiation gets harder, though, even at the end of the Table, it is not as hard as the K series is for silver or the neighbouring elements. Other series of the same type are also known, but it suffices to consider only the two.

**Moseley's Law.**—The K series was shown by Moseley, by the crystal grating method, to consist of two principal lines, though since his time many other weaker lines have been found. The L series comprises usually a larger number, five or more of important intensity, but in each case we may limit ourselves to the consideration of the wave-length of the strongest line. For the K series Moseley found this to be given by

$$1/\lambda = R[1/1^2 - 1/2^2][N - 1]^2 \text{ or } \frac{3}{4} R(N - 1)^2,$$

where N is what is now called the Atomic Number of the element. For the L series the formula is

$$1/\lambda = R[1/2^2 - 1/3^2][N - 7.4]^2 \text{ or } \frac{5}{9} R(N - 7.4)^2,$$

this formula not being so exact as the first. It means that if the square-roots of the frequencies are plotted against the atomic number of the elements we get in each case a straight line, that for the L series being somewhat curved. In Fig. 48 (facing p. 281) is shown a striking photograph due to Moseley for the two principal lines in the K series for a number of successive elements from calcium to zinc, the one next to calcium, scandium, being missing, and zinc being represented by its alloy with copper, brass. The regular increase in frequency  $1/\lambda$ , or decrease in wave-length,  $\lambda$ , as we pass from element to element is well shown.

The explanation from the standpoint of Rutherford's atom and the Bohr theory followed at once. The K lines arise from the return of the electron after excitation or ionisation to the innermost orbit, that is to the K shell next to the nucleus, and the L lines similarly to the L shell next to it. It is impossible to remove such deep-seated electrons, from any element subsequent to neon, except by primary electrical forces of great intensity. All the lines of ordinary optical spectra arise from ionisation of the outermost shells, but the K lines arise from the innermost pair that is complete by helium and the L lines from the second shell of 8 that is complete by neon.

The much greater simplicity of the spectra, especially of the K lines, under these circumstances, and their direct dependence on the atomic number, must be ascribed to the fact that the K electron is so close to the nucleus. The other electrons in the atom, all but one, more or less equally surround it and do not have any resultant influence—that is, their several effects cancel out. Under these conditions we practically have to do with a simple system, like the hydrogen atom itself, except that the + nuclear charge is not unity but the atomic number of the element. Actually, it is one less than this, because the second K electron in the atom neutralises one of its + charges, but the other electrons do not count. In consequence we have practically the first line of a Lyman series with, instead of  $R$ ,  $R(N-1)^2$ . The first line in the K spectrum is due to the fall, into a vacant K position, of an electron from an L position. Similarly the first line of the L series is due to the fall, into a vacant L

position, of an electron from the M ring. But for this series the effective nuclear charge is not (N - 1) but (N - 7·4) approximately, the 7·4 probably representing the number, on the average, by which the nuclear charge is reduced by the K and L electrons.

So that not only were these new spectra linked up in a wonderful way with the optical spectral series given by hydrogen, but a direct method of determining the atomic number, and all it implies in the constitution of the atom, was obtained.

**Optical Spectra.**—It must not be supposed that all the exceedingly complicated spectra given by the elements have now been explained, or can be calculated beforehand by theory. But the latter has given to their interpretation a powerful new weapon, and the explanation and classification of the various possible modes of emission of radiant energy from the atom proceeds apace. But there is one result so intrinsically interesting and important that it cannot be omitted. It refers to the various types of spectra given by the same element under various conditions, a misinterpretation of which, in the case of the "enhanced lines" in stellar spectra, was responsible for Norman Lockyer's theory that in the stars as they cool there is going on a building up of the heavier elements from the lighter ones (p. 32). The "enhanced lines" which Lockyer ascribed to "proto-elements" in the stars are reproducible in the laboratory by intense electric discharges and are now called spark spectra.

The elements of Group I, the alkali metals, have only one valency electron (see next chapter) and give only one type of spectrum, the so-called "arc-spectrum," the "head" line of which results when an electron recombines with the monovalent ion, as  $\text{Na}^+ \rightarrow \text{Na}$ . Group II, the alkaline-earth elements, have two such electrons, and here there is the possibility of two spectra, the "arc-spectrum" as before,  $\text{Mg}^+ \rightarrow \text{Mg}$ , and a "spark-spectrum" in which the intensity of the electrical forces is sufficient to "strip" the atom, leaving only the "core," as  $\text{Mg}^{++}$ . When this unites with an electron to form the monovalent ion  $\text{Mg}^+$ , we have the "head" line in the spark spectrum emitted,  $\text{Mg}^{++} \rightarrow \text{Mg}^+$ .

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Next aluminium, a trivalent element, when "stripped" is  $\text{Al}^{+++}$ . So aluminium gives an arc spectrum,  $\text{Al}^+ \rightarrow \text{Al}$ , a first spark spectrum  $\text{Al}^{++} \rightarrow \text{Al}^+$ , and a second spark spectrum  $\text{Al}^{+++} \rightarrow \text{Al}^{++}$ . The next element is silicon, a tetravalent element, and when "stripped" is  $\text{Si}++++$ . Hence silicon gives four spectra, an arc spectrum, a first, second and third spark spectrum in the same manner.

**The Spectroscopic Displacement Law.**—The reason why series analogous to those found for hydrogen, and with the same value for  $R$ , the Rydberg constant, occur also for other elements, is that a monovalent ion combining with an electron is very like a hydrogen ion, in that its effective positive charge is only 1, whatever the atomic number, because the other electrons surround the nucleus and neutralise all but a single unit of its charge. But for a divalent ion with two +charges, uniting with an electron to form a monovalent ion, we should expect the constant to be  $4R$ , as it depends upon  $E^2$ . For a trivalent ion uniting to form a divalent ion the effective +charge is three, and the constant should be  $9R$ , and for a tetravalent ion, similarly,  $16R$ .

Now something very like this has been found, and is called the Spectroscopic Displacement Law, from analogy with the Displacement Law of radioactive change. Making the allowances given for the values of  $R$  in each case, it is found that there is a general correspondence between, for example, the arc spectrum of sodium, the spark spectrum of magnesium, the second spark spectrum of aluminium and the third of silicon ; also between the arc spectrum of magnesium, the first spark spectrum of aluminium, and the second of silicon; and finally between the arc spectrum of aluminium and the first spark spectrum of silicon. Here, again, only a beginning has been made, and it is to be understood that the rules are by no means universally obeyed. The spectrum of each individual element has still plenty of peculiarities of its own.

## CHAPTER XIV

### THE PERIODIC TABLE

**The Periodicity of Chemical Character.**—The original suggestion of Sir Joseph Thomson (p. 205) has now been developed to account for the periodicity of chemical character of the elements, expressed by the Periodic Law, due originally to Newlands, Lothar Meyer and Mendelejeff, and for the peculiar numerical sequence followed by the successive periods. In passing from one place in the Table to the next, with an increase by unity of the atomic number, the +nuclear charge increases by unity. To preserve the electroneutrality of the atom as a whole, an electron has to be added to its outer region. The key of the solution of the problem is that, in general, the addition of this electron leaves the structure as regards the electrons already there essentially intact. The addition to the nuclear charge, and the increasing central positive charge of the nucleus, of course produce corresponding changes in the scale or size of the atom and the dimensions of the various shells. But in this description these are not considered, and, indeed, attention is concentrated upon the electronic system, the changes in the nuclear charge being always taken for granted.

After a certain number of electrons have been so added, which is at first 8, then 18, and, in the last case, 32, these form a complete shell, and the next electron goes to begin the building up of a new shell outside it. Thus the nucleus may be regarded as surrounded by these concentric completed shells, much as with the layers of an onion, which, in general, do not play any very direct part in the chemistry of the atom. It is the number of electrons in the outermost shell which, in general, fixes the chemical character and the family, or vertical row in the Table, to which the element belongs. This accounts perfectly for the regular periodicity of the chemical properties, so far as concerns the first two short periods of 8 elements. In the later parts of the Table it has to be modified. For the two long periods of 18 elements the two outer-

most shells, and for the longest period of 32 elements the three outermost shells, are being built up by the successive additions of electrons. For certain of the elements in these periods, the electrons directly responsible for chemical character, called, in general, the valency electrons, may be derived from the two outermost shells.

**The Relation with Spectroscopy.**—Another idea underlies this development. The various "orbits," or places in the electronic structure, which the several electrons occupy in the single complex atom in its normal unexcited state, have a close analogy with the several orbits which the single electron of the hydrogen atom can occupy in the excited state preparatory to the emission of the various spectrum lines of hydrogen. Bohr's theory effects in this a great economy of orbits, as compared with any previous conception, for, owing to any interchange of an electron between any two orbits corresponding to one spectrum line, the number of possible lines increases very rapidly with the number of the electrons. Moreover, as regards the outermost orbits at least, each electron may have as many excited orbits as the single electron has in the hydrogen atom. Thus, for example, in the atom of iron, atomic number 26, there are 26 electrons outside the nucleus, but from four to five thousand lines are present in the iron spectrum. The extremely complex spectra of the elements does not require for their explanation, as was before supposed, a correspondingly complex constitution of the normal unexcited atom. In fact, only a few of the possible orbits are represented by the spectra.

The general nature of the development has been that the spectroscopists, from their intensive studies of spectra under all possible conditions and under the highest resolving powers, when many of the lines show a fine structure and are resolved into a multiplicity of separate lines, have fixed the minimum number of normal orbits to explain their results, and, then, this minimum number was found also to account for the total number of elements in the Periodic Table on the simple assumption that no two electrons in the external electronic structure of the atom could occupy precisely the same kind of orbit (Pauli Exclusion Principle, p. 242).

**The Periodic Table.**—A chart of the Periodic Table, with the electronic structures assigned to the several elements, is given in full at the end of the volume, and in this description the general principles rather than the details will be referred to. Hydrogen, with atomic number 1, nuclear charge 1, and a single electron outside it, is usually put before the Table proper, which starts with helium, the second element, of atomic number 2. The structure of hydrogen is the simplest possible. The nucleus,  $H^+$ , is called a proton, and is supposed to be the “ protyle ” out of which all the elements are ultimately constituted (p. 32). It has no electrons in the nucleus, but all the other elements on this view must have as many electrons in the nucleus as the difference between the atomic weight, in terms of H as 1, and the atomic number. Assuming that their nuclei are composed of protons and constituent electrons, the number of the latter is necessarily the atomic weight minus the atomic number. Thus helium has two and uranium 146 nuclear electrons, but with the hypothetical constitution of the nucleus we are not in this chapter at all concerned. Hydrogen is, in many senses, unique, though, its valency being 1, it has in its compounds formal resemblances both with the alkali-metals in Group I and the halogens in Group VII.

In the description of the Periodic Law a “ period ” signifies the horizontal sequence of elements, increasing one by one in atomic number, starting with any of the elements in Group 0 and extending to the element preceding the next element in that group. A family, or group, is a vertical row of chemically similar elements. In the old nomenclature of Mendeleeff, the long periods are divided into two parts, the first part being called the A sub-period and the last part the B sub-period, the A and B members each forming separate families, but this division is becoming obsolete. The three elements joining the ends of the A with the beginning of the B sub-period, Mendeleeff put in Group VIII and called transition elements. But now the term transitional elements is being extended to include all the 10 elements that are, as it were, interpolated into the short period of 8 to make a long period of 18 elements. In the way the places in the Table are usually arranged, there is a fairly close formal re-

semblance, as regards the valency of their principal compounds at least, between the A and B divisions of the same family.

The word "core" is conveniently used to indicate the whole of the completed shells, that is all the electrons except the outermost valency electrons, and this core is, for the fully developed uranium atom at the end, comprised of 7 successive shells bearing the letters K, L, M, N, O, P, Q, from within outwards. The origin of these particular letters has already been noted in the discussion of Barkla's characteristic X-rays (p. 222).

**The Zero Elements as the Points of Electroneutrality.**—By helium, the second element and the first member of Group 0, the K shell of 2 electrons is completed. By the next member of Group 0, neon, the L shell of 8 electrons is also complete, and by argon, the next shell, the M shell, of 8 electrons also, and this brings us to the end of the short periods and the commencement of the long periods. We may, from the consideration of these short periods, first get the general character of the interrelationship between the elements.

The Group 0 elements act, as it were, as the points of reference to the elements on either side of them. Beyond them, in Group I, the alkali-metals, the elements have a single valency electron; in Group II, the alkaline-earth elements, two, and so on. Behind Group 0, in Group VII, the halogens, the outermost shell needs but one electron to complete it, and in Group VI, the oxygen and sulphur elements, two. Chemical affinity, as more nearly discussed in the next chapter, results from the efforts of the atom to complete its core up to that possessed by the nearest Group 0 element. Thus when an atom of chlorine and an atom of potassium combine, the valency electron of the latter goes to complete the core of the chlorine atom. There results two argon cores, with nuclei respectively charged one unit more and one unit less than the argon nucleus, and these are the potassium ion,  $K^+$ , and the chlorine ion,  $Cl^-$ . These hold together by general electrostatic attraction, rather than by individual bonds, the affinity being exerted essentially between the electro-negative or acidic element, chlorine, and the valency electron of the electropositive or basic element, potassium. The

compound is a typically "polar," but it is only one of three distinct types of chemical compound, to be elaborated in the next chapter.

The above holds true to an ever decreasing extent as we pass, on either side, further from Group 0 into the elements more nearly in the middle of the periods. Group I and Group VII, severally, are both composed of elements extremely similar in chemical properties. Group I comprises lithium, sodium, potassium, rubidium and cæsium, and Group VII, fluorine, chlorine, bromine and iodine, and each may be regarded as an almost perfectly harmonious family in the chemical sense, the relations between the members of which first pointed the way to the complete generalisation. But for the other groups, the resemblances become less perfect as we get towards the middle of the periods, and, in particular, the first two members of the groups which belong to the short periods, are generally rather different from the later members which belong to the long periods. Group II, comprising beryllium, magnesium, and the four alkaline-earths, calcium, strontium, barium and radium, are all divalent basic elements, and, as regards the last four, are as similar to one another as the alkali-metals. Group VI, comprising oxygen, sulphur, selenium, tellurium and polonium, are all divalent acidic elements.

But, in passing down any family or group vertically, the basic or metallic character increases and the acidic character diminishes. The members of the family of higher atomic weight are, practically universally, more basic than the first representatives. Thus selenium and tellurium are approaching to a metallic character. A better example we have had already in the difference between protactinium and tantalum, which enabled the two elements to be separated (p. 151). The difference between the first two members and the subsequent ones, already mentioned, was indicated in the nomenclature of Mendelejeff, by terming the former the "typical elements"; but the name is misleading as, in their properties, they are not completely typical of the rest.

**The Short Periods.**—Considering periods instead of families, and taking first the two short periods, we find each successive

member is less basic and more acidic. In the first period we pass from lithium, through beryllium, boron, carbon, nitrogen, oxygen and fluorine, and in the second from sodium, through magnesium, aluminium, silicon, phosphorus, sulphur and chlorine, there being practically perfect correspondence between the succeeding members of the two series. The elements in Group III are the trivalent earth elements, of which aluminium is the commonest. At Group IV we reach the middle of the period with the tetravalent elements, carbon and silicon, and the basic or metallic character is definitely lost. From now on, in Groups V, VI and VII, we pass over to acidic elements with increasing electronegative character. After four electrons have been added the character of the atom reverses. Instead of tending to lose electrons forming positive ions, it tends to combine with more from other electropositive elements, and to use them to bring up its outer shell to the full complement possessed by the next inert gas in Group 0. Thus nitrogen requires three, oxygen two, and fluorine one electron to form a complete neon core.

In this, the electronegative, part of the Table the principal valency is not, as with the electropositive elements, the group number, but eight minus the group number. But the possibility of the element acting, as an electropositive element, with its valency equal to the group number, is not excluded, though the compounds formed are invariably non-polar in character. No simple negative ion with valency higher than two is known, and, as a general rule, it may be stated that the higher the valency the less the tendency to form free ions and polar compounds at all. However, valencies as high as four are known for simple positive ions of some of the heavier metals, such as tin, as in the stannic series of salts derived from  $\text{Sn}^{++++}$ . This must not be confused with the momentary existence of such ions as  $\text{Si}^{++++}$  in intense electrical discharges described in the last chapter, and to be further discussed in Chapter XVIII.

**The Long Periods.**—The difficulties begin to arise when we have to decide upon what may be termed the course of evolution of the elements in the long periods. Here there is now a consensus of opinion, derived not only from the general

chemical and physical character of the elements and their compounds, but particularly from their spectra as interpreted by Bohr's theory discussed in the last chapter. The most important point that has emerged is that, during the passage through what have been termed the interpolated elements in the long periods, the building up of the incomplete outermost shell is suspended, and the new electrons are added to the next inner shell of 8 electrons, swelling the number to 18, before the filling up of the outermost shell is resumed.

**The Principle of Symmetry.**—There is a marked tendency for the atom to assume the greatest possible symmetry as regards the number of electrons in the successive shells, the middle shell tending to have the greatest number, and the successive shells on either side of it to have the same numbers, decreasing from the centre in both directions. This principle accounts not only for the swelling of the under shells in the development of the two long and the longest periods, but also for the particular point at which the change begins, at which the new elements begin to be interpolated into the period. So soon as the outermost shell has two electrons, corresponding with, and symmetrical to, the two of the innermost K shell, the further development ceases, and the electrons go into the shell beneath.

In the change from the short period sequence to that of the long period, the ten interpolated elements are all metallic in character. After this interpolation, the last five elements of the period follow again the normal course in the short periods, the outermost shell of two electrons growing successively from two to seven. The result of this is that the outermost shell of any atom never has more than eight electrons, attaining this number at the Group 0 element. The long periods may be regarded as short periods, in which, after Group II, ten interpolated or transitional elements have been introduced before the completion of the short period is resumed.

**The Transitional Elements.**—In the first long period, these ten transitional elements, introduced after calcium, are scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc, before the normal course of

development is resumed with gallium, germanium, arsenic, selenium and bromine, which resemble very closely their analogues in the short periods. In the second long period, similarly, the sequence after strontium is yttrium, zirconium, niobium, molybdenum, masurium, ruthenium, rhodium, palladium, silver, cadmium, before the normal course is resumed with indium, tin, antimony, tellurium and iodine, which again are analogous to the corresponding short period elements.

In many respects, the transitional elements have distinctive qualities, which are to be ascribed to the influence of the developing penultimate shell. They frequently show variable valency, in which the variation is by single units, as in the cuprous and cupric salts derived from the ions,  $Cu^+$  and  $Cu^{++}$ . Their salts are frequently, as in the last example, coloured, showing a banded absorption spectrum. They are notably paramagnetic and markedly catalytic. Most of the inorganic catalysts commonly used in chemistry are derived from the transitional elements. The VIIIth Group of Mendelejeff, which lies in the middle of the transitional elements, especially has these properties developed in the highest degree. It comprises the iron metals—iron, cobalt and nickel; the light platinum metals—ruthenium, rhodium and palladium; and, in the longest period, the heavy platinum metals—osmium, iridium and platinum.

**The Longest Period.**—The development of the next and longest period of 32 elements can be regarded as proceeding in a precisely analogous manner to that of the two long periods, but with the interpolation of 14 additional elements, after the Group III member, lanthanum. These 14, together with lanthanum, constitute the 15 rare-earth elements, all of which are trivalent earth elements resembling each other with such closeness that their separation from each other, and their identification as individuals, has proved one of the hardest and most laborious tasks of chemical analysis. Lanthanum itself closely resembles yttrium and scandium, the first of the transitional elements of the long periods, and indeed the latter pair and thorium are often classified along with the rare-earths, owing to certain analogies in their

properties. But the next element, cerium, instead of following in character the tetravalent elements, titanium and zirconium, which are the second representatives of the transitional elements in the long periods, does so very half-heartedly. There is an unstable series of salts, the ceric salts, derived from the ion  $Ce^{++++}$ —and traces of this tetravalent character are detectable in the next rare-earth element, praseodymium, but the main salts are trivalent, derived from the ion  $Ce^{+++}$ , and this is true without qualification for all the other representatives.

In lanthanum as in yttrium and scandium, the electron added goes to the under shell, so that the two outermost shells of these elements are represented by 9 and 2 electrons respectively. But then a more interesting new development begins. The two outer, P and O, shells remain at (9) (2), while the next inner shell, the N shell, begins to develop from 18, unit by unit, until at the last rare-earth, lutecium, it contains 32 electrons. Then the P shell resumes its development from 9 normally for the remaining 9 of the transitional elements, and after that the O shell develops up for the 5 elements completing the period, almost exactly as in the case of the two long periods. The slight differences will be noted later.

**The Rare-Earth Elements.**—Just as the transition elements of the long and longest periods are characterised by certain peculiarities of chemical behaviour, the rare-earths also have, as a group, certain characteristic properties. They are paramagnetic, some very strongly, and the salts are often highly coloured. But there is a marked difference in their absorption spectra. These, uniquely for the rare-earth elements, are characterised by narrow bands, often not exceeding 10 Å. in width, which are practically sharp lines. Whereas, in other cases, the absorption spectra consist of broad bands. The characteristic is so remarkable that a prospector in the field can distinguish a monazite sand, or other rare-earth mineral, by simply looking at it in bright daylight with a pocket spectroscope, when the characteristic dark absorption lines of the rare-earths appear in the continuous spectrum. It is supposed that here the internally

developing shell, in which the colour originates, is so deep down in the atomic structure that the outer shells protect it from the influence of the stray fields of the neighbouring atoms, so that the lines remain sharp, instead of being broadened into bands, as is elsewhere universally the case. Glasses, into which traces of these rare-earths have been introduced during manufacture, show these absorption lines very well.

**The Last Incomplete Period.**—The final period commencing with emanation, the last inert gas, comprises only seven places and ends with uranium, the element with the highest atomic number, 92, and atomic weight 238. The most interesting feature here, apart from radioactivity, is that the development definitely follows that of the long periods, rather than that of the last longest period, and this behaviour, since its "prediction" has not been hailed as supporting any particular theory, may be taken to have been unexpected by the atom-builders. Actinium, in Group III, of course corresponds perfectly with lanthanum, the first of the rare-earths, and to a less degree with yttrium and scandium, but, instead of the succeeding elements being, as might reasonably have been expected, close copies of actinium, the sequence through thorium, protactinium and uranium is exactly analogous to that from yttrium, through zirconium, niobium and molybdenum. The three final elements seem to show that again a new turn has entered into the course of evolution, and this unexpected development may be the explanation of radioactivity, rather than any considerations arising directly from the instability of the nucleus through its increasing positive charge. However that may be, it is clear the Periodic Table ends just where it was about to become, from the standpoint of the electronic explanation, exceedingly interesting, not to say impossible.

**The Cubic Atom.**—The structures assigned to the six inert elements in Group 0, on the foregoing considerations, are as follow:

Helium	Neon	Argon	Krypton	Xenon	Emanation
(2)	(2)(8)	(2)(8)(8)	(2)(8)(18)(8)	(2)(8)(18)(18)(8)	(2)(8)(18)(32)(18)(8)

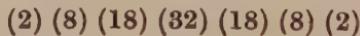
The Principle of Symmetry, already discussed, gives to the evolutionary process the peculiar feature that the outermost shell of the core of each of the six inert gases is always composed of eight electrons. Bearing in mind that in compounds, as distinct from elements, the act of chemical combination results from the effort of each of the combining atoms to make its outermost shell conform to the number in the outermost shell of the nearest inert gas, and that this number is always eight, we have the explanation of the exceedingly simple and effective model atom suggested by G. N. Lewis, and developed by I. Langmuir, known as the cubic atom. It has been undeservedly and somewhat impertinently belittled by physicists because it makes no pretensions to explaining how the electrons are fixed against the attraction of the central nucleus. But such criticism, as we have seen, applies even more directly to the electron or the nucleus itself, and, for chemical purposes, the cubic atom is a better model than the crude astronomical atom of Bohr, or the incomprehensible conceptions of the wave mechanics. These are so commotional that it would seem hopeless to derive from them the effective shape of the atom or the character of the resultant field of force which gives them their chemical and physico-chemical character. They have proved a sad hindrance to the proper developments of atomic chemistry.

On this cubic atom, the *combined* atom is regarded as occupying the centre of a cube, the 8 corners of which are occupied by an "octet" of electrons, and the *act* of chemical combination is regarded as the filling of these octets, by rearrangements among the electrons in the outermost shells of the uncombined atoms, by one of the three methods whereby an economy is effected in the number required, as described more nearly in the next chapter. This cubic atom is capable of representing graphically a surprisingly large proportion of all the known chemical compounds, but there appear to be definite exceptions, in that, in some cases, the number of electrons rises from 8 to 12 and even 16. It is possible that these exceptions may in time receive an alternative explanation.

**The Assigned Electronic Structures.**—In each place of the Periodic Table in the chart, the number of the electrons in

each of the three outermost successive shells is indicated for that element in the same manner as for the inert gases given in the preceding section. But the detailed consideration of these is hardly necessary, as their interest is mainly in the very special interpretation of spectra rather than in the general physical and chemical properties of the elements. The theory of these structures, which is usually called Bohr's Theory of the Periodic Law, is of course the application of Bohr's theory of the origin of spectra to the Periodic Table. But with one notable exception, hafnium, to be discussed at the end of the chapter, it has not contributed any very important addition either to our knowledge of the elements or of their interrelationship. Rather this knowledge has been used to supplement the spectroscopic evidence in the choice of the particular structure assigned. In some cases the choice made seems to do violence to previous conceptions. Thus some of the valencies are derived from the shell below the outermost, as well as from the latter, without any corresponding difference in the chemical value of the valencies. It will suffice, if we briefly consider these cases.

**The Exceptional Cases.**—It is useful to notice that the elements of Group II, beryllium, magnesium and the four alkaline-earth elements, all possess, as detailed in the chart, an absolutely symmetrical structure, derived from those given for the six inert gases (p. 286), by adding an outer shell of (2). Thus radium is:



and it is poetically appropriate, if scientifically uncalled for, that radium, the most interesting element of the lot, should be assigned this æsthetically satisfying constitution. Of more moment is it that these elements form the starting-points at which the transitional elements of the long periods are interpolated. Thus scandium, following calcium, (2) (8) (8) (2), is not (2) (8) (8) (3), as in the previous developments, but (2) (8) (9) (2), one of the three valency electrons being derived from the M shell and the other two from the outermost O shell. The structures assigned to yttrium, lanthanum and

actinium are similarly derived from the symmetrical structures of strontium, barium and radium. But, after this, there are small and unimportant differences, suggested by spectrum considerations, in the development in the three long periods. The transitional elements of the first retain the outermost (2) except for chromium and copper, which are supposed to have only (1) here and an additional one in the shell beneath. For the second long period, the latter type is the more common, only yttrium, zirconium and masurium being assigned (2), and the others (1) except palladium (0) for the outermost electrons. The structure of palladium, (2) (8) (18) (18) (0), is unique, but there is no corresponding chemical uniqueness. For the longest period all the transitional elements are assigned (2) except gold (1). This summarises what may be considered the exceptions to the normal course of development according to the principles already explained.

**The Rydberg Series.**—Although the spectroscopic study has not contributed much to the chemistry of the elements in the technical sense, it has of late achieved a very important advance in accounting for their number, and for the peculiar law which governs the number of elements in the successive periods. In 1914 Rydberg pointed out that the atomic numbers of the inert gases, which are the key elements of the Table, are given by the peculiar series, known by his name,

$$2 (1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 \dots)$$

by taking one, two, three, and so on of the terms within the brackets to get the successive members. This gives 2, 10, 18, 36, 54 and 86, all correct, for the atomic numbers of helium, neon, argon, krypton, xenon and emanation. The explanation of this has been a long and involved story, and the extensions of the quantum principle have been so rapid that it has been difficult to keep pace with them. But now it looks as if the last word has been said. The general solution, as already mentioned, depends on the idea that no two electrons in the outer electronic structure of any atom are exactly alike, and the finding of the minimum number, actually four, of sets of quantum numbers which will represent their orbits.

**The Spectroscopic Interpretation.**<sup>1</sup>—In the original Bohr atom only circular orbits were postulated, and the first differentiation made between the electrons in the separate shells had regard to the ellipticity of the orbits assigned. The principal quantum number, usually denoted by  $n$ , represents the number of half-quanta of kinetic energy, or whole quanta of angular momentum, in the same sense as explained in the last chapter, for the various possible stationary orbits of the hydrogen atom. Thus  $n=1$  for the K shell, 2 for the L shell, and so on up to 7 for the Q shell possessed by the elements of the final period. For the circular orbits, the second quantum number, expressing the degree of ellipticity of the orbit and usually denoted  $l$ , is 0, but a variety of elliptical orbits of increasing degree of eccentricity is possible for which  $l$  varies from 1 to  $(n-1)$ . Thus the maximum number of different orbits so provided for is, for each shell, the same as the value  $n$  for that shell.

But this does not exhaust the differentiation between different orbits in the same shell, for which  $n$  is the same, and two other quantum numbers, representing directional quantities, are needed, but there has been considerable doubt as to their physical meaning. The third quantum number, called  $m$ , is the more difficult to grasp. It has been rendered necessary to account for the effect of magnetic and electric fields in splitting up the spectrum lines into close groups of separate lines, known as the Zeeman and Stark effects, and for this reason it is sometimes distinguished as the magnetic quantum number. It is believed to be connected with the angle made by the plane of the orbit to the direction of the external force and to the direction of revolution of the electron, clockwise or counter clockwise, in its orbit.

We have seen that for any value of  $n$ ,  $l$  may be any integer from 0 to  $(n-1)$ . The rule for  $m$  is that, for any value of  $l$ ,  $m$  may have all the integral values from 0 to  $l$ , reckoned both positive and negative. Since one of the values of  $l$  is always 0, the positive and negative values of which are identical, the possible number of values of  $m$  for each value of  $l$  is one

<sup>1</sup> A useful little book on this topic is *Spectra*, by R. C. Johnson, Methuen's Monographs on Physical Subjects, 1928.

more than twice that numerical value of  $l$ . Let us see how far these three quantum numbers and their rules lead us.

For the K shell,  $n=1$ ,  $l=0$ , and  $m=0$  by the above rules, and hence only one orbit, characterised by these three  $n$ ,  $l$ ,  $m$ , quantum numbers, 1, 0, 0, is possible.

For the L shell,  $n=2$ , and  $l$  may be either 0 or 1. For the first value of  $l$ ,  $m$  is 0, and for the second, either +1, 0 or -1. Hence 4 orbits are possible, characterised as 2, 0, 0; 2, 1, 1; 2, 1, 0 and 2, 1, -1.

For the M shell,  $n=3$ , and  $l$  may be either 0, 1 or 2. There are 9 orbits possible, given by

3, 0, 0; 3, 1, 1; 3, 1, 0; 3, 1, -1; 3, 2, 2; 3, 2, 1; 3, 2, 0; 3, 2, -1; 3, 2, -2

For the N shell,  $n=4$ , and  $l$  may be either 0, 1, 2 or 3. There are now 16 orbits possible, which the reader, if interested enough, should be able to construct for himself from the foregoing examples.

The result of this, then, is to show that for each of the shells of principal quantum number,  $n$ , the number of possible orbits is  $n^2$ .

**The Fourth Quantum Number.**—Still a fourth quantum number is required before the spectroscopist can explain all the possible frequencies of light which an atom can emit, on quantum principles. It is known as the polarisation or spin quantum number, and is perhaps, experimentally, the most suggestive of them all. It is due to a rotation or spin of the electron on its axis, which may be either clockwise or counter-clockwise. This gives the electron polarity and causes it to be the seat of an intense, but localised, magnetic field. At any rate, it is supposed that the electron can, in general, enter into the structure of an atom in one of two ways, depending upon the direction of its spin. Two electrons spinning similarly repel one another both on account of their electrostatic as well as of their magnetic fields. But two electrons rotating oppositely attract one another at close range, when the localised magnetic forces overpower the more diffuse electrostatic field. It is supposed that two oppositely spinning electrons can have the same orbit so far as the other

quantum numbers are concerned, but not two spinning in the same direction. The same idea may serve to explain the non-polar link, discussed in the next chapter.

Interesting evidence of electronic spin has been obtained by experiments started in 1921 by Stern and Gerlach, which consisted in sending a beam of uncharged atoms through a vacuum, under the action of a non-uniform magnetic field, to see if the stream were deflected by the field. The results were unexpected on any existing theory, but have since been interpreted by the wave mechanics. Elements such as silver, the one first done, hydrogen and lithium, in each of which there is a single electron in the outermost shell, are split up by the magnetic field into two beams equally and oppositely deflected, none passing through the field undeflected. Whereas helium, which has a shell of two electrons, oppositely spinning as we shall see in a moment, is undeflected.

**The Pauli Exclusion Principle.**—The effect of this fourth polarisation quantum number on the possible number of orbits in each of the successive shells is simple, as the number before worked out,  $n^2$  for a shell of quantum number  $n$ , is just doubled and becomes  $2n^2$ . This accounts for the two, outside the brackets, of the Rydberg series. Each orbit may be occupied by two electrons so long as their spins are opposite. The fourth quantum number is conventionally represented by the symbols  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . So our single K orbit, 1, 0, 0, now becomes two, 1, 0, 0,  $\frac{1}{2}$  and 1, 0, 0,  $-\frac{1}{2}$ . The two electrons must be spinning oppositely in the helium atom, whereas in the hydrogen atom some may be spinning one way and some the other. This accounts for the positive Stern-Gerlach effect with atomic hydrogen, and the negative one for helium. The helium atom is absolutely symmetrical, and all directions in it are alike.

The Exclusion Principle, which simply states that no electron in the outer electronic structure can have all four quantum numbers the same, makes the maximum possible number of orbits for each shell  $2n^2$ , where  $n$  is the principal quantum number, and, as  $n$  passes through the successive integral values, 1, 2, 3 and 4,  $2n^2$  becomes 2, 8, 18 and 32. This with the Principle of Symmetry, already explained, accounts for

the Rydberg Series and the number of elements in the successive periods of the Periodic Table.

Thus, to take the perfectly symmetrical atom of highest atomic number, radium, No. 88, the K, L, M and N shells of which are filled with the maximum number of electrons, and the O, P, Q shells of which have the same number as the M, L, K shells respectively, we have:

$$2[1^2 + 2^2 + 3^2 + 4^2 + 3^2 + 2^2 + 1^2] = 88$$

In no other subject is there such a confusing set of phenomena, or such a mass of numerical data of unsurpassed accuracy as in spectroscopy, and it is a veritable triumph that the assumptions necessary to account for these should also serve to explain the number of chemical elements.

On the wave mechanics, the first three quantum numbers which have, in the particle aspect of the electron, the significance of quanta of angular momentum, or kinetic energy, in the wave aspect can be related to the three different modes of vibration of a three-dimensional vibrator, such as a sphere of gas. Here the "pitch," or note, of each of the three types of vibration can be expressed as the number of nodal surfaces in the sphere, on which the particles of the gas, though everywhere else in vibration, are at rest. The fourth quantum number seems to be accounted for by the symmetric and antisymmetric wave functions, and to be, in general, connected with the non-polar linkage by pairs of electrons, discussed in the next chapter. But into these almost virgin territories the reader can now seek a more competent guide.<sup>1</sup>

**The Search for the Remaining Missing Elements.**—It is in the field first explored by Moseley, rather than in the older one of optical spectra, that the more important results to chemical science have been obtained. Moseley, we have seen, first called the roll of the chemical elements and determined the number still missing. He fell at Suvla Bay, Gallipoli, at the age of twenty-eight in the first year of the War, and, even in the white-heat of conflict, the whole civilised world experienced a pang of remorse at the untimely end of so rare

<sup>1</sup> *The New Conceptions of Matter*, C. G. Darwin, Bell and Sons, Ltd., 1931.

a scientific pioneer. But, just before, he had applied his method to the determination of the atomic numbers of the rare-earth elements, preparations of the more recently discovered members at the end of the group having been furnished him by Professor G. Urbain of Paris. The latter said of the result, "So the law of Moseley, for the end of the group of rare-earths as for the commencement, confirmed in a few days the conclusions of my twenty years of patient work."

Moseley showed that there were, in all, places for 15 rare-earth elements, from lanthanum, No. 57, to lutecium, the one with heaviest atomic weight, and the last to be discovered by Urbain, which has the atomic number 71. But one was still missing, namely No. 61. There was another vacant place, No. 72, next to and beyond lutecium, and before tantalum, No. 73. In this part of the Table, there had previously been no hint whatever as to the total number of the rare-earth elements, or of the number still unknown. For the rest, Moseley established the existence of vacant places, Nos. 48 and 75, between molybdenum and ruthenium, and between tungsten and osmium, respectively, in Group VII, these being the two missing homologues of manganese. Here, too, though the existence of such missing elements was known to be probable, before Moseley's work this could not with certainty be affirmed, because the sequence in the second long period and in the longest period might well have been different from that in the first long period. The vacant places Nos. 85 and 87, the last representatives of the halogens and the alkali-metals, were formerly thought to belong to elements too unstable to exist (see p. 247). These six, on Moseley's roll-call, were, in 1914, the only remaining missing elements between hydrogen and uranium.

**Element No. 72.**—The vacancy of most interest was that of No. 72, immediately following lutecium. At the time, Urbain had some uncertain indications that, in some of the fractions of this element, there was another rare-earth element present in small quantity, which he provisionally termed celtium. Later the X-ray spectrum seemed to give faint indications of lines which corresponded, by Moseley's law,

to such an element. But it was pointed out by Bohr, as a consequence of the application of his theory of spectra to the elucidation of the structure of the elements in the Periodic Table, that No. 72 ought certainly *not* to be a rare-earth element, but a homologue of zirconium, tetravalent, instead of trivalent, and definitely acidic in character. For it immediately precedes tantalum, a pentavalent acidic element, and it would be unprecedented for two consecutive elements in the Table to have a difference of two in their principal valency. This did not in itself require any special theory, and, without any, one would naturally at the time have said that element No. 72 would most probably closely resemble cerium, which, although trivalent and a rare-earth in the cerous series of salts, has another less stable series, the ceric salts, in which it is tetravalent and very weakly basic. One would perhaps have guessed that No. 72 would be tetravalent like zirconium in its main characteristics, but also would show trivalence and rare-earth character to a minor degree.

However, the theoretical prediction was different, and this constitutes the one outstanding example, already referred to, of the theory adding to our knowledge of the chemistry of the Periodic Law. On Bohr's scheme, the full 32 electrons of the developing inner ring are complete by lutecium, so that the next electron must go to the one outside, and constitute an additional valency. Hence No. 72 should be, definitely, a homologue of zirconium.

**Hafnium.**—The missing element was discovered in 1923 by Coster and Hevesy, working in Bohr's laboratory in Copenhagen, and named hafnium after the ancient name of that capital. It resembles zirconium extremely closely in chemical character. Indeed, what had been regarded by chemists as a single element, zirconium, had always, till then, been a mixture of zirconium with a small quantity of hafnium. Common zircons may contain as much as 7 per cent. of the zirconium as hafnium, and the secondary zirconium minerals, such as alvite and cyrtolith, up to 30 per cent. The average hafnium content of zirconium is about 3 per cent., so that the new element is really fairly abundant. Its chemistry agrees in every respect with its position in the Periodic Table. It

is more basic than zirconium, and is fairly easily separated from it by the fractional crystallisation of the oxychloride. Its atomic weight is 178·6. An interesting photograph of part of the spectrum of hafnium by X-rays is shown in Fig. 49 (facing p. 281).

**Illinium.**—The element No. 61, since Moseley's prediction of its existence, has been looked for by his method. It was found in 1925 in the rare-earths in Brazilian monazite sand, by Professor Hopkins and his co-workers in the University of Illinois, and named illinium. But the discovery has also been claimed by a group of Italian investigators who have proposed for it the name florentium, and so far it does not appear that there has been any authoritative adjudication of the rival claims. It must be remembered that in this work, unlike that in the domain of the optical spectra, Moseley's law definitely predicts the wave-lengths of the chief lines of the new elements, and the claim to discover a new element now may mean no more than being the first to observe certain predicted X-ray spectrum lines. In the case of illinium there is very little else as yet known about it, though it appears to resemble the cerite sub-group of rare-earths rather than the yttrium sub-group. It must necessarily be a long and tedious task before such an element can be separated in any quantity from its numerous close copies.

**Masurium and Rhenium.**—The two missing homologues of manganese, Nos. 43 and 75, were looked for and found in 1925 by Noddack and others in the ores of the platinum metals, and in such minerals as tantalite and fergusonite, being identified by predicted X-ray lines. The first, No. 43, has been named masurium, but so far nothing much more has been heard of it, and its discovery, as a new chemical element, is still incomplete. But the second, No. 75, called rhenium, is now quite a well-known element, and its technical preparation has been undertaken by the firm of Siemens and Halske. It occurs only in very small quantities, but has well defined chemical characteristics. Like manganese, it forms a class of interesting compounds analogous to the permanganates, such as sodium per-rhenate,  $\text{NaReO}_4$ . It forms several oxides

which are more readily reduced to the metal than the corresponding oxides of manganese, reduction being effected by fusing in hydrogen at 800° C. Another class of salts, the rhenates, corresponds to the manganates.

Its isotopic composition has already been determined by Aston. It consists of two isotopes of mass 185 and 187, the heavier being the more abundant, and, in this respect, it constituted the first exception to the general rule governing complex elements of odd atomic number above No. 5, discussed in Chapter XVIII. The atomic weight is 186·3.

**Element No. 87.**—Only two places remain, Nos. 85, between polonium and emanation, and No. 87, between emanation and radium, and, as already remarked, these elements were thought to be too unstable to exist. However, the announcement has been just made (October, 1931) of the discovery of No. 87, the heaviest alkali-metal, by Papish and Wainer, working at Cornell University, Ithaca, N.Y. The most likely source of a rare element is an ore containing its companions on either side of it in the same period, or horizontal row, of the Periodic Table. An instance of this we have just had in the occurrence of rhenium in the platinum metals and tantalum ores. The Cornell investigators chose for their search for No. 87 a samarskite, rich in uranium, and containing, in addition to the elements usually present in this mineral, traces of rubidium and caesium. The mineral was heated in hydrogen chloride gas at 1,000° C., and the sublimate, which contained the chlorides of the alkali-metals, subjected to a treatment to isolate the latter. Fractional crystallisation, first of the chlorates and then of the alums, followed, designed to concentrate the unknown element, if present, with caesium, its nearest homologue. In the X-ray spectrum of this fraction, five of the X-ray lines, calculated by Moseley's law for element No. 87, were observed. This, the first step, therefore indicates that this element exists, and the confirmation will be awaited with great interest by the scientific world. Until this is done, no name will be suggested, but it may be referred to as eka-caesium.

Since No. 87 seems to exist, there is no longer any reason to suppose that No. 85 will not also ultimately be found, and

then there will be not a single element left for the chemist to discover, unless, indeed, such exist beyond uranium. The chemist cannot but feel, like Alexander, that something of the zest of life has departed, for the discovery of new elements, like the discovery of new worlds, has always been a powerful incentive. But no Alexander ever so quickly lost his hold over his conquests. Those of the chemist pass overnight into the pattern, and are taken for granted by model atom builders who, confronted with the originals, would probably have considerable difficulty in recognising them, but who, as long as time shall last, need never fear any similar exhaustion of *their* subject. No work is so fruitful of endless new vistas of research as that not really done, and the cynic might say that the scientist honoured the creation of work and dreaded the prospect of unemployment just as much as the ordinary nigger-driver.

## CHAPTER XV

### CHEMICAL AFFINITY

**The “Free” Elements.**—One of the consequences of present views is that matter and electricity, apart from the individual high-speed electrons and ions dealt with by modern methods, cannot be studied apart. Our knowledge of matter in perceptible amount is necessarily confined to the combination of matter with electrons, which is electrically neutral. It was, of course, long ago recognised that in free elementary substances such as hydrogen, oxygen, chlorine and other gases, atoms for the most part do not exist free, but combine into molecules, composed of two or more atoms of the same kind. But the metals, mercury being a good instance, usually exist monatomic in the gaseous form, as the inert gases do, and many of them can be volatilised. It is paradoxical but true to say that such elements are in the chemically combined state when free, and are often in the free state when combined. For the single atoms are composed of the union of one or more valency electrons with the + ion, and the compounds often exist, when in the liquid state, fused or in solution, with the + ion of the metal quite free. It is the positive ion, rather than the neutral atom, which is the elementary particle of an electropositive element, the atom being the compound of this with an electron, and the nature of the bond of union is the same as chemists have been in the habit of using to express chemical combination.

It seems early to give up our belief in matter as a separate entity and to regard it as built up of + and – charges of electricity, when all that the modern views have done is to show that the positive charge of electricity is intrinsic to matter. The negative charge of the electron is the electron, but, for the positive ion, all the properties of matter are shown as well as the electric charge. It is true one may, by theoretical reasoning, show that the mass of the hydrogen ion, or nucleus of the hydrogen atom, would be explained

if its radius was about  $10^{-16}$  cm., just as that of the electron would be explained if its radius were  $10^{-13}$  cm. But this is to argue in a circle, for the radii in neither case are known, and, according to the wave mechanics, probably meaningless.

The merit of the nuclear atom is its division into an outer region occupied only by electrons and an inner occupied by the positively charged nucleus, the charges being normally equal and opposite. Electrons appear to be fundamental constituents of the nucleus, because their ejection as  $\beta$ -rays results in transmutational changes. Apart from this, there is no ingoing or outgoing between electrons and the nucleus, as there is for the outer region, in the various kinds of ionisation. The latter type of change is reversible and has no power of impressing any corresponding change on the nucleus. Whereas any change of the nucleus is at once followed by a corresponding change in the outer region to preserve electro-neutrality. The types of ionisation are essentially two, the electrons in the inner shells being only influenced by the primary electrical forces, such as generate X-rays, and the electrons in the outer shells, which are responsible for ordinary optical spectra, being those influenced by the weaker secondary electrical forces of chemical affinity. The nucleus, so far, appears to have only two direct experimental properties, mass and radioactivity, including  $\gamma$ -ray emission in the latter. All the older physical and chemical properties of matter except mass are actually properties of the outer electronic region, but this, in turn, is directly governed by the nucleus. The latter produces most of the phenomena we are familiar with through the intermediary electronic system external to it.

**The Magnitude of the Primary Electrical Forces.**—With one exception<sup>1</sup> the magnitude of the forces of repulsion between electrons, and of the forces of attraction between electrons and matter, is insufficiently emphasised in expositions of the modern views. If the charge of a milligram of hydrogen ion,  $H^+$ , could be communicated to a sphere of the size of the earth, it would raise its potential 100,000 volts. If hydrogen

<sup>1</sup> *The Electron Theory*, E. E. Fournier d'Albe, Longmans, Green and Co., 1906.

ions could be got into a closed tube as strong as a modern wire-wound cannon, without being discharged by the walls, they would burst it long before so much was got in as would, in the form of ordinary hydrogen, show the spectrum of hydrogen in a vacuum tube. If a gram of hydrogen ion could be got and kept together in one place, and placed as far apart from another similar gram as the poles of the earth, the repulsive forces between them, although it falls off as the square of the distance apart, would still be, at this distance, equal to a weight of 26 tons. We can, in fact, never hope to be able to deal with either free electricity or free matter except in quite infinitesimal amounts.

**The Real Problem.**—It is here we get to grips with the real problem, the total inadequacy of electrical theory to explain, not matter, but electricity. How does a single electron hold together? It should, according to the laws of electricity, dissipate itself with uncontrollable violence. At long last we find the point becoming recognised, and new laws are being hastily invented for electricity disguised under such phrases as "potential barriers," "reversal of the Coulomb law of force at small distances," "unknown mechanism in Nature enabling  $\beta$ -particles to keep clear of the nucleus" and so on, to get round the awkward fact.

Whereas the only real discovery was the electron, and until we have a clear and definite theory of the atomicity of electricity, it seems a little premature to make any assumption, that may at the moment be the least troublesome way of accounting for this, in order to explain the atoms of matter. It is the attributes of matter applying so unexpectedly and unaccountably to the "electric fluid" that calls first for proper theoretical examination.

**The Arrhenius Theory of Electrolytic Dissociation.**—Whatever may be the ultimate theory of the electric charge that will account for its atomicity, the discovery of the electron throws an entirely new light upon the nature of the ordinary chemical forces, familiar in the ordinary physico-chemical properties of matter. The development began to take its present aspect, however, long before the discovery of the

electron, with the remarkable theory of electrolytic dissociation put forward in 1887 by Svante Arrhenius, resulting in the rise of the so-called "ionic school" of physical chemists, who regarded the electrolytes (the class of chemical compounds comprising the acids, bases and salts) as existing in solution largely dissociated into oppositely charged ions. The view was at first so strange that it was rejected as incredible, not only by most chemists, but even by some of the greatest exponents of electrical science, such as Lord Kelvin. But it is now thoroughly well established.

In reality, it began in 1808 with Davy's sensational isolation of the metals of the alkali group, sodium and potassium, by the electrolysis of fused caustic soda and caustic potash. For this led to the theory of Berzelius, "that the forces of chemical affinity and electricity are one and the same" which to-day has, with a difference, triumphed. The difference is that we now regard chemical affinity as probably a relatively small differential effect, or residuum, of the primary attraction between the electron and matter. The primary forces are electrical, and they are colossal even on chemical standards. What the chemist recognises as chemical affinity is the resultant field left over when the individual oppositely charged particles have combined together to form as stable a system as is possible, and in which the far greater primary forces between the attracting particles have been to all but a relatively small extent neutralised. The reasons why the two oppositely charged sets of particles do not completely neutralise one another and annihilate their charges, and why, after coming as close together as they can, they stop short of actual union, is, as already indicated, entirely problematical and belongs to the same mystery as surrounds the physical explanation of the existence of the electron itself. We saw (p. 219) that this probably is one of the consequences of the existence of energy quanta.

**The Co-existence of + and - Ions.**—The early attitude of the physicists and the chemists to the ionic theory was very natural. To the physicist it seemed incredible that + and - ions should remain permanently in the closest proximity and continually in violent collision with one another without

recombining. This difficulty, though made easier of understanding by the discovery of the atomic character of electricity, is raised in a far more fundamental form by the mere existence of free electricity as electrons, and remains unanswered. To the chemist it seemed equally bizarre to suppose that sodium, for example, could exist uncombined in water without violently reacting with it, but this objection was due to misunderstanding. The atom of sodium is, of course, totally different in chemical properties from the sodium ion. It was soon realised that almost all the ordinary chemical tests for the common elements, by which they are identified in the ordinary reactions of "wet" analysis, are not tests for the elements, but for their ions. Gradually the conception grew up that chemical affinity is not exerted mutually between different elements, but that it is rather the self-contained affinity of each element for electrons which differs from one element to another.

Once the fact is admitted that, in spite of their intense opposite charges, the individual ions do not rush together and neutralise one another, the residual or resultant field of force in the immediate surrounding space is not zero, but varies from one point to another even for a collection of equal numbers of opposite charges, and depends upon how, relatively to one another, the separate charges are orientated. Probably to the early astronomers it must have appeared unintelligible how the sun, moon and planets remain indefinitely up in the sky without falling down. It was quite natural to suppose, as a first attempt, that the mutual repulsions and attractions of the ions are neutralised in a similar manner to the gravitational forces between worlds.

But the difficulties have thereby been merely pushed into the background, and have ultimately to be faced. We may believe that the reason why two opposite charges remain apart without neutralising each other is but another aspect of the reason why the individual charges hold together. We must accept their behaviour as established, and this will make it seem less absurd to postulate a purely static atom with definite constitution and orientation of its component parts. This is required by sciences such as chemistry, which have to deal largely with problems connected with the

architecture and engineering of matter, and for which the excited atoms of the spectroscopist are not only unsuitable but definitely antagonistic to the proper understanding of such subjects.

**The Shapes of Molecules.**—In chemistry, questions of molecular structure are of paramount interest. We wish to know about, not all the internal commotions which produces even in a simple atom a bewildering set of vibrations much more complex than those given out by a grand piano, but its shape, and how it fits with other atoms to form molecules and the shapes these molecules also possess. One of the most remarkable sequels of the structure theories of chemistry has been to show that the structural formulæ assigned to compounds are very much closer to their actual shapes than these formulæ ever pretended to represent. Nor is this only true of solids. To-day such extraordinary properties as the spreading of oil as a film over water, of practical importance in saving life at sea, are known to be due to the shape of the oil molecules. The class of hydrocarbon compounds known as the normal paraffins are comprised of long chains of  $-\text{CH}_2-$  groups with  $\text{CH}_3-$  groups at each end and may contain up to fifty carbon atoms. Such oils do not "spread." They do so if, at one end, there is a group containing oxygen atoms. The natural fats, such as palmitin, stearin and olein, are complexes of glycerin with palmitic, stearic and oleic acids, and the latter are long hydrocarbon chains with a  $-\text{COOH}$  group at one end. The hydrocarbon end is "hydrophobic." That is to say, there is a natural aversion between it and water expressed by the old proverb that oil and water cannot mix. But the other end is "hydrophylic," as the oxygen in it makes it much more like water than a pure hydrocarbon oil. The consequence is that the hydrophylic ends bury themselves in the surface of the water and try heroically to dissolve in it, whilst the hydrophobic ends as obstinately refuse, so that the molecules are "up-ended." In chemistry, as in electricity, like repels like and unlikes come together. But here the likes at the one end are held close together by the attraction of the water for them, and this forces the likes at the other end, the hydrophobic ends of the molecules, close

together. The consequence is that the oil molecules now violently repel one another, instead of aggregating together as a drop, and the oil spreads all over the surface of the water until the film is only a single molecule thick. This alters the surface tension of the water and, as sailors know, has a perfectly wonderful effect in an angry sea in moderating its turbulence. An amazingly small amount of oil is effective. The single-molecule-thick film acts as an elastic membrane over the surface and prevents the waves from breaking. One could not get very far in understanding such phenomena if one had to think of each atom in the molecule as a miniature grand piano.

So it is with all the common properties of matter which make them of use, whether we deal with their cohesion, ductility, hardness, lubricating qualities, grain, texture or resistance to wear. All of the engineering qualities of common materials are structural in nature, and whatever the materials may actually be, that the atoms have shapes in the ordinary sense of the term and that these shapes determine most of their normal material properties, is incontrovertible.

**The Activation of Molecules.**—On the other hand, when we leave the realm of structure and shape, and enquire more precisely as to the nature of chemical affinity—to put it bluntly, why sometimes a given reaction will take place and at other times not, and why such agents as catalysts exert so important an action in determining the course of chemical reactions—we are still only at the beginning. In this field the influence of the Bohr theory of spectra has been more marked, but the real advance was made also by Arrhenius, as far back as 1889. The latter, in interpreting the relation representing the effect of temperature upon the equilibrium reached in a reversible reaction, made the suggestion that before any molecule can take part in a reaction it must be "activated." That is to say, its internal energy must be increased beyond the normal amount, and, without this preliminary "gingering up," it is quite inert. It has been natural to interpret "activation" as a shifting of one of the electrons in the atom or molecule from its innermost and stable quantum orbit to an outer and more distant one, as for excitation preliminary

to spectrum emission, and to try to derive the energy necessary for this change either from radiation or from the energy of thermal agitation of the molecules.

Spectra show clearly that such intermediate stages between stable molecules and completely separated ions exist, or, in other words, that a sort of partial ionisation can occur, in which an electron, while not entirely dissociated from its original combination with an atom, is removed further from it with an absorption of energy. There is little doubt that these intermediate states of high internal energy do play a large part in determining whether or not a substance will react chemically with another. The most natural agent to effect this preliminary activation would be light, or, in general, radiant energy of the correct wave-length and frequency. It is known that the relations between the emission of light and the absorption of energy are largely reversible and that, in photo-electric phenomena, light of the right wave-length will ionise atoms and cause them to emit electrons at definite speeds. But hitherto, although the specific action of light in promoting various reactions is well known, and indeed comprises a special branch of the subject known as "Photo-Chemistry," it does not appear that, in general, light is the real agent in promoting "activation." In fact, the converse seems to have been proved. There is, on the other hand, nothing at all improbable in the origin of the energy being the ordinary thermal agitation of the molecules. After all, nothing but the thermal agitation of the molecules at high temperature is responsible for the emission of ordinary light. This is perhaps the theory now most favoured, but it appears difficult as yet to put it to a really crucial and convincing test.<sup>1</sup>

**Structural Formulæ.**—The dualistic hypothesis of Berzelius supposed that atoms of the elements were positively and negatively charged, the basic and metallic elements being positive and the acidic elements negative. While this works well for electrolytes, it totally fails to explain the ordinary combination of two similar atoms to form the molecule, for example, in the case of the common gases, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and

<sup>1</sup> Compare *Kinetics of Chemical Change in Gaseous Systems*, by C. N. Hinshelwood, Clarendon Press, 1926.

the like, and the carbon compounds of organic chemistry, which are in number as the sands of the seashore. Here, very surprisingly, electropositive elements like hydrogen, in the hydrocarbons, can be replaced, atom for atom, by electronegative elements like chlorine. From methane,  $\text{CH}_4$ , we get by successive replacement of the hydrogen, the compounds,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$ , the last two, chloroform and carbon tetrachloride, being well-known liquids, stable towards attack by reagents, and not in this respect much different from the hydrocarbons themselves. The substitution in fact makes surprisingly little alteration in the chemical properties.

This made chemists for the time abandon any physical theory of chemical affinity, and to represent chemical union by the well-known valency bonds. So long as one is not inquisitive of their nature, they displayed very well the structural features of compounds—*i.e.*, the manner in which the atoms were joined together, or the actual architecture of the molecule, in which the atoms are regarded as bricks, each bonded to either one, two, and so on of the other bricks. It so explained isomerism—that is to say, the existence of such totally different compounds as ethyl alcohol and methyl ether, which have the same total number and the same number of each kind of atom in the molecule,  $\text{C}_2\text{H}_6\text{O}$ . They are, respectively,  $\text{CH}_3\text{—CH}_2\text{—O—H}$  and  $\text{CH}_3\text{—O—CH}_3$ . It accounted correctly for the number of possible isomers for any given collection of atoms, when each atom is given some definite valency or number of bonds of union, though for the acidic elements, the possibility of the atom acting with any one of a number of different valencies, or even with more than one at the same time (tautomerism) had to be allowed. This concentration on the purely formal structure sufficed to enable the carbon compounds of Nature to be artificially synthesised, a knowledge of how the atoms are put together in any natural substance being the essential preliminary step to manufacturing it artificially.

**Stereo-Isomerism.**—It received a tremendous impetus and gain of prestige by the development of stereo-isomerism, consequent upon the theory of the “asymmetric carbon

atom " of Lebel and van't Hoff in 1874.<sup>1</sup> Any molecule, in which the four groups attached to the four valencies of a carbon atom are all different, may show the property of "optical activity," which means that it can rotate the plane of polarisation of light either left-handedly (*lævo-rotary*) or right-handedly (*dextro-rotary*), much as certain crystalline substances had long been known to do in the solid state. The extension of this to liquids and gases indicated a peculiarity in the spatial arrangement of the atoms in the molecule, rather than in the spatial arrangement of the molecules in the crystal. If the formulæ for carbon compounds are represented in three dimensions instead of in two, to account for the equality of the four valencies of the carbon atom, they must be supposed to radiate from the atom at equal angles to one another, and this is the same thing as supposing the carbon atom to be a regular tetrahedron, with the four points of attachment to other atoms at the four corners. Now when the groups attached to the four corners are all different, *i.e.* for an asymmetric carbon atom, there are two distinct ways of arranging them, related to one another much as a left-hand glove is to a right-hand, or as any unsymmetrical object is to its image in a mirror. The two forms are quite distinct, and the one cannot be got from the other by any amount of turning. To derive the one from the other any two of the groups have to be transposed in their respective positions. Thus, the formal structural representation of carbon compounds was shown to have a very much closer resemblance to the actual structure than was at first intended.

The development of stereochemistry, its application to compounds of other polyvalent elements, such as silicon and nitrogen, its extension to ring carbon compounds, and the complete explanation it offered not only of the possible numbers of stereo-isomers, but also as to whether or not they would exhibit the property of optical activity, marks the zenith of the purely structural representation of chemical affinity.

**The Structure of Inorganic Compounds.**—In the closing years of last century and the opening years of this, the most

<sup>1</sup> For the growth of our ideas on these topics, see *The Origins and Growth of Chemical Science*, by J. E. Marsh, John Murray, 1929.

strenuous efforts were made to make this theory of valency universal. Chemists attempted to apply it to mineral or inorganic compounds, as to the organic compounds, in spite of the most obvious and inexplicable exceptions. Thus, for a series of such simple compounds as the oxides of nitrogen, with molecules represented by  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ , which illustrate very well Dalton's Law of Multiple Proportions, the theory gives no real indication of the way the atoms are linked. In carbon monoxide,  $\text{CO}$ , and other carbon compounds, only forced and unlikely explanations can make the carbon atom even tetravalent.

In trying to account for the compounds of mineral chemistry on the bonds-of-valency theory, this period of chemistry resembles nothing so much as attempting to put a boot on the wrong leg. The boot could in a way be forced on, but no one could describe it as a good fit. It made plenty of good examination questions in papers on inorganic chemistry, but contributed confusion rather than clearness to the subject, while the growth of the ionic theory, and the discovery of the electron, showed that the original theory of Berzelius was far more in keeping with the properties of electrolytes.

**Polar Compounds.**—Berzelius supposed that the atoms forming a compound were intrinsically either positive or negative. But this is contrary to experience. Metallic sodium exists in the form of vapour as single atoms, but these are electrically quite neutral. The sodium ion, on the other hand, is the atom of sodium which has lost an electron and so gained a positive charge,  $\text{Na}^+$ . Paradoxically, it is the element here which is a compound, and the ion the free atom of the element. Whereas for chlorine it is the ion,  $\text{Cl}^-$ , that is the compound and the neutral atom the free element. Now, by losing an electron, the sodium, in Group I, becomes identical, as regards the number of electrons in its outer shell, with the inert gas neon in the zero family of the Periodic Table. By gaining an electron, chlorine, in Group VII, becomes identical as regards the number of electrons in its outer shell, with argon, in the zero family. They differ from these inert gases only by possessing, respectively, one more and one less unit of +

electricity in the nucleus. Hence the ions are non-valent, and the compound NaCl is held together, not by any individual bonds of affinity, but by the necessity of being present in equal numbers to preserve electric neutrality.

This point of view receives powerful independent support from the results of the X-ray examination of the crystal. In rocksalt, and in other compounds of this type, the ions and not the molecules are the units of the crystal space-lattice. Moreover, for any one of the ions of either sign, there are a number—six for NaCl, eight for CsCl—of the ions of the other sign symmetrically disposed round it. It is impossible to say that any such unit as NaCl, consisting of two atoms, one

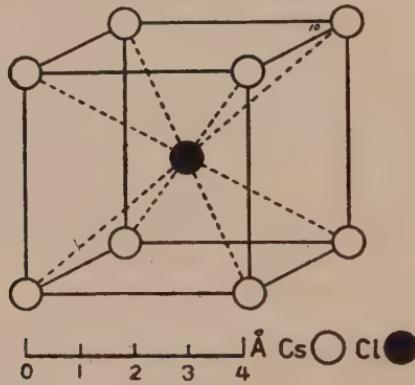


FIG. 50.

of each kind, joined together and not joined to the other atoms, exists at all (see Fig. 44, p. 133). Such compounds are termed polar compounds and the space-lattice of the crystal an ionic space-lattice. Not only the chlorides, but also the bromides and iodides, of sodium and potassium have crystal space-lattices represented by Fig. 44, and naturally one would have thought it quite safe to generalise from such data and to extend it also to the halides of rubidium and caesium.

But this is not true, apparently, for caesium. Fig. 50 shows the elementary unit of the caesium chloride lattice, and it represents, neither the simple cubic lattice nor the face-centred cube lattice, but the third type, the cube-centred lattice. It must be imagined to be repeated indefinitely in all three directions, and then no difference exists between

structures represented by the black and white circles respectively. Each of the 8 white circles, at the corners of the cube containing the black circle at the centre, is, in the completed lattice, shared by 8 cubes, only one of which is drawn, and is at the centre of a cube with 8 black dots at the corners, just as, in the drawing, the black circle is at the centre of a cube with 8 white circles at the corners. Thus, for caesium chloride each atom, whether of caesium or of chlorine, is equally shared by 8 of the other kind, instead of by 6 as in the other cases.

**Non-Polar Compounds.**—But the above represents only one type of chemical union, and at least two other distinct types are now recognised. For the compounds for which the Berzelius theory fails, which do not conduct the electric current in solution, there is a different "bond of union" and the molecules rather than the ions are the unit points of the crystal lattice. These compounds are termed non-polar, and the lattice is termed a molecular space-lattice. Here there has been a distinct new idea introduced, due to G. N. Lewis in the first instance and elaborated by Irving Langmuir, as to the nature of the bond of union, which is termed a "co-valent" link or bond. Each single bond is considered to be due to *a pair* of electrons in common between the two atoms so joined. It is supposed that each atom, instead of losing or gaining, respectively, an electron, half-loses and half-gains an electron, so that each has an equal share over *a pair* of electrons which they divide between them.

We need not take yet very seriously the dynamic aspect of such a bond, which the older views would have attempted to depict by representing both electrons of the pair as occupying the same orbit, which was symmetrical with regard to both the atoms joined. Thus, for the hydrogen molecule, both electrons would be made to revolve in the same orbit round both hydrogen atoms. The phenomenon is probably best regarded as connected with the Pauli exclusion principle (p. 242), which allows two electrons in the outer shell of the atom to occupy the same "orbit," but only when oppositely spinning, so that the resultant magnetic poles attract one another, and overpower the electrostatic repulsion between

the electrons. It is very significant, from this point of view, polar union not being by bonds at all, that the real single bond of union should prove to be the result of the co-operation of *a pair* of electrons.

It is, also, in this very field that the wave mechanics has achieved its greatest triumph, so far, in the prediction of two different sorts of hydrogen gas, H<sub>2</sub>, which, when looked for, were found. That the simplest compound of all, the hydrogen molecule, should be capable of existing in two distinct forms with different physical constants without chemists suspecting it, and that this should have been predicted by a weird magic which hardly even pretends to be mathematics, is perhaps the *coup de grâce* before chemists finally immolate themselves in their own crucibles, and reappear, phoenix-like from the ashes, as a new school of neo-chemists with a permanent wave.

**Para- and Ortho-Hydrogen.**—On the experimental side, the change of specific heat of hydrogen with temperature was not in accordance with what is to be expected for a simple molecule of this type. On the theoretical side, it was predicted that, if the proton, or hydrogen nucleus, had "spin" like the electron, resulting in a definitely orientated magnetic field, there should be two distinct ways of uniting two hydrogen atoms into a molecule, depending on whether the "spins" were similar or opposite. We are warned that this crude picture is really a misdirection, and that the real distinction is that in the one form, called the ortho, "the wave functions are symmetrical," and in the other, called the para, "anti-symmetrical." The important point is that, whatever be the correct description, the two forms ought to exist separately, and not change, the one into the other, so fast as to constitute them "tautomers," as the chemist would say—that is, a mixture of both forms, each perpetually and rapidly changing into the other form and back again. On such a view the anomaly of the specific heat received a quantitative explanation.

Using the difference of specific heat as the test between the two kinds, it was found that, under high pressure at the low temperature of liquid air, the form called para-hydrogen, which is normally present to the extent of only 25 per cent.

of the whole, increased with the lapse of time, and, after a long period, constituted 95 per cent. of the whole. It was then found that the rate of change of the ortho into the para form at low temperature could be accelerated, either by passing an electric discharge through the gas, or by subjecting it to the action of charcoal. The latter in fact "catalyses" the reaction and causes it to proceed to equilibrium much quicker, without otherwise altering its nature. The specific heat of the para form is at low temperature greater than that of the ortho form, and, when the latter changes into the former, there is a large evolution of heat. The para form, when allowed to heat up again to ordinary temperatures, reverts back to the ortho form only very slowly, but the change is hastened by catalysts like charcoal. The two spectra are different, and in the band spectrum of ordinary hydrogen lines due to the para form are weaker than those due to the ortho. The foregoing discovery encourages us to think that the co-valent bond may prove to be due to a pair of electrons with opposite spins or wave functions.

**Modes of Representing Chemical Reactions.**—Chemical reactions are often represented diagrammatically, for the reason referred to on page 237, by means of the Lewis cubic atom. Some simple examples of this can now be given as

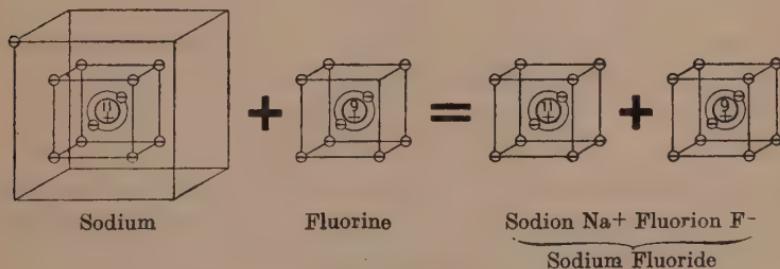


FIG. 51.

illustrations. We may take, first, a typical polar compound, sodium fluoride (Fig. 51), and represent its formation from an atom of sodium and an atom of fluorine. The diagram shows an inner nucleus in each atom, marked with the atomic number, or magnitude of the positive charge, 11 for sodium and 9 for fluorine, surrounded by the K ring of 2 electrons,

and then by the L, or neon, shell of 8 electrons at the corners of a cube, that for sodium being complete and that for fluorine with only 7 of the corners filled. Sodium has an additional electron at one of the corners of the next M, or argon, shell. The act of union, then, is simply that this electron is transferred to the vacant corner of the fluorine cube, producing two identical completed neon cores, but with different nuclei, the "sodium"  $\text{Na}^+$  having one more positive charge in the nucleus, and the "fluorion"  $\text{F}^-$  one less, than the number of electrons, 10, in the complete neon core. But there is no individual union whatever of the two atoms which remain after chemical combination as distinct as they were before.

The next diagram (Fig. 52) is of a typical non-polar combination on the cubic atom model, only the external cubes being represented, the cores and nuclei being always assumed. The two fluorine atoms, by combining together and sharing between them a pair of electrons, effect an economy of

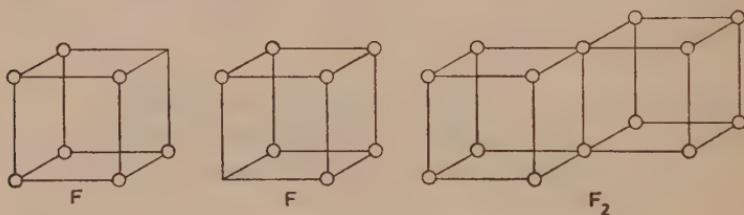
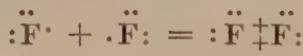
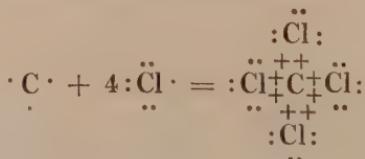


FIG. 52

electrons, so that each atom has now its cube or octet complete. This is more briefly represented as:



unshared electrons being denoted by dots and shared electrons by crosses. The union of an atom of carbon with four chlorine atoms on this system would be written:



Here the carbon atom needs four electrons to complete its octet, having four, and by sharing them all, each with a

chlorine atom, which in turn shares one of its electrons with a carbon atom, all five octets are completed.

Further, the double bond of organic chemistry,  $>\text{C}=\text{C}<$ , may be represented by two carbon cubes face to face, sharing two pairs of electrons, but the triple bond,  $-\text{C}\equiv\text{C}-$ , cannot be represented on this model.

**Intermediate Types of Combination.**—While there is, in the typical examples cited, a very sharp distinction between polar and non-polar compounds, in practice the two types merge into one another by imperceptible degrees. A good illustration of a compound about midway between the two extremes is mercuric iodide. Though a salt, it is ionised to only a very small extent in solution, and it exhibits its non-polar character by forming a number of very interesting complexes with the non-polar carbon compounds of organic chemistry. Its crystal lattice also is intermediate between the ionic and the molecular types, for it has layers of mercuric ions  $\text{Hg}^{++}$ , each of which layers is sandwiched between *two* layers of iodine ions,  $\text{I}^-$ , so the sequence across the layers runs  $\text{I}^-$ ,  $\text{Hg}^{++}$ ,  $\text{I}^-$ ,  $\text{I}^-$ ,  $\text{Hg}^{++}$ ,  $\text{I}^-$ ,  $\text{I}^-$ ,  $\text{Hg}^{++}$ , etc. The union between the mercuric and iodine ions is polar, but in addition there is non-polar linkage between the iodine ions.

Both types of union may, as here, occur in the same compound, and these developments have given to the systematic study of the structure, or constitution, of chemical substances a new and very fruitful direction. Modes of representation and mental pictures at first intended as merely symbolical are, on actual examination by the powerful new methods of X-ray spectroscopy, proving to be far nearer to the literal truth than was at first supposed possible. The familiar and striking differences of character between such typical substances as graphite and diamond, asbestos and talc, iron and steel, chalk and marble, are by this method being reduced to differences in structure, which now can be laid out on the drawing-board to the scale of Ångstrom units,  $10^{-8}$  cm., as the engineer and architect lay out the plans of a mechanism or building.

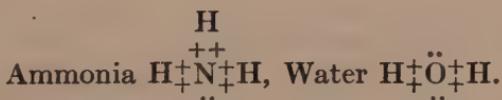
**Molecular Compounds.**—The modern electronic theory of valency has not only been successful in accounting for polar

and non-polar types of compounds. By a very slight extension, it has been found possible to include a group of compounds, at least as important, theoretically, as the other two, which, because the ordinary bond-of-union theory could not account for them, were apt not to be considered to be true chemical compounds at all. They were termed "addition compounds" or "molecular compounds" to indicate the union of compounds together, which were already fully "saturated," that is to say had no bonds of union left over to use for such a purpose. Most of the commoner salts crystallise, for example, from water with a definite number of molecules of "water of crystallisation." These compounds furnish excellent examples of the law of multiple proportions. For instance, copper sulphate occurs usually as "blue vitriol," containing five molecules of water,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Note the comma, intended to indicate that the union was between the salt and the water molecules, not between the constituent atoms. If this salt is dehydrated by heat, it gives the colourless anhydrous compound,  $\text{CuSO}_4$ , but two quite definite intermediate stages,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , exist, each of which has every right to be considered a distinct compound. So it is with hosts of similar compounds.

**Co-ordination Compounds.**—There was here, perhaps, little violence done to the facts by regarding the union as of a molecular rather than atomic character, because all such compounds are readily dehydrated by heat and because no great or obvious difference of chemical character results from the salts combining with water. But it is quite different with a whole class of compounds, which came to be called "co-ordination compounds," to which no known rules of valency could be applied, and for which A. Werner, about the year 1893, proposed a special theory. The feature of this was that in the complex there was a certain central atom, which, irrespective of its ordinary valency altogether, had the power of uniting with a *certain definite number* either of atoms or groups of atoms, quite irrespective again as to whether these atoms or groups were univalent, or whether they were or were not capable of separate existence as whole molecules, like, for example, the "water of crystallisation." This

number was called the "co-ordination number," and it was usually six, less frequently four, and in rare cases eight. Into all the interesting ramifications and consequences of this idea it is here quite impossible to enter. Werner, who died in 1919, devoted his whole life to the development of the theory, and made many striking predictions and discoveries. The prestige of his, at first sight, not very rational theory was enormously enhanced when he succeeded in resolving some of his complexes into optically active forms, but their nature remained to most chemists an enigma. He himself claimed that his co-ordination theory covered the whole of inorganic chemistry. The reason why it is not necessary for carbon compounds, and, equally, the reason why the ordinary bond-of-union theory is so uniformly applicable there, was, he claimed, because the carbon atom is tetravalent, and because its co-ordination number is also four.

**The Electronic Explanation of Werner's Theory.**—It was not till 1923, four years after his death, that the electronic theory of valency was shown by N. V. Sidgwick<sup>1</sup> to apply perfectly to this class of compound. All that was necessary was to extend the non-polar linkage to include the possibility of both electrons in the pair being contributed from the same atom or group. One was the "donor" and the other the "acceptor," and such a linkage is called a "co-ordination link." Since electrons may be contributed by pairs, whole molecules, as H<sub>2</sub>O or NH<sub>3</sub>, which have no free valencies, may contribute both the electrons and so possess combining power. The formulæ for these on the system explained (p. 264) are:



So that the first has what is known as a "lone pair" of electrons in its octet and the second has two such lone pairs.

The elements of the VIIIth Group and their neighbours in the Periodic Table are particularly prone to furnish typical

<sup>1</sup> *The Electronic Theory of Valency*, N. V. Sidgwick, Clarendon Press, Oxford, 1927.

Werner compounds. Thus platinic chloride  $\text{PtCl}_4$  (a polar compound of which the ions are  $\text{Pt}^{++++}$  and  $4\text{Cl}^-$ ), forms many co-ordination or addition compounds with ammonia,  $\text{NH}_3$ . These have remarkable properties. One molecule of the former to two of the latter gives an entirely unionisable and non-polar complex, which may be written  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ . In this, the platinum atom is attached to six groups (atoms or molecules), and its co-ordination number is six. The platinum atom is regarded as surrounded by six pairs of shared electrons occupying positions at the corners of a regular octahedron, and is supposed to have contributed its four electrons to the six pairs. The other eight electrons are contributed, one each by the four chlorine atoms, and two each by the two ammonia molecules.

If we take the complex described as the starting-point, four new complexes result by replacing each of the four chlorine atoms by ammonia molecules, and two more by replacing each of the two ammonia molecules by chlorine atoms. But these compounds are now no longer non-polar. They are ionisable and in a very peculiar way. The first four are :

- (1)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$  with ions  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$  and  $\text{Cl}^-$
- (2)  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$  with ions  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{++}$  and  $2\text{Cl}^-$
- (3)  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$  with ions  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]^{+++}$  and  $3\text{Cl}^-$
- (4)  $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$  with ions  $[\text{Pt}(\text{NH}_3)_6]^{++++}$  and  $4\text{Cl}^-$

In the pair obtained by replacing the ammonia molecules by chlorine atoms, the platinum complex is now the negative ion, and it forms salts with, for example, an alkali metal like potassium. The two are :

- (1)  $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_6]$  with ions  $\text{K}^+$  and  $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$
- (2)  $\text{K}_2[\text{Pt}\text{Cl}_6]$  with ions  $2\text{K}^+$  and  $[\text{Pt}\text{Cl}_6]^{--}$

The last is, indeed, nothing but the well-known potassium platinichloride, which, being relatively insoluble in water, is used in the analytical detection of potassium. We saw (p. 167) that the thallium salt is also insoluble, and this test was the basis of Fleck's identification of actinium and thorium C" with thallium.

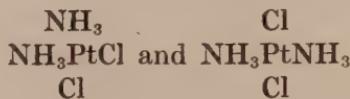
Could any more hopelessly confusing set of relationships be imagined upon the ordinary ideas of chemical valency ? It

shows how wedded the mind is apt to become to a preconceived notion that such amazing complexes as those discovered by Werner did not instantly result in a reconsideration *ab initio* of the theory of valency.

**The Sextuple Werner Valency.**—With the simple extension already mentioned they fit in quite well with the electron theory of valency. When, starting from the non-polar complex  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ , an ammonia molecule joins the complex of six groups, surrounding the platinum atom, it turns out a chlorine ion  $\text{Cl}^-$ , the negative charge on which may be supposed to be derived from the platinum and is compensated for by the complex acquiring an equivalent + charge,  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$ . In this complex we still have six pairs of shared electrons, but the platinum contributes only three, having lost one of its electrons to the chlorine ion, giving the group a single positive charge. The three ammonia molecules contribute six and the three chlorine ions three. For  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{++}$  the platinum has lost two of its electrons to the two chlorine ions, acquiring a double positive charge, and contributes only two to the six pairs, the remaining ten being contributed as regards eight by the four ammonia molecules and as regards two by the two chlorine atoms. So it is with all the other compounds, six pairs of shared electrons surrounding the platinum atom, representing the sextuple Werner co-ordination valency of platinum, exist in all the complexes whatever their charge. For the positive ions, this charge is the number of electrons the complex has to lose to reduce the number remaining always to six pairs. In the case of the negative ions as  $[\text{PtCl}_6]^{--}$ , it is the number of electrons it has to gain from other electropositive elements, such as potassium, to bring up the number to six pairs.

Platinous chloride,  $\text{PtCl}_2$ , the ions of which are  $\text{Pt}^{++}$  and  $2\text{Cl}^-$ , forms an exactly analogous series of compounds in which the co-ordination number is four instead of six, and the platinum atom is at the centre of a group comprising four pairs of electrons. The complexes are (1)  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ , (2)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ , (3)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , (4)  $[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{K}$ , (5)  $[\text{PtCl}_4]\text{K}_2$ , in which the third is the non-polar compound, and in the other four cases the platinum complex is either

a divalent or monovalent positive or negative ion. In these, the platinum is regarded as in the same plane as the ring of four co-ordinated groups, because compounds of the type of (3) above, though not capable of existing in optically active forms, are capable of two geometrically isomeric forms, represented by:



It is a matter of great importance that this hitherto mysterious and confusing set of compounds should have received such a satisfactory explanation, and an extraordinary achievement that such a simple extension of our ideas should have sufficed for the purpose.

**The Nature of Chemical Affinity.**—The chief contribution which the discovery of the electrons and nucleus of the atom has made to chemistry is that they give us a rational conception of the nature of chemical forces. The Lewis cubic atom might be the atom rather than a mere model. Consider an atom with one corner of its octet unfilled. In the direction of that corner the nuclear charge will be less than neutralised, and in all other directions rather over-neutralised. But the field due to the excess + charge will be localised in direction, whilst that due to the deficient + charge will be diffuse. So that the localised field will attract an additional electron to the atom more strongly than the diffuse field will repel it. So, also, for a monovalent positive ion, the excess positive charge of the nucleus over that of the core of electrons will give a diffuse field, uniform in all directions. If an additional electron is brought up to it to form the neutral atom, part only of this field will be exerted in the direction of this electron. The diffuse field in all the other directions will still to some extent persist, so that the forces holding the electron will be weakened and it will be easily detached. In general, the opposite charges being localised at various points, they do not entirely neutralise one another, but for a neutral atom there is a residual field of greater or less intensity, positive in some directions and negative in others.

It is this residual field, rather than the primary electric forces, which we recognise as constituting what we call chemical affinity. But we are only now beginning to understand why the opposite charges remain apart without neutralising one another, or why they appear to yield a definite resultant as though their position was definite. In the astronomical atom one would expect the residual fields to average out, unless, indeed, every one of the myriad atoms in this heavenly choir sings in exact unison with all the others !

## CHAPTER XVI

### THE ENUMERATION OF MOLECULES AND ATOMS

**Brownian Movement.**—The physicists of last century were much engaged in the task of enumerating the actual number of molecules in a given quantity of substance. To them it would have appeared a perfectly hopeless aspiration to be able actually to see and count individual atoms, which radioactivity has now rendered possible. But, before considering these methods, a peculiarly interesting and instructive example of a method of indirect enumeration by a happy combination of theoretical reasoning and experimental skill will first be described. This we owe to Jean Perrin who, in the opening decade of this century, interpreted the Brownian movement of the microscopist as nothing but the perennial agitation of the molecules, which they possess in consequence of, and which indeed is, their heat energy. This agitation is, for the molecule of hydrogen or other gas, far too rapid to be put directly into evidence. The velocity of the hydrogen molecule at ordinary temperature is 1·8 kilometres, rather more than a mile, a second, and for other gases inversely as the square root of their density in terms of that of hydrogen. In the Brownian movement the motion is slowed down sufficiently to be visible under the microscope on account of the bigness of the “molecules.”

The phenomenon was discovered by the naturalist, Brown, shortly after the invention of the achromatic objective. It is observed when any turbid fluid, containing suspended particles sufficiently small, is examined under a sufficiently high-power objective. The smaller the particles the livelier is their perennial agitation, and it is difficult to believe that the particles are not alive. The Brownian movement is an ocular demonstration of the real perpetual motion of the molecules of matter. This, on the kinetic theory of gases and the dynamical theory of heat, constitutes the ordinary heat

energy of matter—not, of course, to be confused with radiant energy. Modern thermodynamics does not deny the possibility of perpetual motion. Indeed, the whole universe is one grand example of it. It denies the possibility of a perpetual motion machine—that is to say, any arrangement which is capable of converting continuously the perfectly chaotic agitation of molecules, which constitutes heat energy of uniform temperature, into useful work, or the co-ordinated motion of masses of matter in definite directions, as in any machine.

**The Law of Equipartition of Energy.**—This great generalisation of physics simply states in the first place that the average kinetic energy of a molecule, due to its heat energy, is independent of its mass. The average speed of different molecules at the same temperature is, therefore, inversely proportional to the square root of their mass. This law Perrin perceived must apply far more generally than to the particles a chemist thinks of as molecules. The physical molecule is the actual free moving particle which moves as a unit, and this is quite irrespective of its nature or composition. According to the modern kinetic theory, these molecules are colliding with one another millions of times a second, but these collisions do not, in any system in a steady state, affect the average energy of the molecules, or the average speed at which they move. This applies whether the moving particle is a molecule of gas or liquid, a mote dancing in the sunbeam, a particle in a nebula, or a microscopic particle suspended in a muddy liquid or emulsion. The physical molecule is simply the unit that moves independently, collides with others and retains its identity during and after its encounters with its neighbours.

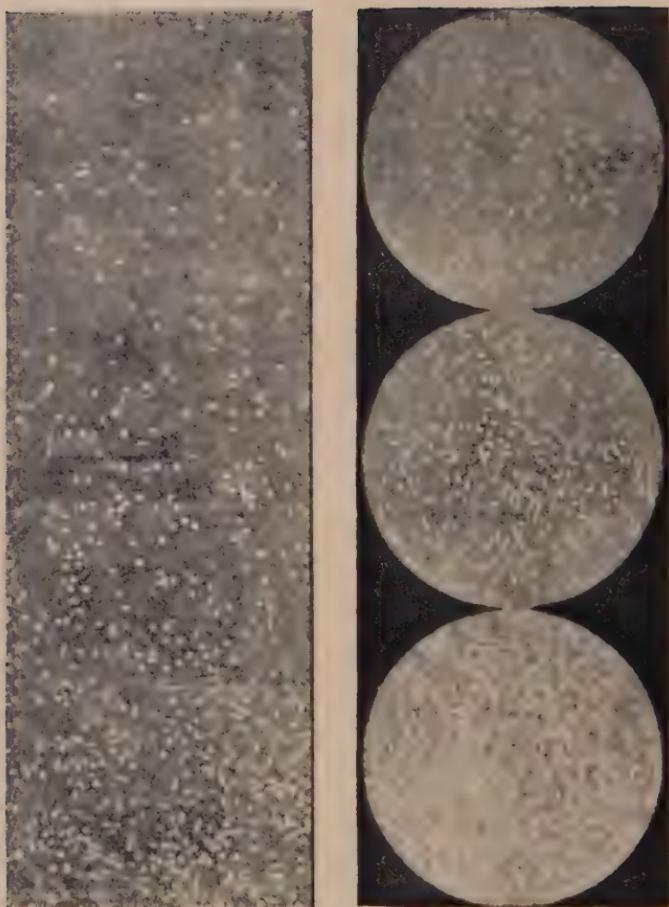
The kinetic theory gives readily enough the average velocity of the molecules of gas, as it is simply that velocity which the whole mass of the gas must have to account for its heat energy. Though on the relative masses for different molecules it is definite, it tells us nothing as to the absolute masses of the individual molecules. The enumeration of molecules, and determination of their absolute masses by the aid of the Brownian movement, depends on determining by direct observations the mass of the particles in a uniform emulsion,

and then comparing this mass with the mass of the hydrogen or any other gas molecule. The method by which Perrin achieved this last step is one of the most beautiful illustrations of scientific reasoning.

**The Law of Rarefaction of the Atmosphere.**—Consider the law of rarefaction of the atmosphere as you ascend, first observed by carrying the mercurial barometer, newly invented by Torricelli, up the Puy-de-Dôme in the Auvergne, and which can now be observed by anyone with a moderately sensitive pocket aneroid, by simply carrying it upstairs. The pressure decreases in a geometrical progression as the height ascended increases in an arithmetical progression. As in the consideration of radioactive change, which follows a similar law, we may speak of the “half-height” as the height to which you must ascend for the barometer to fall to one-half its surface reading, which is the height at which one-half of the air is still above you and one-half below. It is about 6,000 metres, or nearly 20,000 feet above sea-level. For hydrogen or carbon dioxide, this half-height would be just as many times greater or less than for air, as hydrogen is lighter, or carbon dioxide is heavier, than air. Thus the half-height for hydrogen would be  $14.4 \times 6,000 = 86,400$  metres. This is one of the deductions from the law of equipartition of energy and the kinetic theory.

If the law of equipartition can be extended to such relatively enormous particles as those that constitute an emulsion, in passing from the bottom of the fluid upwards there should be a rarefaction in the number of suspended particles in unit volume exactly corresponding with the rarefaction of the atmosphere in going up the mountain. Until this generalisation was made by Perrin it was not even known whether there would be any such rarefaction at all—whether the particles of an emulsion would not, in a state of complete stillness, continue to be uniformly distributed in height indefinitely, owing to their lively Brownian agitation, or whether they would not in time all settle out at the bottom, under the force of gravity. Whereas a calculation showed that particles large enough to be visible under the microscope should thin out very rapidly in height, if left in an undisturbed state,





**FIG. 53.—DRAWINGS BY J. PERRIN OF DISTRIBUTION IN HEIGHT OF COLLOID GRANULES**

The left-hand drawing is for granules of gamboge ( $0.6\mu$  diameter; 4 levels taken every  $10\mu$ ).

The right-hand drawing is for granules of mastic ( $1\mu$  diameter; 3 levels taken every  $12\mu$ ).

and that this rarefaction should be obvious in the layer of about 1/10th of a millimetre (1/250th inch), which is conveniently examined under the microscope.

**Perrin's Experiment.**—Thus the problem was this. Prepare a uniform emulsion, that is to say one with spherical particles as nearly as possible all of one size, and this Perrin did for emulsions of gamboge, and also mastic, by an ingenious process of fractional centrifugalisation. Measure the diameter of the particles under the microscope, and the density, both of the substances of which they consist and of the fluids in which they are suspended. Then their effective or apparent weight in the fluid in which they are immersed can be calculated. Lastly, in a microscopic cell, sealed with a cover-glass and left undisturbed long enough for the particles to settle down to their equilibrium distribution in height, measure on the microscope focussing screw what depth has to be traversed in focussing upwards for the number of particles visible in the field of vision to be reduced to one-half, that is the "half-height" for the emulsion. This apparently difficult operation was in fact easy by reason of the very quality of the high-power objective which is normally a great defect, namely its extremely shallow depth of focus. Actually only those particles in an exceedingly thin layer are visible at all, as all the rest are too out-of-focus to give an image.

**The Result.**—Drawings showing the results of two experiments of Perrin are shown in Fig. 53. Fig. 54 is a diagram of the simple disposition employed. It will be seen that in the exceedingly small heights of  $10\ \mu$  and  $12\ \mu$  ( $\mu$  being the microscopist's unit of length, viz. 1/1000th of a millimetre) a striking variation occurs in the relative abundance of the particles. The photographs on the left refer to gamboge particles of  $0.6\ \mu$  and those on the right to mastic particles of  $1\ \mu$  diameter. Under these novel circumstances the law of rarefaction was found to be exactly the same as for an atmosphere of gas—as the height increases in arithmetical progression, the density or concentration, that is the number of particles per unit volume, decreases in a geo-

metrical progression. It was easy to find the "half-height" for any of the emulsions.

In one series with gamboge granules of  $0.14\ \mu$  diameter the half-height was 0.1 millimetre. Thus these granules weigh as much more than the molecule of hydrogen as 86,400 metres is greater than one-tenth of a millimetre, that is to say 864 million times as much. The apparent weight of these granules

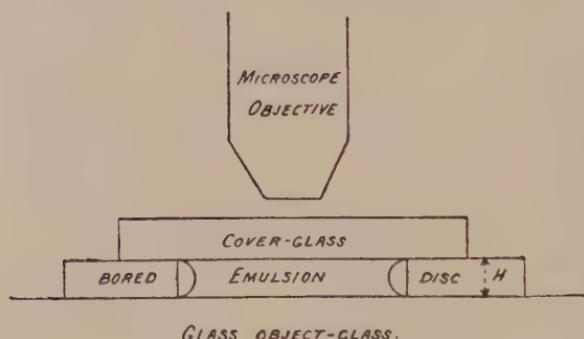


FIG. 54.

suspended in water, though extremely minute, was readily and certainly found, since they were spherical in shape, from their density and diameter, as measured by the microscope in a variety of ways. It was  $1/400,000,000,000,000$ th of a gram. Hence the weight of the hydrogen molecule is  $2.9$  million-million-millionths of a gram. The weight of the hydrogen atom is  $1.45 \times 10^{-24}$  gram according to this estimate.

**Avogadro's Number.**—The value generally now accepted as the best of all the modern determinations is rather more than this, namely  $1.65 \times 10^{-24}$  gram. It is usually expressed by its reciprocal,  $6 \times 10^{23}$ , which is called Avogadro's number in honour of the Italian physicist and chemist, Amedeo Avogadro, to whom we owe the generalisation that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. For it expresses, not only the number of atoms in the gram of hydrogen, but the number of molecules in the gram molar weight of any gas—that is to say, in 2 grams of hydrogen, 32 grams of oxygen and so

on. The same number, Avogadro's number, usually denoted  $N$ , relates the atomic charge  $e$  to the faraday,  $F$  (see p. 186). That is  $F = Ne$ . Since the faraday has been very accurately determined by the ordinary voltameter, a determination of  $e$  is also a determination of Avogadro's number,  $N$ , and the most accurate value for the latter has been obtained by Millikan by this method.

**The Determination of  $e$ .**—The experiment which was the sequel to a long series of researches by the Cambridge physicists, and a refinement upon them, was of a very curious character. It depended on making a fine spray of oil droplets, isolating one of these in the field of an ultra-microscope, and compelling it by appropriate environment to catch ions. Once it had caught an ion and acquired a charge, either + or -, its slow fall under gravity, as observed by the measuring microscope, could be arrested and reversed by the application of a suitable electric field. By such means it could be hung up in the air indefinitely like Mahomet's coffin, and the same ultra-microscopic droplet could be watched for hours at a time.

A sequence of events was observed, perhaps among the most remarkable ever made in physics, which entirely depended on the fact that the droplet could never catch less than a whole  $e$ , and its charge, + or -, could only vary by integral multiples of  $e$ . The magnitude and sign of the charge on the droplet made no difference whatever to its rate of fall under gravity so long as no electric field was operating. But the speed at which it was pulled up again after falling depended upon the number of  $e$ 's in its charge, which could only vary by integers, not continuously. In this way perhaps the most direct and convincing proof of the atomicity of the electric charge was ocularly demonstrated. The speed at which it was pulled up by a field of known strength varied *abruptly* from one rate to another, as the charge changed. From this and the speed of the fall of the drop when no field was on, which was always the same, the magnitude of the charge could be deduced. In 60 consecutive days' observations, which agreed to a maximum error of 0.5 per cent., no smaller change of charge was ever observed than  $4.774 \times 10^{-10}$  electrostatic

units, and since the faraday is  $2 \cdot 893 \times 10^{14}$  electrostatic units, Avogadro's number by this method is  $6 \cdot 06 \times 10^{23}$ .

**The Spintharoscope.**—We may now consider the direct enumeration of atoms that radioactivity renders possible. The energy of the single  $\alpha$ -particle, and to a less striking degree that of the single  $\beta$ -particle also, is sufficiently great to produce an effect that can be detected. For the case of the  $\alpha$ -particle it is, for example, sufficient to produce a flash of light when it strikes a zinc sulphide screen, easily visible to the eye in the dark when the screen is observed through a lens. The

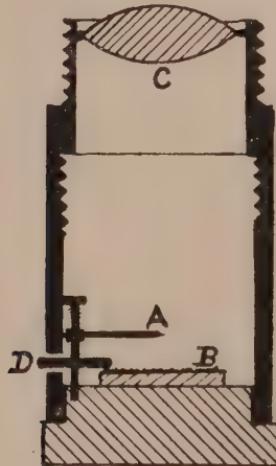


FIG. 56.

first discovery of this effect was made by Sir William Crookes, who devised an instrument, which he called the spintharoscope, to show it. A photograph of the instrument is shown in Fig. 55 (facing p. 125) and an explanatory diagram in Fig. 56. It consists of a tube about the size of a reel of cotton, in the upper end of which is screwed a holder containing a lens C, which, by means of the screw, can be focussed on a piece of zinc sulphide screen B mounted on a disc closing the lower end of the tube. Close above the screen is mounted a needle, A, the tip of which has been touched by a radium preparation and carries an infinitesimal quantity of radium. The distance of the needle tip from the screen can be varied by turning

the head D of a screw which projects through a slot in the tube.

On examining the screen through the lens in the dark it will be seen that the luminosity of the screen is not continuous, but consists of bright momentary flashes of light or scintillations, closely resembling in appearance a swarm of meteors. The whole instrument can be purchased from the opticians for a few shillings, its comparative inexpensiveness being due to the practically infinitesimal quantity of radium it contains. The same, of course, is true for the radium watches, in which the hands and figures on the dial can be made sufficiently luminous for the watch to be read in the dark by the expenditure of, at most, a few pennyworths of radium or mesothorium. But in the spintharoscope a pennyworth would be far too much.

The luminosity of the zinc screen under radium rays deteriorates with age fairly quickly, owing to the intense bombardment spoiling the zinc sulphide. But the radium does not wear out, even in a lifetime, and if a new screen is inserted into the spintharoscope after the old has become insensitive, the radium will be found as active as ever. Although it is belching forth  $\alpha$ -particles like a Maxim gun, the unweighable and invisible trace of radium will keep it up without any very notable diminution for centuries. Over a period equal to the whole Christian era, little more than one-half of it will be used up. No better illustration can be found of the almost incredible minuteness of the ultimate particles of matter and of the colossal latent stores of energy in the atom which radioactivity has disclosed.

Those who have to guide the destinies of nations might do worse than take a peep through the lens of a spintharoscope and spend the rest of the day in the contemplation of its implications. Even scientific men, who, of all people, might be expected to be the first to realise the consequences of their own discoveries, in their private lives still think, act and counsel others as though it is only by the most heroic exertions that anyone survives in the struggle for existence. For generations now, and, indeed, ever since the harnessing of ordinary fuels, the struggle has, like the Oxford and Cambridge boat-race, been of traditional and symbolic rather than physical

significance. After having struggled so long to exist, humanity now exists to struggle.

**Electrical Methods of Enumerating  $\alpha$ -Particles.**—Both scintillation and electrical methods have been developed for the accurate counting of the number of  $\alpha$ -particles expelled by a radioactive substance in a given time. The latter were developed first by Rutherford and Geiger. They depend on the magnification of the ionisation produced by the individual particles, by making use of the phenomenon of ionisation by collision first recognised by Townsend, up to the point at which each  $\alpha$ -particle can produce sufficient ionisation to be detectable by a sensitive electrometer. The principle has already been explained (p. 102). In an electric field of sufficient strength, especially when the pressure of the gas is reduced, the original ions, produced by the  $\alpha$ -particles in passing through the gas, themselves acquire sufficient velocity and kinetic energy to ionise the molecules of the gas they strike, upon their own account. Actually the negative ion, being rather the lighter, acquires this power somewhat sooner than the + ion, and so long as it alone is operative, the ionisation produced by the  $\alpha$ -particle is very greatly magnified but still remains finite. If the electric field is made but a little stronger, the + ions also acquire the same power, and the ionisation then rises without limit, so that a spark passes through the gas. In practice it is possible to magnify the original ionisation something like a thousand times before this occurs.

At first only a very small number of  $\alpha$ -particles a minute could be counted by this means. The source of  $\alpha$ -particles from a radium C preparation, for example, was placed at the end of an exhausted tube many metres long with a tiny window of thinnest mica at the other end, so that, of the whole number expelled, only an infinitesimal, but accurately determinable proportion—of the order of one in a hundred million—passed through the window into the ionisation chamber, where its effects were magnified by a powerful electric field. Helium was found the most suitable gas to use in this chamber, and an ordinary quadrant electrometer was first used to detect the effect.





FIG. 48.—MOSELEY'S DIAGRAM OF X-RAY SPECTRA OF THE ELEMENTS (K SERIES).

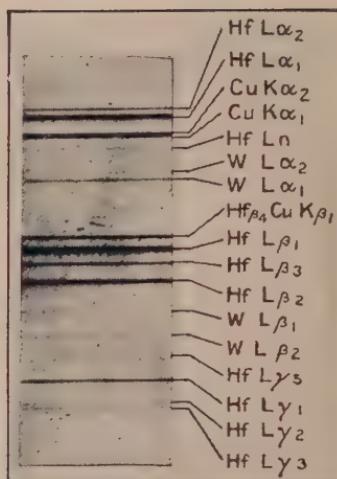


FIG. 49.—X-RAY SPECTRA OF HAFNIUM (L SERIES) WITH K LINES OF COPPER AND L LINES OF TUNGSTEN FOR COMPARISON.

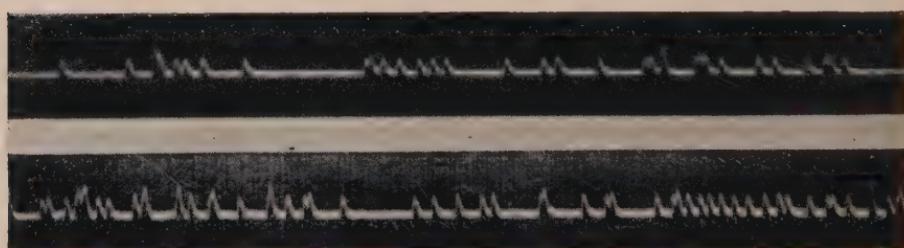


FIG. 57.—PHOTOGRAPHIC REGISTRATION OF  $\alpha$ -PARTICLES WITH RUTHERFORD-GEIGER COUNTER AND STRING ELECTROMETER.

The upper record corresponds to the entrance of particles at a rate of 600 per minute into the counter, the lower to a rate of 900 per minute.

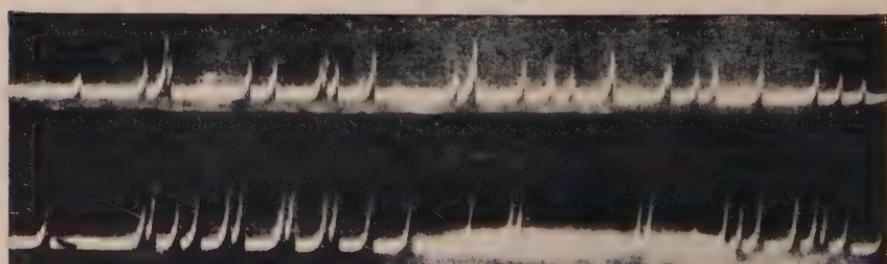


FIG. 58.—REGISTRATION OF  $\alpha$ - AND  $\beta$ -PARTICLES WITH GEIGER POINT COUNTER.

The upper record shows the registration of  $\beta$ -particles; the lower the registration of  $\alpha$ -particles

But great improvements were gradually made. A recording string electrometer, with very rapid period of oscillation and high damping factor, replaced the ordinary instrument, and the rate of counting could thereby be enormously increased. The arrival of each  $\alpha$ -particle is signalled by a sudden kick or jerk of the electrometer needle, which is magnified in the usual way by a mirror and beam of light, and recorded on a moving photographic film. In Fig. 57 the record of the electrometer is shown, in the upper film for a rate of 600  $\alpha$ -particles a minute, and the lower film for a rate of 900  $\alpha$ -particles a minute.

Another improvement was due to the invention of the Geiger point counter, which makes use of a very sharp needle point charged to a high potential. If an  $\alpha$ - or  $\beta$ -particle passes in the neighbourhood of the point a discharge, which can be plainly seen, under the microscope in the dark, as a flash, occurs at the point, and this can be recorded by the string electrometer as before. The peculiar feature here is that the flash discharge is of much the same intensity whether produced by an  $\alpha$ - or a  $\beta$ -particle, so that the method extends the possibility of enumeration to the latter. This is shown in Fig. 58 in which the upper record is for  $\alpha$ - and the lower for  $\beta$ -particles. This method has also been found invaluable in the study of the new cosmical rays (p. 334).

**Valve Methods.**—More recently the ordinary wireless valve has been impounded into the service of recording  $\alpha$ -particles. By appropriate methods, the original ionisation produced by a single  $\alpha$ -particle may be amplified up to the amount required to produce a sound in a telephone or loud-speaker. The great advantage here is that the method enables the speed of recording to be still further increased. The method, originally used by Greinacher, has been brought by Wynn-Williams and others, working with Lord Rutherford, to a high degree of perfection. Electrical methods, by "thyatron valves," have been applied to the counting as well as to the recording, and the rate of counting increased to some thousands a minute.

A particularly ingenious differential method, due to Lord Rutherford, has been the means of further advances. The

stream of  $\alpha$ -particles traverses two shallow ionisation chambers, one immediately behind the other, connected up electrically in such a way that the effect of the  $\alpha$ -particles passing through the one is almost exactly neutralised by their effect in passing through the other. Thus, this differential arrangement records only those  $\alpha$ -particles which traverse the first but stop before they reach the second, and in this way the presence of a few  $\alpha$ -rays of shorter range among a much larger number of longer range has been put into evidence. The main stream of  $\alpha$ -particles may be passing through at the rate of many thousands a minute, but only the few  $\alpha$ -rays of range just sufficient to enable them to traverse the first, without reaching the second chamber, are recorded.

After having been looked for in a great variety of ways for many years, the short-range  $\alpha$ -rays which, theoretically, should be expelled in the minor branch change of radium C when the RaC" product results (p. 173) have at last (1931) been experimentally detected. They exist in the proportion of one in 4,000 of the main radium C'  $\alpha$ -rays, and their range, 4.1 cm., agrees with that deduced, before they were observed, by the Geiger-Nuttall relation from the calculated period of the single change in which they result.

**Scintillation Methods.**—Contemporaneously with the development of the electric method, the scintillation method has also been made a valuable and accurate means for the enumeration of  $\alpha$ -particles, zinc sulphide, and sometimes diamond, being used as scintillators. The simplicity and efficiency of this method is remarkable. When it is considered that the electrical effect has to be magnified something like a thousand times before it can be registered by the most sensitive electrical instrument, and that the human eye is easily able to detect the effect of the single  $\alpha$ -particle without amplification, by the flash of light it produces in the zinc sulphide crystal, some idea may be obtained of what a delicate and efficient instrument the eye is. In this it is aided by the extraordinary efficiency of the zinc sulphide crystal as a converter of the energy into visible light. It is estimated that about one-quarter of the whole energy must be turned by it into light energy, and, moreover, the wave-length or colour

of the light is exactly at the maximum of the scoptic luminosity curve for the dark-adapted eye.

For accurate counting by this means, not more than three or four  $\alpha$ -particles a minute must strike the screen, the eyes must be rested by remaining half an hour in complete darkness prior to counting, and one observer cannot count for more than a short period without long intervals of rest in between counting periods.

**Results of Enumeration of  $\alpha$ -Particles.**—A very large number of observations, both by scintillation and electrical methods, have been made in order to evaluate the number of  $\alpha$ -particles given by the gram of radium (element) per second. The values vary from  $3\cdot4$  to  $3\cdot7 \times 10^{10}$ , the highest value being considered the most probable. This is for the  $\alpha$ -particle from radium itself, and it must be multiplied by four to give the total number for radium in equilibrium with its products as far as radium C.

If we may assume that the period of average life of radium is accurately known to be 2,800 years ( $7\cdot25 \times 10^{10}$  seconds) and its atomic weight is 226, Avogadro's number, N, can be evaluated from the above figure. It is the number of atoms in 226 grams of radium. Hence, since each  $\alpha$ -particle emitted corresponds to the disappearance of one atom of radium, and in the complete disintegration of 226 grams,

$$226 \times 3\cdot7 \times 10^{10} \times 7\cdot25 \times 10^{10} = 6\cdot06 \times 10^{23}$$

$\alpha$ -particles are emitted, this number equals N. The exact correspondence with Millikan's value, so obtained, is due to the choice of  $3\cdot7 \times 10^{10}$  for the number of  $\alpha$ -particles emitted per second, and is the reason why this value is supposed to be the most probable. The mean of all the results would make N somewhat less, but not nearly so much less as the value obtained by Perrin from the Brownian movement.

**The Indeterminacy of Disintegration.**—All these methods of detecting and counting individual  $\alpha$ -particles, that is to say, the individual disintegrations of the atoms, bring into prominence one very important feature of the disintegration process. The mathematical interpretation of the law of disintegration,

that the same definite proportion of the radioactive atoms remaining in existence always break up in the unit of time, whether we study the beginning, the middle or the end of the process, is that the individual act of disintegration is entirely indeterminate and governed by the laws of probability alone. It is only the average period of life (which is the reciprocal of the proportion disintegrating in the unit of time) that is definite, and then only when a sufficiently large number of disintegrations are considered, so that individual effects are averaged out.

This is strikingly demonstrated by actual experiments on counting, and the determination of the actual intervals of time between the successive disintegrations. It is true that, just as with games of chance, there appears at first to be all sorts of "runs of luck," and any set of observations dealing with a small number only of successive disintegrations will appear to give regularities governing the time intervals between successive disintegrations. But over a long enough period, when sufficient numbers are counted, all irregularities are smoothed out, and we get the pure probability law for emission, random both as regards time and space.

These and similar experiments negative the possibility that there can be any gradual or progressive change in the nature of the atom leading up to and ultimately resulting in its disintegration. Nor can there be any effect on the neighbouring atoms produced by the break-up of the atom. The complete independence of the process from any known influence makes it difficult, if not impossible, to assign any reason for the break-up of the atom at all.

That the period of future life of an atom does not at all depend on the length of time it has already lived may be simply and directly demonstrated by experiment. The average life period of radon, for example, may be measured: (1) for radon newly born, which was not in existence a short time previously, by examining the radon regrown from a large quantity of radium in the period of a few seconds from the time when the radon was completely removed; (2) for radon that has already been in existence many times the average period of life, by allowing a large amount to decay and then determining the rate of decay of the small fraction left after

many weeks. Such experiments have proved that there is no change in the period of average life. An atom that has escaped disintegration a long time is not thereby any the more likely to disintegrate.

The idea of Laplace, that if perfect knowledge existed of the state of the universe and of every atom in it at one instant, a perfect mathematician could predict its state and that of every atom in it at any future time, even when the disturbing element of life and free-will is excluded, does not accurately represent the actual behaviour of radioactive atoms. Indeterminacy seems to be essentially a part of the nature of atoms, and for this and similar reasons physicists are tending to regard all the definite laws of Nature in the same way as the law of radioactive change, as the result of random events, in which each event individually is a law to itself, but for which over a sufficiently great number of events there is a definite average result. There has been much discussion of, but little actual advance in our knowledge of, the cause of radioactive disintegration, and the reason for this atomic indeterminacy. The laws of thermodynamonics, similarly, are pure statistical or probability laws, and the idea has been somewhat loosely extended to energy-quanta, though the sharpness of spectrum lines seems a direct proof of the opposite.

**Wilson's  $\alpha$ -Ray Tracks.**—By far the most beautiful as it is also the most direct method of studying the individual  $\alpha$ -ray is due to C. T. R. Wilson, who discovered a simple method of rendering their tracks in the air or other gas visible to the eye and capable of being photographed. For this purpose it suffices to send them through dust-free air supersaturated with moisture. As is well known, dust particles and similar large nuclei play a large part in the precipitation of moisture from a supersaturated atmosphere, and this function is also displayed, under well-defined conditions of supersaturation, by the ions themselves, although these are molecular in size. In absence of dust, the ions cause the excess moisture to condense upon them as minute drops. If there are many ions we get a Scotch mist; if few, a miniature thunder shower. The usual way of inducing the condition of supersaturation

is to expand suddenly a saturated atmosphere, when the chilling produced by the sudden increase in volume causes the same quantity of air to be incapable of holding as much water vapour as before, and, in the presence of dust or ions, the excess is deposited at once. The absence of dust is easily secured by expanding air in a closed vessel a few times over water, when the dust nuclei are carried down by the rain. If, then, the air is irradiated by any of the ionising rays, each successive expansion is accompanied by the appearance of a fog or cloud. If, for example, a needle-point containing a trace of radium or other substance emitting  $\alpha$ -rays is placed in the chamber, on expansion we have the appearance well shown in Fig. 59. Each individual  $\alpha$ -particle traversing the air at the moment of expansion forms in its path a dense column of ions upon which the excess moisture instantly condenses, revealing the whole passage of the particle. These tracks illustrate all the peculiarities of the  $\alpha$ -rays discovered by Bragg and others. They are, for the greater number, almost perfectly straight lines becoming more rather than less distinct along their path and then ending abruptly. But a few show sudden bends usually near the end of their range. In the magnified photograph, Fig. 60, in addition to the  $\alpha$ -ray track may be seen faintly the end of a  $\beta$ -ray track. These are always very much fainter than the  $\alpha$ -ray tracks because the ionisation they produce in gases is much less intense, and they are usually wavy or zigzag, the light  $\beta$ -particle being readily deflected from its course by its encounters with the molecules. In Fig. 61 is shown, side by side, the normal straight  $\alpha$ -ray track and one with two abrupt changes of direction. They illustrate the occasional wide-angle deflections suffered by the  $\alpha$ -particles from which so much has been learned as to the structure of the atom. C. T. R. Wilson's own description of the last photograph may be compared with that for the  $\alpha$ -particle by Sir William Bragg already quoted (p. 107).

"The  $\alpha$ -particle has thousands of encounters with atoms of the gases in the air in each millimetre of its course by which ionisation is brought about, as we know from measurements made with the electrical method, and in accordance with this the cloud particles (which are simply ions magnified by con-



FIG. 59.—WILSON PHOTOGRAPH OF  $\alpha$ -PARTICLES.



FIG. 60.—SINGLE  $\alpha$ - AND  $\beta$ -PARTICLES.



FIG. 61.—DEFLECTED  
 $\alpha$ -PARTICLE.

*To face p. 286.*



densation of water) are so closely packed that they are not separately visible in the photograph. It is remarkable that only two encounters out of the many thousands occurring in the course of its flight should succeed in deviating the particle visibly from its course, and that in these cases the deviations should be quite large."

In Fig. 62 (facing p. 292) one of Wilson's photographs for a single fast  $\beta$ -ray and for a number of slow  $\beta$ -rays is shown. The fast  $\beta$ -rays often traverse several cms. of air in straight paths without being deflected, and the density of ions produced along their paths is slight. This, as in the case of the  $\alpha$ -particle, increases with the time the ionising particles spends in traversing the atoms ionised, and therefore increases as the velocity decreases. The slow  $\beta$ -rays show much more pronounced tracks, and these are in no case even approximately straight. The tracks produced by  $\gamma$ -rays show no trace of the original  $\gamma$ -rays, but consist of a large number of slow  $\beta$ -ray tracks similar to those of Fig. 62 along the path of the  $\gamma$ -rays (p. 124).

## CHAPTER XVII

### THE ATOMIC NUCLEUS

**H-rays.**—The phenomenon of occasional large-angle single scattering, when the nucleus of the  $\alpha$ -particle comes into close collision with the nucleus of an atom in its path, naturally must depend very much upon whether the atom struck is heavier than, equal in mass to, or lighter than the  $\alpha$ -particle. In the last two cases, especially, interesting results are to be predicted by the ordinary principles of dynamics. Thus an  $\alpha$ -particle striking an atom of hydrogen cannot be deflected by the collision through a greater angle than  $14^\circ 29'$ , owing to the mass of the hydrogen atom being only a quarter of that of the  $\alpha$ -particle. But if a direct “head-on” collision occurs, the centre of the atom struck lying in the path of the  $\alpha$ -particle, no deflection of the latter will occur, but the lighter atom in front will be projected forward with the speed 1·6 times that of the  $\alpha$ -particle striking it. It will instantly be ionised to  $H^+$ , and its range in air, both by reason of its greater velocity and single charge, may be expected to be about four times as great as that of the  $\alpha$ -particle producing it.

Such long-range particles, generated when  $\alpha$ -rays traverse hydrogen, were observed first by Marsden in 1914, and subsequently studied in detail by Rutherford. They are conveniently termed H-rays. Generated by  $\alpha$ -particles of radium C' of range 7 cm., they have a maximum range of 28 cm. of air. Even in absence of hydrogen gas, a few such rays are always generated, owing to the presence of such impurities as water in the screens or other materials through which the  $\alpha$ -rays pass.

**Collisions in Helium.**—For the case of helium gas there is no distinction between the nucleus bombarded and the  $\alpha$ -particle. Here dynamical considerations lead to the result that the maximum angle of deflection cannot exceed  $90^\circ$ , and, after the collision, no means exists to decide which of the two particles was the bombarding and which the bombarded.

In the case of a "head-on" collision the rôles are simply transposed: the  $\alpha$ -particle is reduced to comparative rest and the helium atom struck goes on at the same speed and in the same direction as the original  $\alpha$ -particle.

But a very interesting prediction from the wave mechanics atom has been made as regards the distribution of the angles of scattering of the  $\alpha$ -particle in helium. Twice as many should go off at  $45^\circ$  to the original direction of the  $\alpha$ -particle, and correspondingly less at other angles, than the older dynamics predicts, owing to the wave functions for the system as a whole being in a symmetric mode. But for the collisions of two electrons, for which the wave functions are anti-symmetric, only half as many  $45^\circ$  angles should be found as the older dynamics requires. The prediction has been completely verified as regards the  $\alpha$ -particle, but the other case is much less easy to settle by experiment.

**Artificial Disintegration of Light Elements.**—The experiments on the collisions between  $\alpha$ -particles and light atoms paved the way for much the most important result that has yet transpired from this work, namely, the artificial disintegration of light atoms by  $\alpha$ -particles. This was first observed for the element nitrogen. It was found in 1922 that when  $\alpha$ -particles were passed through this gas, H-particles were observed, to the extent of a few per million  $\alpha$ -particles, which had a greater range in air than the H-particles furnished by hydrogen, and which traversed up to a maximum of 40 cm. of air. This removed at once the chief doubt that must otherwise arise as to the genuineness of the results observed, for hydrogen, in the form of moisture, is an impurity that would be difficult absolutely to exclude in such work. The fact that the range is greater than for the H-particles given by hydrogen itself, showed conclusively that the H-particles did not originate in impurities. The identity of the H-particles observed in this and other cases was made probable by experiments on their deviability in a magnetic field, which showed them to be positively charged particles and to be deflected by the magnetic field to an extent to be expected if they were singly charged hydrogen nuclei moving with a velocity estimated from their range.

A systematic study of the light elements showed that whereas all probably (at least, according to some observers) give out hydrogen nuclei, the effect is the more marked and the ranges of the H-particles are the greater for the elements of odd atomic number than for those of even number. For helium, beryllium, carbon and oxygen, none whatever could be detected in the experiments at the Cavendish Laboratory, but investigators in the Vienna Radium Institute claim to have obtained them from nearly every element examined. The two sets of experiments and the methods used are not the same, and it does not appear that the one set of observers have tried to repeat those of the other using their methods. There is, however, agreement that, up to potassium, atomic number 19, the elements of odd number give the clearest and most unequivocal evidence of actual disintegration under bombardment. Boron, nitrogen, fluorine, sodium, aluminium and phosphorus, give H-particles of range greater than 28 cm. in air, which cannot therefore be ascribed to possible impurities. The range of the H-particles is greatest for aluminium, being no less than 90 cm. of air for those emitted in the forward direction. This indicates that the H-particle has an energy *greater* than that of the  $\alpha$ -particle striking the nucleus, and shows that the effect cannot be merely a mechanical one. In such cases the  $\alpha$ -particles must act as the trigger releasing an internal store of energy in the atom struck. Part of the energy of the H-particle emitted from an aluminium nucleus must arise from the internal energy of the nucleus itself, as in the primary disintegration in which the  $\alpha$ -particle is expelled. About two to three times as many H-particles are emitted by aluminium in the forward direction of the  $\alpha$ -particle as in the backward direction.

Rough estimates of the total numbers of H-particles emitted in the various cases have been made. For nitrogen, per million  $\alpha$ -particles of 7 cm. range totally absorbed in passing through the gas, as many as twenty nitrogen atoms are estimated to be disintegrated and to emit H-particles; for aluminium, the corresponding number is eight; for chlorine, argon and potassium not more than one; while, for elements heavier than potassium, the possibility of disintegrating them at all is not admitted by the workers in this country.

**Odd and Even Numbered Elements.**—These experiments have added to the evidence that has been accumulating that the elements of even atomic number are in many ways distinguished from those of odd atomic number, and the difference is possibly to be sought for in the lesser stability of the latter. It is most interesting that, in the earth's crust, the even numbered elements are far more abundant than the odd numbered, and the whole of the latter, which are, of course, as numerous as the others, only account for 12 or 13 per cent. of the total crust. Excluding aluminium, sodium and potassium, the proportion contributed by all the other odd elements is almost negligible. The experiments which show that, under bombardment with  $\alpha$ -rays, a hydrogen nucleus is emitted, possibly explain the difference, for they show a much greater tendency for the elements to change from odd number to even than the contrary. We know little as yet as to the fate of the nucleus from which the H-particle is ejected, whether it captures or absorbs the  $\alpha$ -particle or not after the collision. But, in either case, the atomic number of the element must be changed by one unit, being decreased by one if the  $\alpha$ -particle is not captured, and increased by one if it is. Since the odd elements show the emission of H-particles more easily, it is clear that the nett effects of these processes in nature must be a steady conversion of elements of odd atomic number into even to a greater extent than the converse, and this perhaps accounts for the relative scarcity of the odd elements. We shall have to deal with other differences between the two types of elements when their isotopes are considered in the next chapter.

**Cloud Photographs of  $\alpha$ -Particle Collisions.**—Wilson's beautiful method, described in the last chapter, has been adapted for the purpose of photographing, or rather cinematographing, these rare encounters between  $\alpha$ -particles and atomic nuclei. For this purpose a large number of  $\alpha$ -ray tracks are cinematographed by two cameras in two directions at right angles. From an examination at leisure of the film, the pairs of photographs which show evidence of direct collisions may be selected, and the actual tracks of the colliding particles in three dimensions reconstructed on stereoscopic principles. The great rarity of the phenomenon makes it

necessary to take an enormous number of photographs to secure even a few examples of actual disintegration and ejection of a proton, or H-ray, from the disintegrated nucleus, though a large number of ordinary forked tracks occur. The work has been done by Blackett in this country and Harkins in America, and some examples of the former's photographs are given. About 23,000 photographs, showing 270,000 of the longer and 145,000 of the shorter  $\alpha$ -rays were taken with thorium C+C' as the source of  $\alpha$ -rays, in nitrogen gas, to which some oxygen was added. But only eight of them showed the actual ejection of the proton from the nitrogen nucleus.

Fig. 63 is a Wilson photograph of the  $\alpha$ -rays passing through hydrogen, and shows an ordinary elastic collision of the  $\alpha$ -particle with a hydrogen atom. An  $\alpha$ -particle on the right, in the lower half of the picture, has struck a hydrogen nucleus and has suffered only slight deflection. The hydrogen nucleus is seen going off at a sharp angle to the left. Fig. 64 is for  $\alpha$ -particles passing through helium, and the photograph shows the bombarded and bombarding particle going off at right angles to one another, with nothing to indicate which was the original  $\alpha$ -particle and which the helium nucleus struck. In Fig. 65 the stereoscopic picture shows, for  $\alpha$ -particles passing through oxygen, a normal elastic collision, without disintegration, between the  $\alpha$ -particle and an oxygen nucleus. Fig. 66 shows one of the excessively rare collisions of an  $\alpha$ -particle, passing through nitrogen gas, in which a proton is ejected from the nitrogen nucleus. The fainter track is that produced by the proton, and the heavier that produced by the nitrogen nucleus. It is evident that, after the collision, this nitrogen nucleus has encountered another nitrogen nucleus and has been deflected again.

The point of most interest about these rare photographs of artificial disintegration accompanied by the ejection of a proton is that in no case yet has the  $\alpha$ -particle producing the phenomenon survived the collision and given a third track. It is considered almost certain that it is absorbed by the nitrogen nucleus struck. If this is so, it means that the nitrogen atom of mass, 14, and atomic number, 7, has gained a helium nucleus and lost a hydrogen nucleus. It must therefore become an

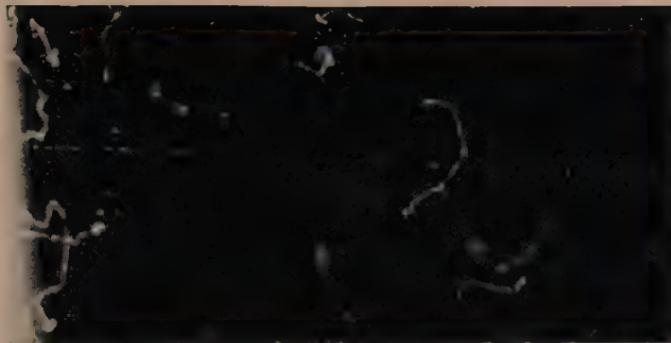


FIG. 62.—FAST AND SLOW  $\beta$ -PARTICLES.



FIG. 63.



FIG. 64.



FIG. 65.



FIG. 66.

COLLISIONS OF  $\alpha$ -PARTICLES WITH, FIG. 63, A HYDROGEN ATOM; FIG. 64, A HELIUM ATOM; FIG. 65, AN OXYGEN ATOM; FIG. 66, A NITROGEN ATOM, DISINTEGRATING IT. THE LAST TWO ARE STEREOSCOPIC PHOTOGRAPHS.  
BY P. S. BLACKETT.



isotope of oxygen, of mass, 17, and atomic number, 8. Such an isotope is now known (p. 302) to exist, from the evidence of the band spectrum of oxygen.

**The Nature of the Nucleus.**—Though, in a general way, the excessively minute dimensions of the nucleus is in accord with the electrical theory of the origin of mass, it cannot be said that there is any quantitative agreement in this respect. Lord Rutherford, from his general results on scattering, distinguishes between the nuclei of the heavy elements, beyond copper in the Periodic Table, and the lighter ones. For the former the collisions with  $\alpha$ -particles conform to the Coulomb law of repulsion, in which the repulsive forces vary inversely as the square of the distance between the centres of the colliding nuclei up to the closest distances of approach between them even with the swiftest  $\alpha$ -particles. For the latter, this is not true, except for  $\alpha$ -particles of the lowest range and velocity that can be studied.

The experiments on the collisions between  $\alpha$ -particles and hydrogen nuclei and helium nuclei receive an interpretation if it be supposed that the  $\alpha$ -particle is an elastic oblate spheroid, moving in the direction of its minor axis, which is about  $4 \times 10^{-13}$  cm., the major axis being some three and a half times greater. Whereas the hydrogen nucleus or proton acts as an elastic sphere of about  $4 \times 10^{-13}$  cm. diameter. This makes the electron and proton of practically the same size, whereas, if the mass of the proton is a consequence of the inertia of its charge, its diameter should be  $1/1840$ th that of the electron. There is evidence that in the collision of  $\alpha$ -particles with light atoms, for which the Coulomb law does not hold for the closest distances of approach, the  $\alpha$ -particle must penetrate into the nucleus struck, and this may account for its power of occasionally disintegrating the lighter atoms of odd atomic number.

It has been considered probable that the proton, emitted during artificial disintegration, exists in the atom as a satellite revolving round the main central nucleus. This serves to account for the large proportion ejected in the backward direction. Also since protons, as well as helium nuclei, are invariably present in the nuclei of elements of odd atomic

number,<sup>1</sup> this may be the reason for the latter being more easily disintegrated.

For the heavy elements, such as copper and beyond, since Coulomb's law is obeyed, it is concluded that the two nuclei do not interpenetrate. If we define the closest distance of approach as giving approximately the maximum radius of the nucleus bombarded, a difficulty arises. For this method would make the radius of the uranium nucleus about  $4 \times 10^{-12}$  cm. On the conventional view that this nucleus is built up of 238 protons and 146 electrons, clearly the uranium nucleus must be considered a fairly close-packed assemblage.

A simple calculation by classical dynamics, however, is sufficient to show that the radius of the uranium nucleus must be at least  $6.3 \times 10^{-12}$  cm. For the central charge is  $+90e$ , after it expels its first  $\alpha$ -particle. The argument is directed to ascertain at what distance from the centre of the uranium nucleus the  $\alpha$ -particle ejected must start, if initially at rest, to acquire the velocity and kinetic energy with which it is expelled, by the repulsion of the central charge of the uranium nucleus.

The nearer it is to the centre the greater the speed at which it will be ejected. To be ejected at its actual speed, the distance must be considerably greater than  $4 \times 10^{-12}$  cm., viz.,  $6.3 \times 10^{-12}$  cm. If, on the other hand, it has a velocity of its own in the nucleus to begin with, through moving in an orbit, the distance from the centre at which it must start will be greater than this. If the interpretation of the experiments is correct, the classical laws seem to break down.

On ordinary mechanical principles, however, independently of the particular nature of the mechanism, if a particle is expelled from a nucleus at a certain velocity, when it is fired back at the nucleus at the same, or at a greater velocity, it should be able to penetrate the nucleus. Whereas the experiments seem to show that for the uranium nucleus even the fastest  $\alpha$ -particles are unable to penetrate into it.

**The Wave Mechanics Theory of Atomic Disintegration.—** On the wave mechanics, apparently, there is no such thing as an impossibility, and, in this respect, at least, it should appeal strongly to the type of mind most in evidence in the

<sup>1</sup> See Table of Isotopes, Chart of the Periodic Law.

world prior to the pragmatic justification of scientific conceptions. It supposes the nucleus to be surrounded by a potential barrier, through a reversal of the Coulomb law of repulsion at small distances. But, on the wave mechanics, the barrier is not an absolute one, as it would be in classical mechanics, but a probability barrier. There is a definite calculable probability of an  $\alpha$ -particle inside the barrier being able to "leak through" it, although on classical conceptions it would be completely unable to surmount it. It is as if, although no athlete can clear a barrier ten or twenty feet high, and the greatest distance any one of them can jump is six feet, yet, if you get enough athletes together, one will occasionally clear the barrier by some unsportsmanlike method of sneaking through it. Clearly this depends as much on the barrier as on the athlete, and from the wave mechanics standpoint both conspire to defeat impossibility.

Nevertheless this theory purports to be able to account for the disintegration of the radioactive atom by this conception, and claims to get better quantitative agreement than other theories for the Geiger-Nuttall relation between the period and the range of the  $\alpha$ -particle expelled. It does not seem so far to have given any new information, or elucidated the one clear exception to the Geiger-Nuttall relation, radioactinium and actinium X. But as it does not attempt anything so ordinary as the explanation of the known in terms of the unknown, but, like relativity, tries rather to explain the known in terms of the unknown, this is perhaps too much to ask of it. The "explanation" seems to amount to little more than fitting certain calculated numbers to the special cases.

**Long-Range  $\alpha$ -Particles.**—Closely connected with this subject is another which is now being intensively studied, and which was alluded to on page 103. In addition to their normal  $\alpha$ -particles, radium C' and thorium C' both emit a few of much greater range. Per million of normal  $\alpha$ -particles in each case, thorium C' emits 34 of range 9.78 cm. of air and 189 of range 11.66 cm., and radium C' emits 17 of range 9 cm. and 5 of a variety of ranges up to 11.5 cm. It appears that these originate in the actual disintegration of the radioactive nucleus, and not, as in the case of the long-range H-particles just dis-

cussed, in subsequent collisions of the  $\alpha$ -particles with nuclei in their path.

A very beautiful cloud photograph of the rays of thorium C+C', obtained by Fraulein Lise Meitner and Dr. K. Freitag, is shown in Fig. 67. It will be seen that among the great numbers of rays of 8·6 cm. range, a few of the longer ranges, both 11·6 and 9·8 cm., are clearly visible.

The phenomenon has recently (1931) been minutely studied, both for the case of radium C' and of thorium C', by the aid of the differential valve method of recording  $\alpha$ -particles described on page 281. The thorium C' long-range  $\alpha$ -rays appear to be much more homogeneous, as well as more numerous than those from radium C', and to consist of only two well-defined types. The longer range type of range 11·66 cm. is the most energetic  $\alpha$ -ray known. Its velocity corresponds to a potential fall of 5·3 million volts—that is to say, a stationary  $\text{He}^{++}$  ion would have to move between two points differing in potential by 5·3 million volts in order to acquire the energy and velocity of the longest range  $\alpha$ -particle. These rays have now been examined as closely as the corresponding radium rays, which were done first, and all the previous conclusions have been confirmed.

In the long-range  $\alpha$ -rays of radium, no less than nine types have now been distinguished. The type of 9 cm. range, which comprises more than three-quarters of the whole, is accompanied by one type of shorter and seven types of longer range, which are not uniformly distributed as regards their ranges, but fall into definite groups. The theory is advanced that these rays originate from the radium C' atom, when it is still in an "excited" state. The fact that the phenomenon is shown only by the two shortest-lived radio-elements, the periods of which are estimated to lie between a millionth and a billionth of a second, makes it appear plausible that in these cases the atom has not always had time to settle down from the consequence of the preceding disintegration—that is to say, from the emission of the  $\beta$ -particle from the C members in the disintegration in which the C' members originate.

**The Excited Nucleus.**—Quantum ideas have now invaded the interior of the nucleus and, though this may appear at



FIG. 40.—LAUE SPOT DIAGRAM OF ZINC SULPHIDE.



FIG. 67.—LONG-RANGE  $\alpha$ -PARTICLES OF THORIUM C'.

*To face p. 296.*



first sight fantastic, in view of the quantum explanation that has been advanced in this book (p. 219) as to why an electron falling into a nucleus must come to a stop before it reaches it, it is not really so, and the invasion has justified itself by the results. Just as, if we approach the earth from outer space, the force of gravitation reaches a maximum at the surface and falls to zero as we penetrate to the centre, so inside the nucleus the electric field must decrease to zero at the centre. The centre, in fact, corresponds to a point at infinite distance outside, and as we pass from the centre outwards, the electric field will increase just as in passing from an infinite distance outside to the surface. We have a curiously inverted condition of things inside, for, as we approach the centre, the force, instead of increasing inversely as the square of the distance, now decreases proportionally to the distance. It is clear, whether we deal with electrons or positively charged particles, that if quantum conditions apply, they will be totally different from those that obtain outside. But no one as yet seems to have worked them out. The paradoxical deductions of the wave-mechanics are, at present, all the fashion, whereas here it would appear that something reasonably straightforward as regards the nature of atomicity might be discovered.

As detailed in the next chapter, atomic nuclei are now regarded as almost wholly constituted of helium nuclei and electrons, in other words, of potential  $\alpha$ - and  $\beta$ -particles. Nothing seems yet to have been hazarded as to the latter, but the former are regarded as occupying quantised orbits. Just as for the electrons in the outer region of the atom these are normally in states of lowest total energy. But the potential  $\alpha$ -particles may also be in "excited" states of higher total energy, being evicted to these from the normal or "ground" level with an absorption of energy. The agency effecting this was first sought in the  $\beta$ -ray ejected in a  $\beta$ -ray change. But now, as detailed in the last section of this chapter,  $\alpha$ -particles on their ejection in an  $\alpha$ -ray change are also considered to be effective.

As regards the explanation of the long-range  $\alpha$ -particles, it is supposed that some of the  $\alpha$ -particle "levels" in the resulting atom remain disturbed after the ejection of the

$\beta$ -particle for an appreciable, though quite short, time. If the second disintegration, in which the  $\alpha$ -particle is emitted, takes place before the atom has settled down, instead of the  $\alpha$ -particle coming from its normal "level" in the nucleus, it may be at the moment of disintegration still in an excited state and be expelled, in consequence, with a higher speed and kinetic energy.

In fact, as the reader will recognise, there is here beginning a very interesting application of the ideas that have become current since the Bohr theory of the origin of spectra, in which chemists have already sought the explanation of the "activation" precedent to chemical change, to the case of the radioactive changes that occur within the nucleus. The theory is tentative in its present form and is associated with an interpretation of the origin of the  $\gamma$ -rays on the same lines.

**Theory of the Origin of the  $\gamma$ -Rays.**—It is known that the  $\gamma$ -rays, which appear to accompany the  $\beta$ -ray transformation, as of radium C into radium C', in reality are subsequent to it. They are now ascribed to the "jump" of an excited  $\alpha$ -particle, put into a higher level by the  $\beta$ -ray emission, back again into its normal or ground level. Thus we have two really quite independent processes going on, which lead, according to which occurs first, either to the emission of a long-range  $\alpha$ -ray or to the emission of a definite  $\gamma$ -ray. What corresponds to the "activation" of the molecule, preceding chemical change, is here the primary emission of the  $\beta$ -particle. This "activates" the radium C' atom produced. But, the time, on the average, in which the potential  $\alpha$ -particle remains in the higher level is very short, and only a few of the total number of RaC' atoms disintegrate while in this state.

For these few, the long-range  $\alpha$ -particle is expelled, the excess energy, over that of the normal  $\alpha$ -particle of 7 cm. range, being that absorbed by the  $\alpha$ -particle in the activation process. The vast majority of RaC' atoms settle down before they disintegrate, and in this settling down they emit the energy absorbed in the activation process as a single quantum of  $\gamma$ -ray energy.

It follows from this explanation that there should be correspondence between the various frequencies, or wave-

lengths, of  $\gamma$ -rays emitted and the excesses of kinetic energy possessed by the various types of long-range  $\alpha$ -rays over that possessed by the normal  $\alpha$ -rays. Some such correspondences appear to exist. But it also has to be supposed that "settling down" may not result in the emission of  $\gamma$ -rays, but frequently in the emission of the homogeneous secondary types of  $\beta$ -ray accompanying the disintegration, which were referred to in the opening paragraph of Chapter VIII.

The later work on the rays of thorium C' and actinium C has not revealed any connection between the long-range  $\alpha$ -rays and the  $\gamma$ -rays, of the kind found for radium C', and it appears that in these cases the phenomena may not be of the same type. Alternatively it may be said that, owing to the excessively short period of thorium C', even as compared with radium C', the excited atoms have less chance of returning to the normal state before disintegration. The  $\gamma$ -rays given by thorium C' are much weaker than those from radium C', as they should be on this theory. Also the long-range  $\alpha$ -rays are more numerous.

The subject has become exceedingly complex, and it is perhaps hardly to be expected that the exceptional long-range  $\alpha$ -rays can be explained before the normal  $\alpha$ -ray emission is better understood. Also the doubt remains whether the exceedingly penetrating  $\gamma$ -rays, put into evidence by absorption methods, may not have too short wave-lengths to be effectively resolved by the crystal grating method (p. 123).

So far no work has been done on the  $\beta$ -rays of abnormally high kinetic energy comparable with that recently done for the long-range  $\alpha$ -rays. It is possible, as has already been indicated, that they also are to be regarded as exceptional in the same sense as the long-range  $\alpha$ -rays, and to have a similar mode of origin.

**Short-Range  $\alpha$ -Particles.**—The theories just described, applying quantum ideas to the nucleus, not only explain the emission of the long-range  $\alpha$ -particles, but they predict<sup>1</sup> that some of shorter range than the normal should be emitted, if the expulsion of an  $\alpha$ -particle, like that of the  $\beta$ -particle,

<sup>1</sup> *Constitution of Atomic Nuclei and Radioactivity*, by G. Gamow, Oxford Clarendon Press, 1931.

is able to put the nucleus in an excited state. For, in this case, the energy absorbed in excitation will be at the expense of, instead of being added to, the energy of the  $\alpha$ -particle expelled. In addition to  $\alpha$ -rays of velocity and range lower than normal, there will be also an emission of  $\gamma$ -rays, as the excited nucleus settles down. The energy of disintegration will be, in fact, divided between  $\alpha$ -rays and  $\gamma$ -rays, so that the former which produce the latter will themselves be of lower velocity and energy than those  $\alpha$ -rays which do not excite the nucleus.

Even before this prediction, evidence of this effect was obtained in 1929 by Rosenblum, working in Paris, with an enormous electromagnet, capable of deviating the  $\alpha$ -rays into a complete semicircle of 25 cm. diameter. This itself was a feat never before attempted for the  $\alpha$ -rays. The method was introduced in 1913 for the easily deviable  $\beta$ -rays by Danysz, and is called the focussing method. For a diverging pencil of rays, if coiled by the field into similar circular paths, after starting to diverge, converges again, and comes to a focus half-way round the complete circle.<sup>1</sup> The experimental advantage gained cannot be overstated, as powerful divergent pencils of rays may be used, instead of weak narrow ones canalised by fine slits. It has proved invaluable in the study of the  $\beta$ -rays. Aston's successes, detailed in the next chapter, are also due to a very similar effect.

In this way Rosenblum examined the homogeneity of several types of  $\alpha$ -ray. Whereas those from RaA, RaC', RaF, and ThC' all proved to be completely homogeneous, those from ThC, of range 4.3 cm., were not. He found them to consist of two distinct groups, differing only by one part in 300 in velocity, the faster being only one-third as numerous as the slower. In addition, three other groups of velocities, 97.2, 96.1, and 92.8 per cent. of the fastest, were present in minute relative numbers, respectively 2, 1.5, and 0.4 per cent. of the whole.

Gamow, who explains them on the above theory, has shown that the energies of these various groups of  $\alpha$ -rays

<sup>1</sup> Incidentally, this is well shown in Fig. 35 (p. 118). If, in the lower picture, the two circles on the left are followed, it will be seen that they intersect when half-way round, and they may be regarded as the boundaries of a divergent pencil of  $\beta$ -rays, focussed by the magnetic field.

correspond exactly on quantum principles with the wavelengths of six types of homogeneous  $\gamma$ -rays emitted by the complex, ThC. So that it would appear that, in this case, only about one-quarter of the  $\alpha$ -particles succeed in escaping without exciting the nucleus. The rest raise it to various excited levels corresponding with diminution of their own energy and with the energy of the emitted  $\gamma$ -rays.

Evidence of a similar heterogeneity of the  $\alpha$ -rays for AcC, obtained subsequently by the new valve methods, has been already described (pp. 171 and 281). The phenomenon at first appeared to be confined to the disintegration of elements of odd atomic number, and it has been predicted that the  $\alpha$ -rays of protactinium will probably also show a similar heterogeneity. But Mme. Irene Curie-Joliot, a daughter of Mme. Sklowdowska Curie, even more recently, in an examination of the range of the  $\alpha$ -rays of radioactinium, by the Wilson track method, has shown them to consist of two groups in about equal proportions, differing from one another by about 3 mm. in range. Since then, actinon has also been stated to give two groups of  $\alpha$ -rays differing by about 3 mm. in range. In these cases, also, a  $\gamma$ -radiation is known to accompany the emission of  $\alpha$ -rays.

**The Neutron.**—A number of discoveries in this field, made in the last two years, have now (1932) been interpreted as due to the "neutron," that is, to an uncharged atomic nucleus consisting of a proton and an electron in close union. Beryllium, under bombardment with  $\alpha$ -particles, unlike other light elements which give protons as H-rays, has been found to give a weak radiation, probably of quite new type, *more penetrating than the  $\gamma$ -rays*, and this new ray gives, on passage through the light elements, H-rays or similar swiftly recoiling atomic nuclei.

It has been suggested by Chadwick that it is the neutron, travelling at a speed estimated as one-tenth of light. Its very great penetrating power is explained by its absence of charge, since it is to be expected that such a projectile would pass freely through the outer electronic structures of atoms without ionising them. But in the rare collisions with atomic nuclei it should act like an  $\alpha$ -particle, occasionally disintegrating them. If this is correct the neutron should prove an invaluable new weapon in the study of the nature of the nucleus.

## CHAPTER XVIII

### THE ISOTOPES OF THE INACTIVE ELEMENTS

**The Non-Radioactive Isotopes.**—The existence of a nucleus in the atom, as an independently variable component of the atomic structure, comes chiefly into evidence, for the elements that are not radioactive, through the existence of isotopes among these elements. Indeed, our most definite knowledge of the nucleus and the part least dependent upon theories as to its nature comes from the exact study of the mass relations between the individual isotopes that make up the chemical elements. By far the larger proportion of the 64 elements as yet examined are mixtures of from two to as many as eleven different isotopes, which differ in extreme cases by as much as 12 units of mass. Only 22 of the 64 are "simple" or "pure" elements, and the probability is that many of these will ultimately be found to contain isotopes in too small proportion yet to have been revealed. This has happened for carbon, oxygen, and probably nitrogen, which, so far as the positive ray method of analysis can tell, are homogeneous. But recently, from observations on the band spectra, carbon, in addition to the atom of mass 12, has been found to have a few of mass 13, though the proportion can only be one or two parts in a thousand at most. Oxygen, similarly, appears to contain isotopes of mass 17 and 18, in addition to the main constituent of mass 16, and these are estimated to be present in proportion 1:10,000 and 1:1,250 respectively. It is estimated that the mean atomic weight of oxygen is about 1.25 parts per ten thousand greater than it would be if it were a homogeneous element with all the atoms of the same mass as the majority. This is a very small difference, but it becomes of importance as oxygen is the standard on which all the other atomic weights are now universally expressed.

The general prevalence of isotopes among the elements shows how little the ordinary chemical and physical properties of matter depend on the atomic nucleus. Otherwise it could

not have occurred that chemists for centuries should have taken these composite mixtures for homogeneous elements. Even now we know their isotopic composition it is difficult, if not impossible, to effect even a partial separation, and only two or three have been actually separated to a detectable extent. Apart from the newer methods of determining the masses of the individual atoms by the magnetic and electric deviation of their ions, the only methods available for revealing isotopes are diffusion processes, unidirectional distillation in a practically perfect vacuum (p. 179), and band spectra.

**Band Spectra of Isotopes.**—In recent developments, band spectra are playing an increasingly important part, because they are capable of detecting the existence of isotopes in much smaller quantity than the other methods. For spectra that arise through electronic changes in the atoms, the mass of the latter does not enter to a sufficiently great extent to be of importance, and the atomic spectra of isotopes are, at least to an exceedingly close approximation, identical. But band spectra are molecular rather than atomic in origin, and for these the mass of the molecule has an appreciable influence on the frequency of the light. Thus, for the case of an element like chlorine, with two isotopes of mass 35 and 37, there will be three superimposed band spectra, corresponding with the molecules  $\text{Cl}^{35}\text{-Cl}^{35}$ ,  $\text{Cl}^{37}\text{-Cl}^{37}$  and  $\text{Cl}^{35}\text{-Cl}^{37}$ . The case is simpler for hydrogen chloride, where only two forms,  $\text{HCl}^{35}$  and  $\text{HCl}^{37}$ , can exist, and it was with this that the effect was discovered.

Careful investigation with modern instruments of high resolving power is capable of analysing these superimposed band spectra, and, as has happened for carbon and oxygen already, can reveal isotopes in quantity too small to be otherwise appreciable. As this method is quite recent, similar results are to be expected in the case of other elements now classed as "simple" or "pure." Nitrogen has now been suspected by this method to have a small proportion of the isotope  $\text{N}^{15}$ . If this is so, it proves the first exception to the rule for odd number elements, referred to later.

**The Parabola Method.**—The original method of positive ray gas analysis, due to Sir Joseph Thomson, depended on the

action of the magnetic field and the electric field being "crossed," so that they deflected the beam in directions at right angles to one another and to the direction of the beam. In this way the beam was spread out into a curved surface, and, if received on a photographic plate normal to the original direction of the rays, produced, for each different value of  $m/e$ , a different parabolic trace, from which the value of  $m/e$ , and therefore of  $m$ , could be deduced. The method has been replaced by a more accurate one due to Aston, but still has a certain special usefulness as well as an historical interest.

Fig. 68 is a diagram of the apparatus, in which A is the bulb, and D the anode. The cathode B has a hole bored

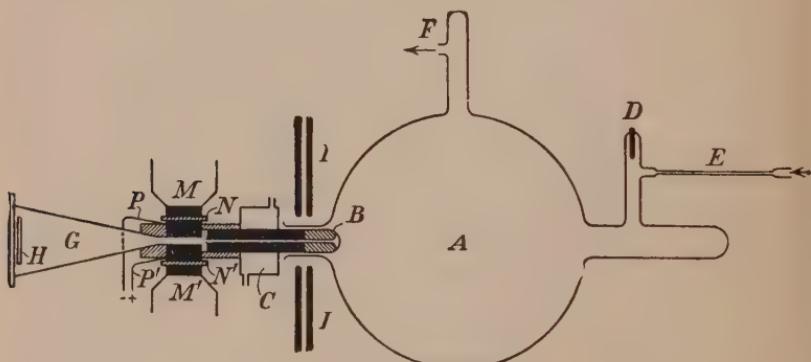
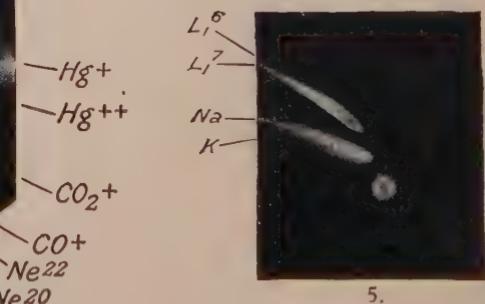
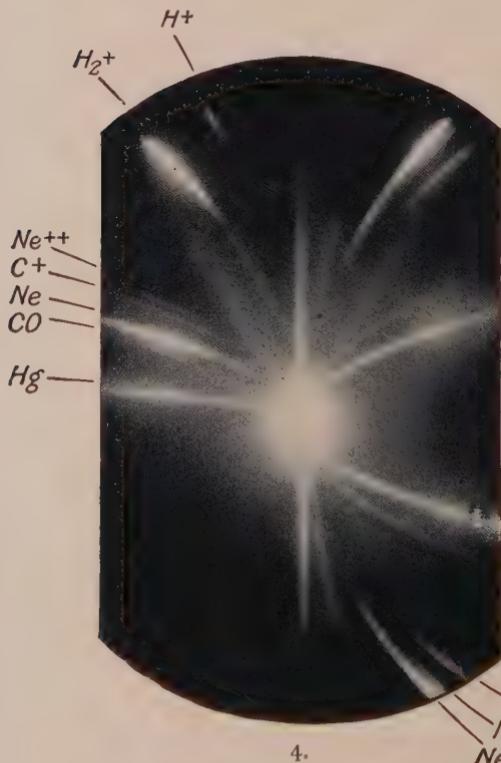
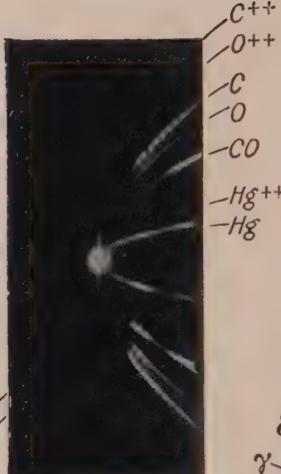
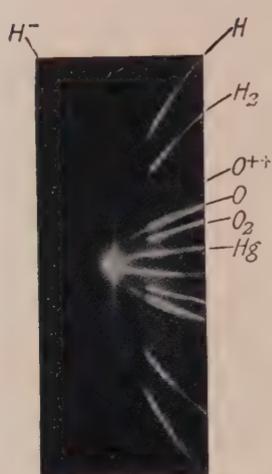


FIG. 68.

through it, canalising the positive rays which pass through the perforated cathode during the discharge. The beam traverses the tube behind the cathode on its way to H, which is either a fluorescent screen or a photographic plate, passing through the electric field between the parallel plates, P, P', and between the poles of the electromagnet, M, M'. Soft iron screens, I, I', shield the discharge bulb from the effect of the magnet.

Fig. 69 shows a collection of representative parabolas obtained by Aston by this method, with the nature of the positive ions producing them shown in many cases at the sides. The magnetic field deflects the rays in a vertical and the electric field in a horizontal direction. Nos. 1 and 2





The Parabolas of Neon.

The Parabolas of Lithium.

FIG. 69.—REPRESENTATIVE POSITIVE RAY PARABOLAS.

To face p. 305.

are for the ordinary gases, hydrogen, mercury vapour, oxygen and carbon compounds, normally present in the discharge bulb. These are duplicated as regards the top and bottom halves by reversing the magnetic field for the two exposures. No. 4 is of the greatest interest in the present connection. The right-hand half has the top and bottom duplicated as in Nos. 1 and 2, the photograph in the top left-hand quadrant being an entirely separate exposure with a weaker magnetic field and the electric field reversed. They refer to neon. The main parabola due to neon, of mass 20, is the lowest in the right-hand bottom corner, and it is accompanied by a much fainter companion on its upper side which is due to the isotope of mass 22. Since the atomic weight of neon is 20·2, this heavier isotope must be present to the extent of some 10 per cent. of the whole. This discovery, though of course it was not, till later, interpreted as being due to an "isotope" of neon, was made in 1913, contemporaneously with the general recognition and explanation of isotopes from the Displacement Law and the nuclear theory of the atom. No. 5 is a more recent result showing the parabolas of the two isotopes of lithium, Li<sup>6</sup> and Li<sup>7</sup>.

**Aston's Method.**—The improved method of Aston differs from the parabola method, mainly in that the electric field and magnetic field deviate the path of the positive rays in the same plane, instead of in planes at right angles. The rays are first deviated by the electric field in one direction and then by the magnetic field through an angle three or four times as great in the opposite direction. This peculiar disposition brings in an experimentally invaluable result. The beam of positive rays, however carefully canalised, is necessarily divergent, and to try to minimise this by using still narrower slits is to reduce correspondingly the intensity of the rays to the point at which long exposures are necessary, and the results too feeble to detect the weaker components. The arrangement described brings in a focussing effect, whereby the divergent beam is made to converge again to a sharp image of the slit at different positions, depending on the value of  $m/e$ , along a certain plane where the photographic plate is placed. This is shown in Fig. 70.

The beam of positive rays is shown as a dotted line passing through the canalising slits,  $S_1$ ,  $S_2$ , and then through the electric field between the parallel plate,  $P_1$ ,  $P_2$ , to the central point  $Z$ , at which it is represented as deflected through an angle  $\theta$  downwards, the actual deflection being of course gradual. From  $Z$  it is shown as a slightly divergent pencil passing through the magnetic field represented by the circle with  $O$  as centre, being turned upwards between  $3\theta$  and  $4\theta$ , and falling on the photographic plate,  $FG$ , at  $F$ , the plane

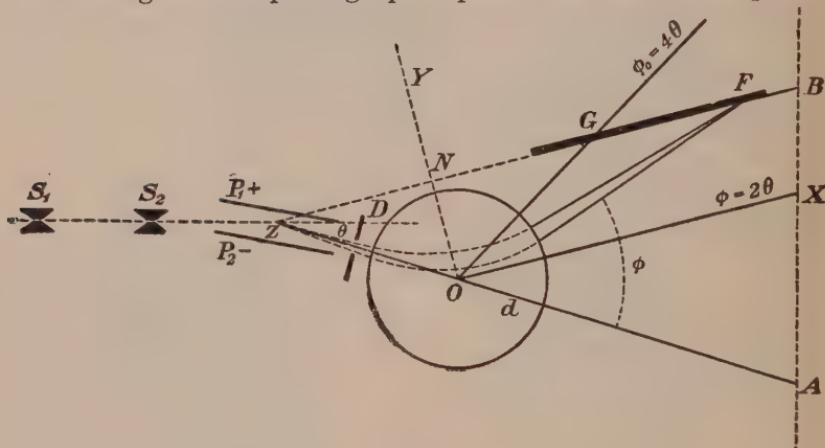


FIG. 70.

of which passes through the centre point of the electric field,  $Z$ . The easily deviated rays, with small  $m$ , fall near  $G$ , and the difficultly deviable ones with large  $m$  near  $F$ . The result is that each kind of particle registers an image of the slit on the photographic plate at a position depending on its mass—strictly on its mass divided by its charge (p. 187)—and one obtains a photograph of sharp lines, as in a spectrum, in which the individual lines represent not wave-lengths but masses. Hence it is termed a mass spectrum.

**The Mass Spectrograph.**—The instrument by which it is obtained is termed a mass spectrograph. Fig. 71 represents a diagram of the construction, and Fig. 72 a photograph of the original Mass Spectrograph set up in the Cavendish Laboratory, 1919. In the first  $B$  is the discharge bulb,  $C$  the concave perforated cathode,  $A$  the anode, and  $D$  a

quartz bulb serving as anti-cathode to protect the glass walls of B from the impact of the powerful beam of cathode-rays. The photographic plate is W, T is a lamp for printing on the plate a fiducial spot through the tube R to record the exact position of the plate in the apparatus, I<sub>1</sub> and I<sub>2</sub> are charcoal bulbs, cooled in liquid air during an experiment to improve the degree of vacuum, and V an arrangement for winding the plate up to enable several photographs to be taken on the one plate without removing it from the apparatus. In the photograph, Fig. 72, the induction coil is under the table, the high potential lead from it being shown connected to the anode, A, L being the high potential leads to the parallel plates, suspended from above, G the rotary mercury pump to exhaust the apparatus, C a small gas reservoir in

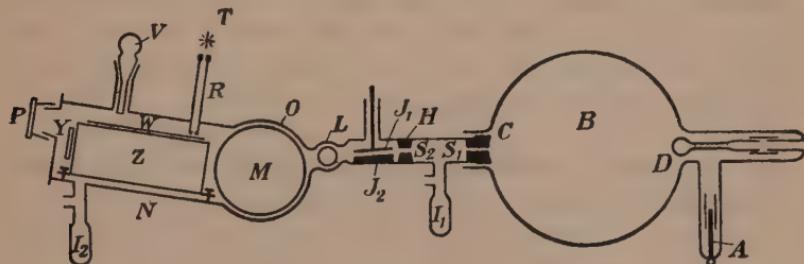


FIG. 71.

which the gas under examination is stored, and S a soft iron shield to protect B from the influence of the magnet. A new apparatus, with which a much higher degree of accuracy has been attained, has since been built, so that now, in favourable cases, the atomic masses of the individual isotopes, or mass numbers as they are called, can be determined to an accuracy of 1 in 10,000, an accuracy only approached in the finest atomic weight determinations of the chemist.

As already explained (p. 187), and well illustrated in Fig. 69, No. 3, the Multiply Charged Parabolas of Mercury, the charge on the ion may be either  $+e$ ,  $+2e$ ,  $+3e$  and so on, and the terms "first order," "second order," "third order" . . . spectrum are used to distinguish the corresponding lines, by analogy with grating spectra. The task of distinguishing between the various orders is not difficult to the experienced investigator. A peculiarity of the method is that, as in

the production of spark spectra (pp. 225 and 232), an ion need only have a momentary existence, sufficient to traverse the tube at high velocity, to record its mark on the plate and, hence, many ions are shown which have no stable permanent existence as chemical compounds. Typical of these is the "first carbon group," due to  $C^+$ ,  $CH^+$ ,  $CH_2^+$ ,  $CH_3^+$  and  $CH_4^+$ , with mass numbers 12, 13, 14, 15 and 16, the last being also shown by the ion  $O^+$ . Usually, in a fresh tube, these are followed by 17 and 18, due to the ions  $OH^+$  and  $OH_2^+$ , of water vapour. This group furnishes a valuable set of lines of known mass number to which to refer those of unknown mass, as hydrocarbons are invariably present in the tube, from the vapour of the grease necessary to lubricate the taps. A "second carbon group," due to ions containing two atoms of carbon, is found, corresponding to every integral mass number between 24 and 30. By comparison with such and similar known lines the mass numbers of the unknown isotopes have been determined.

**The Isotopes of Neon, Chlorine, Argon and Krypton.**—Fig. 73 (facing p. 310) illustrates a series of eight separate mass spectra, numbered I to VIII, taken with the original instrument, some of them of as great historical interest as the plates of the astronomer that record the first appearance of a new planet in the solar system. No. I is for neon, and, in addition to the carbon reference lines, it shows the strong line due to  $Ne^{20}$  and the weak line due to  $Ne^{22}$ , first observed by the parabola method, with beautiful clearness. Nos. II and III, for chlorine, were an even more crucial test, since this element, with the fractional atomic weight, 35.46, had been early marked down as probably a mixture of isotopes, and these photographs first proved it. No. III shows a group of four lines of mass numbers 35, 36, 37 and 38, as well as 20 due to neon from the last experiment, and 44 due to  $CO_2^+$ . These four lines are due to the two isotopic forms of chlorine,  $Cl^{35}$  and  $Cl^{37}$ , and of their hydrogen compounds,  $HCl^{35}$  and  $HCl^{37}$ , already alluded to. Plate II shows also two faint second-order lines at 17.5 and 18.5 due to  $Cl^{35}++$  and  $Cl^{37}++$ . Since there are no corresponding lines for 18 and 19, this is one of the proofs that the former lines, 36 and 38, are due to

the hydrogen compounds and not to other chlorine isotopes, since compounds show the second-order lines but rarely. A further proof was obtained by the parabola method, which frequently shows, particularly with electronegative elements like chlorine, negative parabolas oppositely disposed to the positive ones. These practically never appear with compounds. The negative parabolas due to  $H^-$  can be clearly seen in Fig. 69, No. 1, and those due to  $O^-$  and  $C^-$  faintly in No. 2. Negative parabolas corresponding *only* with  $Cl^{35-}$  and  $Cl^{37-}$  were obtained. No. IV, Fig. 73, for phosgene gas,  $COCl_2$ , is confirmatory, as it shows, in addition, the lines 63 and 65, corresponding with  $COCl^{35+}$  and  $COCl^{37+}$ .

Nos. V and VI are for argon, and show, in addition to the main isotope  $A^{++}$ , 20, and  $A^+$ , 40, in No. VI, a faint line at 36, due to  $A^{36+}$ . The atomic weight of argon is 39.94, and the lighter isotope, of mass number 4 units less than the main one, is only present in minute quantity. No. VIII for krypton, with atomic mass 82.9, revealed the extremely complex composition of this gas, no less than six isotopes of mass numbers, 78, 80, 82, 83, 84 and 86 being shown by their first-order lines and the last five by their second-order lines also.

**The Atomic Weight of Hydrogen.**—Spectrum No. VII, showing four separate photographs lettered *a*, *b*, *c* and *d*, is in a different category. They were designed to test the chemists' atomic weight of hydrogen, 1.00775 on the O=16 standard, by comparing it with helium, the atomic mass of which is nearly integral, 4.0022 on the oxygen standard. By this time it had been found that all the mass numbers of individual isotopes, to the degree of accuracy this first instrument was capable of, were practically exact integers on the oxygen standard, and it was desired to see if hydrogen was really an exception. The method was so to adjust the fields as to "bracket" the line due to the one ion between two due to the other, with which its mass was to be compared. In *a*, *b* and *c*, this was done in such a way that, if the mass of the ion in the centre was exactly twice that of the mass of the other, it would be exactly midway between the other two.

For *a* and *c*, in which the hydrogen molecule,  $H_2^+$ , is brack-

eted between two hydrogen atoms,  $H^+$ , it is, as it should be, midway. But in *b*, in which the helium atom,  $He^+$ , is bracketed between two hydrogen molecules  $H_2^+$ , it will be seen that it is much closer to the one than to the other. In *d*, the hydrogen molecule is bracketed between two helium atoms, and again it is seen displaced to the side. By these ingenious methods, Aston was able exactly to confirm the atomic weights assigned by chemists to hydrogen and to helium, and to show that, on the oxygen standard, hydrogen departs from unity by nearly eight parts in a thousand.

**Table of Isotopes.**—The table of isotopes, printed to the left of the chart of the Periodic Table at the end of the volume, shows the results of these and similar experiments brought up to the date of writing, November, 1931, but new results are continuing to appear, with no evidence as yet that the possibilities are exhausted. Most of the results are due to Aston, but a few are due to Dempster of Chicago by a rather different technique. Sixty-four of the possible 92 elements have, so far, been examined, and, of these, only 22 (21 if nitrogen is excluded), have proved to be entirely "pure" or "simple" elements. The rest are mixtures of isotopes, tin being, so far, the most complex, containing 11 isotopes with mass numbers varying over a range from 112 to 124. It is even possible that, with more sensitive methods of detecting infinitesimal amounts of other isotopes, such as the band spectrum method already described, hydrogen may ultimately prove to be the only really homogeneous element!

Every element up to zirconium, atomic number 40, figures in the list, but of the 52 subsequent, so far only 24 are included. The main experimental difficulty, which has precluded these from examination, appears to be in getting them to give positive ions sufficiently abundantly for the purpose, but no doubt in time these difficulties will be surmounted. Perhaps the most interesting point that emerges is the marked difference between the elements of even and odd atomic number. Of the former, only helium, beryllium, titanium and uranium are homogeneous elements. Uranium, which has just been done, is stated to be homogeneous, at least up to a limit of from 2 to 3 per cent. Of the 30 others, no less



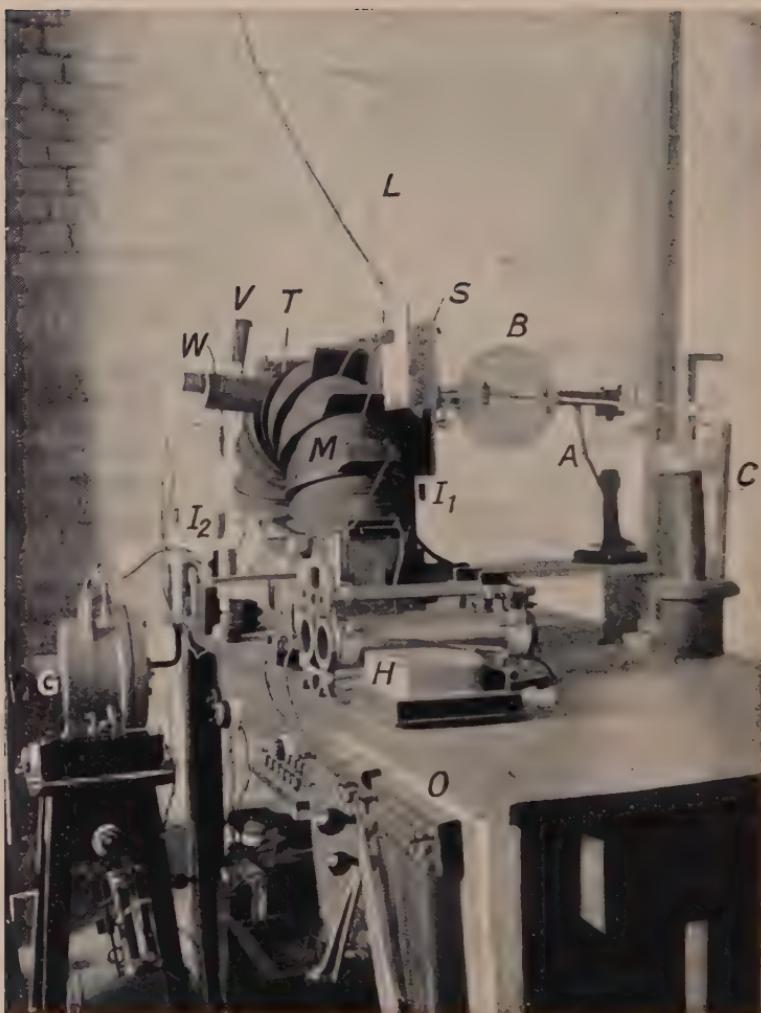


FIG. 72.—PHOTOGRAPH OF THE ORIGINAL MASS-SPECTROGRAPH SET UP IN THE CAVENDISH LABORATORY IN 1919 BY F. W. ASTON.

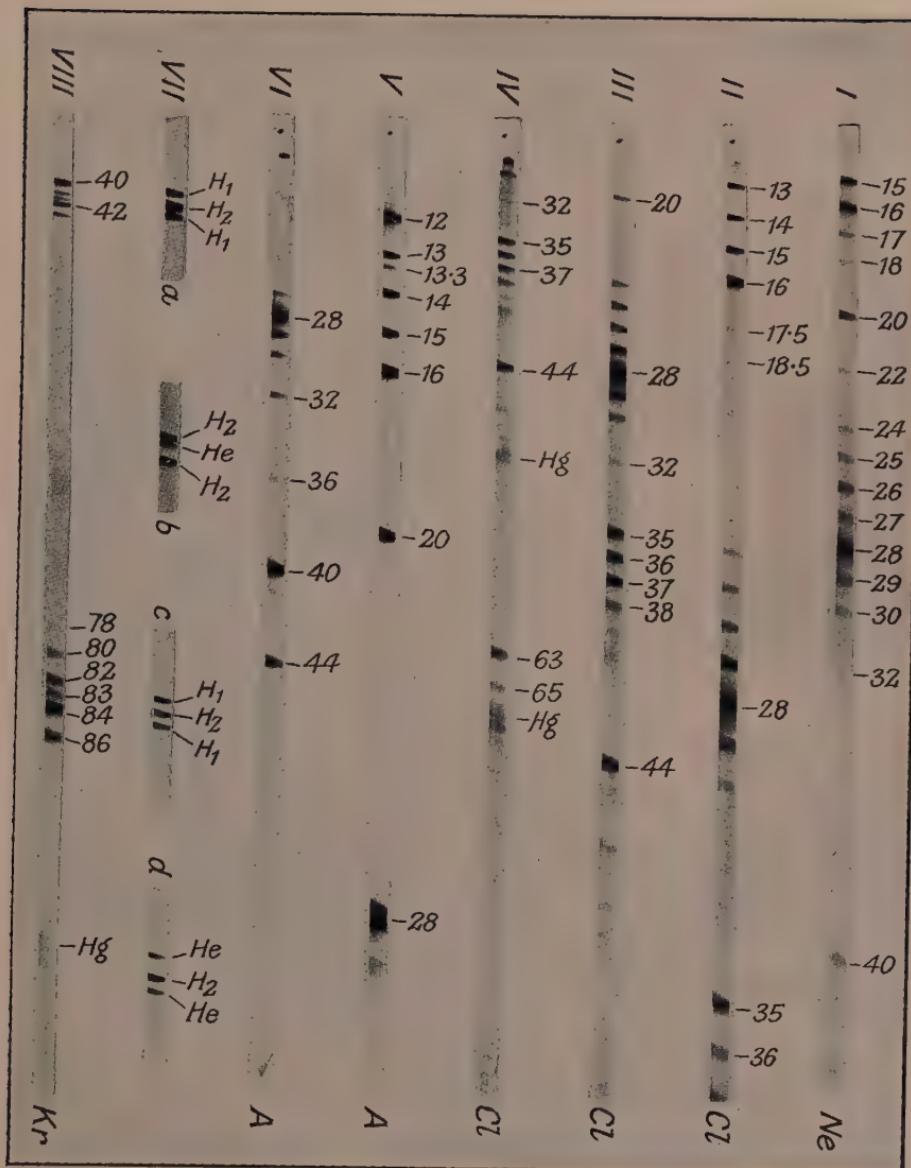


FIG. 73.—MASS SPECTRA OF NEON, CHLORINE, ARGON, KRYPTON, HELIUM AND HYDROGEN BY F. W. ASTON.

To face p. 310.



than 133 isotopes exist, an average for each of between 4 and 5.

Of the 30 odd numbered elements, no less than 17 are homogeneous, and the remaining 13 are all alike in possessing only two isotopes, the mass numbers of which are always two consecutive odd numbers. Moreover, except for the first two, lithium and boron, and the last two, rhenium and thallium, for which the converse is true, the lighter isotope is the more abundant of the two. Thus, the composition of chlorine, with two isotopes of mass number, 35 and 37, is typical of 12 other elements, and in no case yet is an odd numbered element known with more than two isotopes. This is probably the most interesting and suggestive generalisation that has come out of this part of the work, and, as yet, no explanation has been forthcoming.

**Isobars.**—As results accumulated, isotopes of different elements with the same mass number have been found and are now fairly common. These are called isobars. The first example is chromium and iron, each of which have isotopes of mass number 54, and after this, isobars become numerous. All three isotopes of tellurium are isobaric with isotopes of xenon. Up to 100, only 15 mass numbers are missed, and from 9 to 37 there is a run with every number represented. After 50, only 5 remain unrepresented. There would thus appear to be considerable flexibility about the constitution of the nucleus, especially as it becomes more complex. The constituents can form stable aggregates in a large number of different ways. This naturally raises the question whether the isotopes of the same element, with the same mass number, are always really homogeneous—a further complexity which, at present, would absolutely defy experimental detection. But it seems only reasonable to suppose that two nuclei might have the same mass and nett charge and yet be differently put together, so that, if transmutation were possible, they might be transmuted into different elements. But nothing short of actual transmutation would suffice to reveal this difference, if it exists. This must, however, be borne in mind in weighing the validity of the lead ratio method of estimating the age of minerals, discussed in the next chapter.

In the branching at the end of the thorium series we seem to have a clear example of this. For in each branch an isotope of lead, of mass number 208, results. It is unlikely, owing to the very different energies lost by the nucleus in the two branches, that they are identically constituted.

**The Resuscitation of Prout's Hypothesis.**—Since, to a very close approximation, all the elements so far examined, except hydrogen, have integral mass numbers in terms of the oxygen standard, Prout's hypothesis, as mentioned in Chapter III., that the elements are essentially all built up out of hydrogen as the primary constituent, or "protyle," has once again come to the fore. On modern views the high value for hydrogen itself is definitely to be expected. For it is the only element, if this hypothesis is correct, in the nucleus of which are no constituent electrons. It is the pure positive atomic charge,  $+e$ . The helium nucleus, if it is really compounded of four hydrogen nuclei, or protons—to use the term coined to suggest this hypothesis—since the atomic mass is four and the atomic number two, must necessarily have in its nucleus two constituent electrons, in addition to the two forming its external K shell. It can be shown that, in compounding a nucleus out of four protons and two electrons, the attractions of the protons and electrons for one another will outbalance and overcome the mutual repulsions between the protons and between the electrons respectively. In its formation, therefore, there will be a loss of energy, and this is tantamount to a loss of mass, whether on the older theory of the electromagnetic origin of mass, or upon the newer and broader theory of relativity. The actual difference of mass, between the helium atom and four hydrogen atoms plus two additional electrons, is 0.030 of a unit, and this corresponds to an evolution of energy of  $0.03 \times 9 \times 10^{20} = 2.7 \times 10^{19}$  ergs (p. 198). This is for the formation of the gram-atom of helium, 4.0022 grams, from hydrogen and electrons, and corresponds, per gram of helium, to an evolution of energy of about 160,000 million calories. This is some forty times greater than is evolved in the disintegration of a gram of uranium (p. 199). Atom for atom, however, the evolution from uranium is about one and a half times as great as for

helium, since the uranium atom is sixty times as heavy as that of helium, and this is, perhaps, the more scientific way of computing it.

**The Structure of the Nucleus.**—These considerations have not been without repercussion upon our views as to the constitution of the nucleus and upon the nature of radioactive change. For the nearly integral relation between the mass numbers of all the other isotopes suggests that the main change of mass must occur in the compounding of hydrogen into helium. In the nuclei of all the other elements, complete helium nuclei rather than protons are presumably the immediate constituents, and probably there are few or no free protons present. This may account for the fact that, in the radioactive changes, helium nuclei and not protons are expelled, whereas in the artificial disintegration of nuclei by bombardment with  $\alpha$ -particles the converse is true. If a radioactive nucleus were built up from protons an enormously greater evolution of energy would result than if helium nuclei were the starting material, and, therefore, the ejection of a proton from the nucleus, instead of an  $\alpha$ -particle, might actually require energy to be supplied, even when the ejection of the  $\alpha$ -particle would liberate energy. In the artificial disintegrations, this necessary energy is, at least in part, supplied by the  $\alpha$ -particle.

These and similar considerations underlie the significance of the mass numbers of isotopes as a measure of the internal energy of the nuclei, and the importance of determining them to the very highest degree of accuracy attainable. For this purpose a new mass spectrograph was built. With this a large proportion of the isotopes have had their mass numbers determined to an accuracy of one or two parts in 10,000. Viewed by the canons of atomic weight determinations this is a surprising feat, but, from the standpoint of the relations between mass and energy, the accuracy is by no means too great, for we have seen (p. 199) that the whole energy emitted by uranium in its sequence of radioactive changes only corresponds to a loss of one in 5,000 of the mass.

**The Packing Fraction.**—By far the most important generalisation in this field, and one of the most important made this

century, has attended these more exact determinations. It has transpired that the whole number rule is not exact, but that there is a perfectly regular and systematic departure from it, as we proceed from one end of the Periodic Table to the other. The departure from the integral value of the mass number may be either positive or negative. It is expressed in parts per ten thousand of the whole mass and is termed "the packing fraction." It represents the mean fractional gain or loss of mass per proton of the nucleus, as compared with the protons in the oxygen nucleus as standard. Thus, for hydrogen, it is 77·8. For arsenic, the mass number of which is 74·934, it is -8·8.

Considering the broad features of the generalisation first, there is a relatively rapid decrease in the packing fraction with increase of atomic number from hydrogen to elements in the neighbourhood of mass number 16, where it passes through zero and becomes negative. The elements from mass numbers 40 to 80 lie on the minimum range of the curve, with packing fraction from -8 to -9 units. Then there is a slow increase, until for elements of mass number of the order of 190 it again passes through the zero value, and for mercury, the element with highest mass number yet determined, it is again slightly positive, +0·8. It is expected that all the elements of atomic weight above 200 will show a positive packing fraction, increasing slightly from mercury to uranium.

Certain consequences follow at once if we accept the equivalence of mass and energy. The elements of intermediate complexity and atomic weight are those of minimum internal energy, and to transmute any of these into elements, either of lower or higher atomic weight, would require external energy rather than yield it. Whereas the transmutation, whether of heavy elements or of light elements, into those of intermediate atomic weight would yield energy, as in the case of the radioactive elements. We have already considered an extreme case, the transmutation of hydrogen into helium.

The description given explains the broad trend of the packing fraction in passing through the Periodic Table. But for the light elements, below mass number 20, the odd and even elements lie on two separate curves. The odd elements de-

crease in packing fraction relatively abruptly, from hydrogen with the value 77·8, through lithium, 17, boron, 10, to oxygen, the standard for which is zero. The even-numbered elements start with helium, for which the packing fraction is only 5·4, and pass through carbon, 3, to oxygen, zero. After oxygen there is little if any difference between the odd and even elements. For chlorine the packing fraction is -5 and for argon -7. This may account for the greater ease with which the odd-numbered elements of low atomic weight are disintegrated by bombardment with  $\alpha$ -particles.

**The Isotopes of Lead.**—Special interest attaches to the isotopes of lead which Aston has recently been successful in unravelling, using the volatile compound, lead methide. Still more recently the long-awaited isotopic constitution of uranium has been ascertained, using the hexafluoride. For ordinary lead, three isotopes were observed, of mass numbers 206, 207 and 208. The last was the most abundant, the relative proportions being estimated as 4:3:7. The possibility is not entirely excluded that other isotopes in small quantity, of mass numbers 209, 205, 204 and 203, may exist. For lead derived from the uranium mineral, bröggerite, the 206 isotope was in far the greatest abundance, 207 being faint and 208 hardly visible, the proportion of the 207 isotope being estimated at 10 per cent. Aston concluded that the 206 isotope must be the end product of uranium, and the 207 probably that of actinium.

If this is accepted, it fixes many things. The atomic weight of actinium, if its disintegration sequence has been fully unravelled, must be 227 and that of protactinium 231. Since it is known that, of the uranium atoms now disintegrating, 3 per cent. do so through actinium, and Aston's result indicates that, of the uranium atoms that have disintegrated, 10 per cent. have done so, we can, if we know the total age of the mineral, determine the period of the parent of actinium, actino-uranium. The consensus of opinion is that the mineral bröggerite, which is from one of the oldest geological formations, is probably about a thousand million years old. This makes the period of actino-uranium only one-tenth as great as that of uranium I, and the present proportion

of actino-uranium in the mineral only 0·3 per cent. The original proportion, a thousand million years ago when the mineral was formed, would have been 1·5 per cent.

These proportions are too small to have produced the effect, deduced by Joly from his studies of the uranium pleochroic halos (p. 114), that the disintegration of uranium has been proceeding more rapidly in past times. The uranium clock, on this account, would certainly have been running a little faster a thousand million years ago than it does now, but only inappreciably so.

**The Homogeneity of Uranium.**—On the other hand, the result for uranium, that it consists, certainly to within 2 to 3 per cent., of only one isotope of mass number 238, has settled a very important doubt as to the validity of the uranium-lead ratio as a measure of geological time, which arose from the recognition of isotopes. Suppose that the isotope of uranium, uranium I, responsible for the production of radium and lead had only been, like the radioactive isotope of potassium (p. 179), in minor proportion. The estimates by this method of geological time would have had to be reduced in the same proportion as that between the radioactive isotope and the whole uranium. The direct determination of the essential homogeneity of uranium seems to preclude this and to confirm the essential accuracy of the radioactive time scale.

**The Separation of Isotopes.**—The only elements which so far have been separated, even to a small extent, into their separate isotopes are neon by Aston and chlorine by Harkins and others, by fractional diffusion through porous septa, and mercury and potassium, by Hevesy, by the method of unidirectional distillation in a long free-path vacuum, described under the radioactivity of the latter (p. 179). The extent of the separation is followed by measuring the change of density of the two parts into which the material has been separated, and it is always, even after a laborious number of repetitions of the process, extremely small. Thus mercury, respectively two to three parts in ten thousand lighter and heavier than the mercury started from, is the best so far obtained, and these methods hold out no hope of effecting a

complete separation. A great deal of work has been done, both before and after the discovery of isotopes, to see if the atomic weight of an element depends at all on the nature of its source or the locality from which it was derived, but with negative results. This shows that the isotopic composition of the elements is uniform throughout Nature, so far as experiment can yet show.

Possibly boron with two isotopes, 11 and 10, may be an exception to this, as there is a certain amount of evidence that different specimens show slightly different atomic weight. It is, also, owing to the large relative difference of mass of the two isotopes, the one for which any such effect is likely to be the most pronounced.

## CHAPTER XIX

### RADIOACTIVITY AND THE UNIVERSE. COSMICAL RAYS

**Radioactivity and Geology.**—There is no subject in which the interpretation of radioactivity has been of deeper influence than geology, both on the theoretical and practical sides. The older geologists had always contended that in order to account even for a single epoch of geological history tens or hundreds of millions of years must elapse. The older physicists denied the possibility of the earth having existed so long, principally on two grounds: firstly, that there was no known process for maintaining the heat of the sun for as long as a hundred million years; and secondly, because the actual temperature gradient of the earth's crust as you penetrate inwards is inconsistent with any other view than that it was incandescent a hundred million years ago. The difficulty as regards the former objection, the maintenance of the heat of the sun, remains unanswered, but, as regards the latter, the situation has been completely reversed. The enormous heat generated by radioactive changes makes it difficult to understand, not why the interior of the earth is as hot as it is, but rather how it can possibly have existed for the periods demanded by the geologists without becoming incandescent. On the practical side, the ratios of lead and helium to the radio-elements in rocks furnished, as we have seen, a veritable geological clock which confirmed the most extended estimates of the geologists as to the past age of the earth.

The determination of the radium in the representative rocks of the earth's crust was early undertaken by Joly and the present Lord Rayleigh, and the investigations were subsequently extended to their thorium content also. The average proportion of radium in the earth's surface materials is now taken to be about  $2 \times 10^{-12}$  gram of radium per gram. This corresponds with an equilibrium amount of uranium of 6 parts in a million, and the average proportion of thorium

is about double this. The igneous rocks contain, on the average, considerably more radium than the sedimentary. That this may be of the utmost practical importance was shown by Joly in connection with the piercing of the Simplon Tunnel, where the unexpectedly high temperatures encountered in the interior nearly wrecked the enterprise. The mean proportion of radium in the rocks encountered was  $7 \times 10^{-12}$ , and this unusually high radium content, assuming the same composition to extend in depth below the tunnel, is quite sufficient to account for the high temperature gradients encountered.

**The Heat of the Earth.**—The actual loss of heat from the earth's surface, by cooling to outer space, would be supplied by a mere skin, fifty miles or less thick, of rocks of the same composition as those at the surface. If we include potassium as well as uranium and thorium, owing to its relatively large amount, the thickness required is greatly reduced. Unless the central core of the earth is free from radioactive material, there is no escape, on present knowledge, from the rather startling conclusion, that the interior of the earth must be steadily getting hotter with the lapse of time, and that one day the whole earth will again become incandescent.

For the reasoning by which Kelvin, for a cooling globe, showed that 100 million years ago the earth must have been incandescent, now that we know it contains self-heating radioactive materials, applies the other way. Owing to the very poor heat conductivity of solid rocks, the internal heat cannot escape except very slowly, and the interior temperature must therefore be steadily increasing. This might go on, it is estimated, for hundreds of millions of years without the surface temperature rising appreciably. But unless there is some unknown compensating factor at work, the ultimate fate of such a world as ours must be much as is represented in Biblical and other tradition, for the crust must ultimately break up and the whole become incandescent. This phase would be relatively short-lived owing to the rapid loss of heat by radiation as soon as the crust melted. Another crust would rapidly form and another geological age would be inaugurated.

**The Present Theories of Geologists.**—The view most favoured to-day by geologists is that the earth, as regards its surface temperature and the processes at work upon it, has been in much the same condition as now for seven or eight hundred million years at least. The figure of 1,500 million years is regarded as the most probable estimate of the age of the earth in its present state. To account for its high average density, which is 5·66, more than twice that of the surface materials, it is necessary to suppose that the surface rocks do not extend very far in depth. The earth is probably a mass of nickel iron at the core, similar in composition to the metallic meteorites, and its crust corresponds to a layer of lighter slag which covered it when it was molten, and which has since solidified. Earthquake waves tell us also something about the interior and point to a change of composition and elastic constants at no very great depth from the surface.

In this way the necessity of believing in a periodic alternation of geological and incandescent ages is escaped. The effects of radioactive heat are confined to the partial fusion of the magma underlying the great mountain ranges, where the pressure resulting from the weight of the uplifted areas would probably lower the fusion-point of the rocks and cause them to melt first in these regions. It is true that the first effect of pressure would be to raise the melting-point of most rocks, but at very high pressure, owing to the much greater compressibility of liquids as compared with solids, it is probable that this effect would be reversed.

The view is a conservative one, in accord with the general “uniformitarian” standpoint of the geologist, that the earth has arrived at its present condition by slow and gradual changes rather than by large-scale catastrophic events. It must be remembered also that we have no actual knowledge of the effect of such great pressures as exist in the interior upon radioactivity, and it is just possible that this might tend to prevent the atoms disintegrating. The periodic uplifting of mountain ranges is a relatively quick and locally catastrophic process, whereas their levelling is the work of the slow agents of denudation and weathering with which we are more familiar.

**The Cyclic Changes of the Earth's Surface.**—The geologists distinguish four great cycles each of from 150 to 200 million years' duration, upon which are superimposed twenty smaller cycles each of about 30 million years' duration. We are supposed to be living at the end of one of the greater revolutions, in which the Alps and Himalayas were uplifted. The accumulated heat in the interior periodically escapes by an outflow of molten magma to the surface, where it parts with its heat rapidly. This is followed by the consolidation of the rocks and their contraction, resulting in the weaker being folded and deformed. At present the underlying rocks, except for local areas in the neighbourhood of volcanoes, are solid, and the accumulation of heat in the interior is recommencing. This is shown by the evidence of earthquake shocks, which are transmitted, not only along the curved surface of the earth's crust, but by a straight "P3" route through from one point on the globe to another, penetrating below the surface often to great depths. If these depths were molten such earthquake waves could not take this route. But, after the lapse of a period, estimated at some 30 million years, these rocks will again melt and flow out to the surface at the edges of the continents, and this cycle has been repeated, at regular intervals of 30 million years, at least twenty times in the more accessible and recent half of the earth's geological history.

Radioactivity provides the key to the solution of these regular cycles of change, but the discovery of them is entirely due to the work of the geologist, and, indeed, the disentanglement and chronology of these periods from the study of the records of the rocks may be said to constitute the framework of geological science. Professor Joly says:<sup>1</sup>

"Reviewing the surface history of the earth, we find a record of periodic flooding of the continents, followed after long periods of time by retreat of the transgressional seas, and then by a great epoch of mountain building and volcanism; succeeded finally by quiescence and such conditions as now prevail, wherein the land is above sea-level and the only surface activities are those of rain and rivers, frost and thaw."

<sup>1</sup> *The Surface History of the Earth*, J. Joly, Oxford, Clarendon Press, 1925, p. 89.

Thus a cycle is completed but only to be merged into a succeeding cycle in which the seas once more gradually steal in over the lower continental levels."

There seems little doubt that his view that the cycles correspond with the accumulation of heat of radioactive origin in the solid substratum, and its dissipation during fusion of this, is the correct physical explanation of the geological cycles.

**The Age of the Earth.**—There are many methods of arriving at an estimate of the time-scale of geological processes, but none are so direct or, probably, so reliable as that from the ratio of lead—and, to a lesser degree, helium—to the uranium and thorium in minerals from the rocks of various geological horizons. We have seen that the recent determination of the essential homogeneity of uranium by Aston has removed from this method the most obvious element of uncertainty as regards the absolute measure of the time-scale, the doubt that uranium might, like potassium, prove to be a mixture of isotopes, with uranium I, the parent of radium and lead, only a minor proportion of the whole. Even so, the less obvious and less likely possibility must not be entirely forgotten, that uranium may be a mixture of isotopes of the same mass but different nuclear constitution, of which only one is radioactive. At present there seems no way of obtaining evidence on this point. The anomaly of the unexplained discrepancy in the "fit" of the uranium haloes (p. 114) has still to be borne in mind.

As a matter of fact, there is a clear discrepancy between the ages calculated from the Pb/U and from the Pb/Th ratios. The latter, even in some of the cases least open to objection, leads to an age of the mineral only a third as great as the former. To account for this a very ingenious, if somewhat special, theory has been propounded, based on the fact that uranium, as we saw (p. 151), is a more basic element than thorium. When lead is formed in a uranium mineral it may be expected to combine with the uranium as lead uranate,  $PbUO_4$ , a highly insoluble compound. The action of percolating water upon a uranium mineral, and, in general, the processes of alteration and weathering, are more likely to

dissolve the uranium than the lead and the result would be to increase the Pb/U ratio. Whereas, corresponding "thorates" do not exist. The lead formed in a thorium mineral will remain as oxide or silicate, both of which are fairly soluble, so that here percolating water may be expected to dissolve the lead oxide, rather than the thorium oxide, one of the most insoluble of substances, and this would decrease the Pb/Th ratio.

**The Lead Ratio.**—For this reason, the authorities have more and more come to rely upon the Pb/U ratio for minerals containing but little thorium in their estimate of the absolute duration of geological time, probably because this ratio gives on the whole the longest and the most consistent ages. Assuming the real periods of uranium and thorium are exactly known, the lead ratio will be of the nature of a maximum estimate, both on account of the possibility of lead having been present as an initial constituent of the mineral, and, for uranium minerals, on account of weathering possibly having increased the Pb/U ratio. By careful selection of the materials examined, and by comparison of a large number of independent results, these sources of uncertainty may be minimised. The helium ratio, on the other hand, must necessarily be a minimum estimate, because no helium can have been present when the mineral was formed, and because, in the long course of its history, some will certainly have escaped into the air. But it gives a useful check on the general accuracy of the results. The determination of the age of a mineral from its lead ratio, assuming of course no lead was present initially, is made by means of the simple approximate formula:

$$\text{Age} = [\text{Pb}/(\text{U} + 0.38\text{Th})] \times 7,400 \text{ million years.}$$

The ratio of the quantity of lead, Pb, is taken to that of the uranium, U, increased by adding 0.38 times that of the thorium, Th, to allow for the difference of the periods of uranium and thorium and their different efficiency as lead producers, and this ratio is technically called simply "the lead ratio."<sup>1</sup>

<sup>1</sup> The alteration of this factor from 0.38 to 0.25 has been advocated by more recent workers.

This formula applies when the lead ratio is only a few per cent. of that of the radio-elements. For higher ratios a more exact formula must be employed. Each 1 per cent. of the lead ratio, reckoned as above, thus corresponds to a period of 74 million years.

The results obtained by this method show that the beginnings of the Tertiary epoch date back some 60 million years; the Upper Palæozoic strata, from Devonian to Permian, range from 205 to 375 million years; and the Pre-Cambrian rocks fall into three groups at 600, 900 and 1,050 million years, respectively, with another not very well defined group at 1,260 million years.<sup>1</sup>

**A Maximum Estimate of the Earth's Age.**—An interesting method of calculating the maximum possible age of the earth, provided only that no process of synthesis or regeneration of the radio-elements has taken place in it since it was born, is from the ratio of the total quantity of lead in the earth's crust to that of the total uranium and thorium. This ratio is estimated as 5: 4: 10. On the assumption that all the lead has been formed from the uranium and thorium, the time that would be required is 3,000 million years. This is only twice as great as the best estimate of the actual age of the earth, since the formation of the solid crust. It is chiefly of interest in showing how very much younger the earth *must be* than the sun and the universe in general, according to modern theories. The astronomers seem to be oscillating with a rather bewildering frequency between periods of some ten thousands of millions of years and periods some five hundred to a thousand *times* greater than this, as the probable duration in past time of the sun and stars.

Incidentally it may be noted that any such extended periods as these demand that in the sun the reproduction of the radio-elements must have been going on before the earth separated from it, at most 3,000 millions of years ago, and therefore are probably going on there to-day. Thus if the view is correct that the period of actino-uranium is only one-tenth of that of uranium I, we must conclude that it was being formed in the sun at least up to a comparatively short period before the

<sup>1</sup> A. Holmes, *The Age of the Earth*, Benn's Sixpenny Library, No. 102.

earth was ejected from it. It is not difficult to believe that, during the birth of the earth, the lead, as a very easily reducible metal, was to a large extent segregated in the central metallic core, and that originally the crust contained little or none. We thus know fairly definitely that the earth was *not* in existence as a separate planet 3,000 million years ago. The belief that the sun and stars have existed vastly longer periods than this is, however, much more speculative.

**The Age of the Sun and Stars.**—The most definite evidence brought forward for supposing that the universe has existed many millions of millions of years is that the stars in their proper motions seem to approach to the condition of equipartition of energy for the molecules of a gas. As this can only be brought about by their feeble gravitational action upon one another, on the rare occasions when they approach each other sufficiently nearly to exchange momentum and kinetic energy, these enormous periods are indicated. To account for the maintenance of solar and stellar energy over such long periods, there is no source adequate, except the actual annihilation of matter into radiation in accordance with the Einstein law of equivalence between energy and mass. Sir James Jeans has been a powerful advocate of this view.<sup>1</sup>

The chief evidence for it is the general relation that exists among stars between their mass and luminosity, the larger stars being enormously the brighter. Considering their vast numbers, there appears far less difference between the masses of stars than might have been expected. Excluding highly exceptional stars—the “red giants” and “white dwarfs,” to be later discussed—the range of the “main series” stars, as they are termed, seems to extend from something like ten times to one-fifth or one-tenth of the mass of our sun. Whereas their luminosity or “candle-power” varies over an enormously greater range, from hundred-thousands to hundred-thousandths of that of our sun’s luminosity. The luminosity seems broadly to be connected with the mass, stars twice the mass of the sun being on the average eight times as

<sup>1</sup> *The Universe Around Us*, Sir James Jeans, Cambridge University Press, 2nd edition, 1930.

luminous, and those one-half the mass of the sun being only one-eighth as luminous.

**The Annihilation Hypothesis.**—If the Einstein relation is accepted, then the energy apparently radiated from the sun, apart altogether from the question of its origin, corresponds to a loss of mass of 400 million tons a second. But so great is the sun's mass, that, even at this rate, it would last 15 million million years. The relation between mass and luminosity shows that the loss of mass would not be uniform in time, but enormous for a heavy star and almost negligible for a small one. This general view accounts well for the law of the dependence of luminosity upon mass, as otherwise there is no obvious reason why stars of the same mass should not have all degrees of luminosity.

For masses ten times as great as that of the sun, the radiation would be so enormous that this part of the life of a star would be lived through at relatively lightning speed. Whereas for masses much less than that of the sun the radiation is so reduced that the life is almost indefinitely prolonged. Thus the theory sets an upper limit not only to the possible size of the stars but also to their possible past age. This limit, Jeans calculates, is at about 100 times the sun's mass and seven or eight million million years.

The piece of evidence now most relied upon concerns the class of close twin stars known as the spectroscopic binaries. It can be shown theoretically that in the condensation of a nebula into a star, the shrinkage of the matter will produce an increase in the angular momentum of rotation, which may be expected to result, as a rule rather than as an exception, in the fission of the star into two. Moreover, in course of time, the distance between the two parts will slowly increase, and their mutual orbits will become more and more elliptical. Spectroscopic binaries are numerous, and classification of them according to their distance apart, and the ellipticity of their orbits, reveals the interesting fact that the masses of pairs of stars near together are, in general, much greater than that of those further apart. The conclusion is drawn that those which have been in existence longest and drawn apart from one another furthest, have lost the greater part of their

original mass by radiation, a process that requires millions of millions of years.

On the other hand, as reverted to later, modern views are making the life-history of a star much more eventful than the old, which depicted a uniform, inevitable and undignified declension towards senility and death. The phenomena of novæ and white dwarfs make it appear that, during the star's normal life, there occur periods of sudden and amazingly profligate outbursts. These are succeeded by prolonged relapses into what is, virtually, "cold-storage," during which the radiation is so reduced that such periods hardly count in diminishing the mass and future span of life of the star.

**The Tidal Theory of the Origin of Planets.**—The present theory of the origin of the planetary system is also due to Jeans, and differs in one important respect from earlier theories. For the process of the ejection of planets by a parent sun is now regarded, not as a normal, but as a highly exceptional event in cosmical evolution. It can only occur when a sun of greater mass passes within a distance of two or three times its diameter from one of smaller mass. The tidal action between the two then will draw out from the smaller sun a cigar-shaped protuberance of gaseous matter, which, after the larger sun has passed on its way, will proceed to condense into planets.

The chances of such a close approximation of two suns, owing to the enormous scale of the universe, are vanishingly remote. Even if the stars have already existed for millions of millions of years, the chances are that not one in a hundred thousand of them will yet have given birth to planets. Whereas the fission of a star into a binary system is regarded as a more or less normal occurrence. Hence the present view is that very few indeed of the suns can have planetary systems analogous to ours.

The theory receives confirmation from the fact that the largest planets, Jupiter and Saturn, are those with intermediate orbits. The nearer and the more remote planets, on this theory, should both be, as they are, smaller than those in the middle of the series. This has been confirmed by the recent discovery of the extra-Neptunian planet, Pluto, which appears

to be quite a small planet, of the same order of size as the earth. On the other hand, the more recent announcement of the discovery of another extra-Neptunian planet comparable in size to Uranus, would, if it is confirmed, tell against the theory. For the cross section of the cigar-shaped filament being greatest in the middle and smallest at both ends, the quantities of matter available for condensation into planets must follow a similar distribution, as we go outward from the sun.

**Difficulties of the Annihilation Theory.**—Hitherto, it has been supposed that the composition of the earth is necessarily the same as that of the sun, as no one doubts that the earth has originated from the sun. But this is the first difficulty the annihilation theory of the origin of cosmical energy has to meet. For nothing is more certain than that the process of annihilation of matter is not proceeding at any appreciable rate on the earth, or it would be too hot for human habitation. Neither does it seem to be in accordance with our present knowledge of atomic structure to suppose that temperature, at least any temperature likely to exist even in the interior of the sun, will promote the process of annihilation. The theory is driven back on special and apparently unlikely hypotheses as to the nature of the supposed process of annihilation of matter into energy, which do not seem to be in any way supported by any body of scientific opinion or evidence.

The first is that the atoms of matter undergoing annihilation are not any of the kinds known to us. The plain fact is that in the atomic structures known to us, in which electrons and presumably protons form stable intimate systems, the electrons and protons continue to coexist indefinitely without annihilating each other. It is supposed that annihilation must be a property of unknown elements, and these are considered to be elements lying beyond uranium in the Periodic Table, with an atomic number estimated to be in the neighbourhood of 95. The second special assumption is that such atoms are so completely segregated in the interior, that at the moment of the birth of the earth from the sun, they are not drawn up by tidal action, but only the elements as far as atomic number 92.

A further objection to the hypothesis seems to be that it came into being in order to explain the maintenance of the energy of the stars over periods of the order of millions of millions of years. True, if the universe has been in existence so long, and if it has been radiating energy uniformly in all directions at anything like the rate at which we now receive the radiation from the sun and stars here on earth, there seems no possible source adequate for the purpose but the Einstein equivalence of matter and energy. But the theory stands or falls by its ability to account for the generation of heat in the interior of the stars. Whereas the only evidence of annihilation that has so far been cited in support of its taking place is in the explanation of the origin of the cosmical rays, about to be discussed. These, it is certain, do not come and could not come from the interior of the stars, as they could not escape without being transformed into radiation of ordinary frequency. They must originate in practically empty space. So that even if the hypothesis of special elements existing in the interior of the stars is accepted, it still does not account for the origin of the cosmical rays which it is claimed furnish actual evidence of the process. Clearly the two problems are and should be kept distinct. Possibly the theory has unduly restricted itself, by too ready an acceptance of our existing views of atomic structure, which make it improbable that the high temperatures and pressures prevailing in the interior of a star would in any way promote the annihilation. We have no knowledge of how matter would behave under such conditions, and it would seem more natural to assume that they favoured the process for the ordinary elements than to invent new elements for the purpose.

**Novæ and White Dwarfs.**—Before discussing the cosmical rays, two very interesting and possibly connected astronomical phenomena may be mentioned as finding their interpretation in present views of atomic structure. These are the novæ, or new stars, which with fair frequency make their appearance in the heavens, and the white dwarfs, a remarkable type of star of which, as yet, but few examples are known, but which are probably quite abundant. The modern habit of regarding the universe as a sort of glorified example of the kinetic theory

of gases, with the stars wandering about in an immense empty space just like the molecules of a rarefied gas, has brought into prominence the comparative frequency with which new stars appear in the heavens. These new stars, if known before, are usually quite faint stars which suddenly, in the course of a few hours or days, blaze out into unmistakable brilliance, and, after a few months or years, fade away back to their original brightness. On rare occasions they may be so bright as to be visible in daylight. But, as telescopic objects, they are quite frequent, 80 having been recorded in 1929 in the nebula of Andromeda alone.

Modern kinetic theories of the universe negative the view that they can be produced by actual head-on collision between stars, as was first thought, and opinion tends to the conclusion that they are normal events in the history of a star, so frequent that every star in the course of its history may become a nova at least once.

The white dwarfs, of which only some five examples are yet known, are exceedingly faint, being only a few hundredths of the luminosity, and of the diameter of the sun. The light is similar in spectrum quality to that of the ordinary stars, and their excessive faintness must be ascribed to their small area. All except one are the companions of bright stars, Sirius B, the faint companion of Sirius A, the brightest star in the firmament, being the best-known example. The exception is known as van Maanen's star and it is the smallest known, being of diameter comparable with the earth, but of mass estimated at one-fifth that of the sun, so that its density is 66,000 times greater than that of the earth. The weight of most of these stars is given from the orbits in which they revolve round one another, and the remarkable fact emerges that, in spite of their small size, their weight is comparable with that of their brighter companion. Thus Sirius B is 0·85 and Sirius A 2·45 times the weight of the sun, the latter being 26 times as luminous as the sun, and the former only 26/10,000ths as luminous as the sun. The spectrum shows that the stars are of not very different temperature, so that it follows that the diameter of Sirius B can only be approximately 1/50th of that of Sirius A. This has recently been confirmed by the application of an otherwise unproved theorem due to

Einstein, that there should occur in the spectrum of a star a shift to the red side depending upon its weight and diameter. On this basis, the density or specific gravity of the matter comprising Sirius B is over 50,000 times that of water, or over 2,000 times the density of platinum, the densest material known to us on earth. Since Sirius A and B almost certainly must originally have been one star that has undergone fission, the difference between them is arrestingly remarkable.

**The Stars and the Atoms.**—The only way in which matter of the kind we know could become as dense as this is by the complete stripping off of all the external shells of electrons surrounding the nucleus of the atom, right down to and including the innermost K shell. The nuclei and electrons, in such completely ionised or “stripped” atoms, then lead an entirely independent existence, analogously to the independent existence of sodion and chlorion in fused salt. Given sufficient external pressure the whole matter would collapse into a very small fraction of the volume the actual atoms occupy in the states known to us.

Sharply contrasted with the exceptional stars, just considered, are others known as the “red giants,” including some of the brightest stars in the sky, of which Antares and Betelgeux are the best-known examples, for which the colour shows that they are of relatively low surface temperature. Yet, in spite of this, they appear to be radiating energy much faster than the average stars of which our sun is typical. It was pointed out, first by Herzsprung, that red stars are *either* giants *or* dwarfs, and this division was later extended by Russell to the classification now known usually by his name. Russell showed that, as the temperature increases and we pass from red, through orange-yellow, white and blue stars, or more strictly through the various types of spectrum recognised by astronomers as indicative of increasing temperature, the difference between dwarfs and giants, extreme for the red stars, lessens, so that the two branches come nearer together, and for white or blue-white stars of the temperature of Sirius they meet. But just here we have the new and, at present, entirely exceptional type of white dwarfs appearing, with a totally different and more minute order of “dwarfness,” as

compared to the smallest red dwarfs. These astronomical generalisations as to the constitution of the stars have now received an elegant explanation in accordance with the modern theory of the structure of the atom. The abrupt changes in the magnitudes, brightness and densities of the stars have their parallel in the abrupt changes in the characteristic secondary X-rays of Barkla in passing through the elements of the Periodic Table.

It has been said that the modern theory of the atom with its successive shells of electrons, extending outwards with diameter increasing according to the square of the number of shells, is writ large across the heavens for those with eyes to see. The stars have been classified according to the extent their component atoms have been ionised, or stripped of their successive shells of electrons. At one extreme are the "red giants" like Antares and Betelgeux, of relatively low temperature but enormous size exceeding one hundred times that of the diameter of the sun, in which the process of "stripping" has not proceeded beyond the M ring. At the other extreme are the "white dwarfs" in which the atoms must, for the most part, be stripped completely, leaving only the bare nuclei. Intermediate are the vast majority of "main sequence" stars, of which our sun is typical, in the interior of which the atoms retain their K shells, but all the outer electrons have been shorn off.

**Stellar Evolution.**—Much difference of opinion still exists among astronomers and mathematical physicists as to the actual processes of stellar evolution and even as to the dynamics of the interiors of stars of which these processes are the consequence. But a broad general view has been developed by E. A. Milne, which links up the abrupt changes of configuration of the star that must attend each stage in the "degeneration" of the atom, as shell after shell is ionised away, with the appearance of novæ. It has naturally been concluded that in the novæ we are actually witnessing the sudden collapse of a star from one state of configuration to the next most degenerate stage. By cooling, the initial configuration becomes unstable. The diminishing kinetic energy of the atoms due to their falling temperature and the decreasing radiation

pressure, which sustain the materials at a given distance from the centre against their gravitational attraction, become insufficient. But instead of a slow contraction as the older hypotheses assumed, we have a sudden collapse and the appearance of an ephemeral new star, until the excess energy for the new state has been radiated away and the star resumes again its normal existence as a new type.

If this is so, it would seem that the most likely fate of the earth and its inhabitants is not any of those chilly methods of slow extermination, due to waning sun-power, which the second law of thermodynamics holds over us, but, rather, a swift obliteration when the last defences of the atoms in the interior of the sun, which are still holding out in a losing battle with old age, collapse, and the sun suddenly becomes a nova preparatory to a prolonged period of deflation and strict economy as a white dwarf. Indeed, Sir James Jeans is by no means happy about the future, for the sun appears to him to be already skating perilously near the left-hand edge of the main sequence of the Russell diagram with nothing between it and the group of white dwarfs in the extreme left-hand bottom corner. Fortunately, the imminence of the danger has to be considered with reference to the astronomical rather than the historical time scale.

It is significant that the spectrum of a nova, after it has returned to its pristine brightness, is that of the O or Wolf-Rayet type, which shows that its temperature is then as high as any encountered in the study of the stars. It may have shrunk to a tenth of its former diameter, that is to one-hundredth of its former area. But since its brightness is much the same as at first, its intrinsic surface brightness must have increased a hundredfold. Presumably, therefore, it will again lose mass rapidly and may again expand to a star of ordinary dimensions at a later date, to repeat, on an ever-diminishing scale until it is finally exhausted, the astronomical parallel to the "trade-cycle" of inflation and deflation.

**The Expanding Universe.**—On the other hand, the rapidly gaining belief that the universe is expanding, at an alarming rate, which is derived from the study of the remote extra-

galactic nebulæ, has produced a revulsion of feeling among astronomers proper against the view that it has been in existence for millions of millions of years, and a tendency to favour something more nearly the period assigned to the age of the earth. With each new accession of telescopic power, the speed of recession of the confines of the universe increases, if we are to judge by the reddening of the spectrum of the most distant nebulæ. The latest data refer to nebulæ so distant that it is estimated that their light takes 100 million years on its way to us, and these appear to be receding from us at something like the speeds, 12,000 miles a second, hitherto, among material projectiles, the monopoly of the  $\alpha$ -particle! At this rate the universe is estimated to be doubling its size every 1,400 million years, that is in about the estimated age of the earth in its present condition. Even if we do not take very seriously the suggestion of one distinguished astronomer, the Abbé Lemaître, that the universe originally began as a single giant atom which has disintegrated in a super-radioactive manner, the whole process of expansion to its present size would only occupy a mere 10,000 million years at most, and though we may be as lavish as ever as regards the future, clearly we have to be severely economical as regards the past. Besides, with a more concentrated universe to begin with, the law of equipartition of energy among the stars' proper motions is only to be expected. The main plank of the supporters of the English as against the American "billion" of years of past duration is now itself in need of support. The annihilation theory, which arose of necessity to account for the duration, now, lest its style be too severely cramped, has to cling to the duration as necessary for itself.

**The Cosmical Rays.**—Let us conclude with some facts. It was not until 1910 that Gockel, taking an electroscope up in a balloon several times to heights of 4,500 metres, first made the observation which, in due course, has led to the establishment of the existence of the cosmical rays. But the discovery illustrates very well the scientific obsession for pursuing the most trifling and infinitesimal effects right up to and beyond the present limits of detection. When you have reduced to the utmost possible limit the "natural leak"

of an electroscope, to what is the residual leak, below which it is impossible to go, really due? As far back as 1902 a Canadian investigator named Cook, working in Rutherford's laboratory in Montreal, was putting a polish on the inside of the brass vessels used for such electroscopes, in the attempt still further to reduce their natural leak, that even the most conscientious and fastidious experts of culinary science had never before achieved. But there always remained a residual ionisation unaccounted for. It corresponded with the production of only two or three pairs of ions per second per cubic centimetre of volume.

The radioactive matter in the earth, and in the metals of which the instrument was made, the radium and thorium emanations in the air and their active deposits, all produce a certain contribution to the ionisation, even in the absence of all other radioactive substances. Though by far the greater part of the natural leak, or natural ionisation, of the air was thus accounted for, a small residual effect of the order stated remained over. In some experiments of McLennan the measurements were made far out on the frozen surface of Lake Ontario. In others, tons of lead were piled round the instrument to shield it from the earth's radiation. But it was not till Gockel showed, in 1910, that the effect definitely begins to increase at high altitude, that there was any suspicion that ionising radiations were reaching us from above. The balloon experiments were continued by Hess, and later by Kolhörster, and even by 1912 it had been shown that a penetrating radiation is reaching the atmosphere from above in increasing intensity, as one ascends, which does not come from the sun, as it is undiminished at night and unaffected by a solar eclipse.

**The Work of Millikan.**—In 1925, Millikan and his co-workers continued the experiments to greater heights with free balloons, carrying recording instruments only, and attained the elevation of 15.5 kilometres, where only 8 per cent. of the air is above and 92 per cent. below. They showed that the effect did not go on increasing with greater heights, but began to fall off again at the highest reached. This is a familiar phenomenon with penetrating rays, which probably

do not ionise directly, but by virtue of the softer secondary radiation they generate in their path. Owing to the production of these, the ionisation effect will increase for the first layers of an absorbing medium, until the two types come into equilibrium, one with the other, after which the regular absorption occurs. These experiments showed that the 8 per cent. of air left above were not sufficient to produce the full ionising effect. At lower levels, the absorption due to the air begins to tell, so that, in going up, the effect at first increases to a maximum and then diminishes.

Great improvements were made in due course in the electroscopes used for this work. By very large instruments, filled with air, or better carbon dioxide, under high pressure, the small effects may be magnified, since they are proportional to the mass of gas in the electroscope. In addition, automatic recording electroscopes were used, which supply a photographic record of the position of the gold-leaf and its rate of discharge. A great step forward was taken by Millikan and his colleagues, who took the electroscopes up high mountains, and sunk them to definite depths below the surface in the glacier-fed lakes of the Rockies and Andes, the waters of which should be entirely free from radioactive contamination. The absorption of the rays by the air at these high altitudes is much reduced, 5,000 metres of air being equivalent to a depth of 5 metres of water. The ionisation at these high altitudes amounted to 20 (pairs of ions per c.c. per second), but on sinking the instrument in the lake it was found steadily to diminish to one-quarter in 15 metres (50 feet). At 60 metres depth of water it became too small for the further decrease to be measurable.

**Recent Work.**—Later experiments were carried out by Regener, with very much larger and more sensitive instruments, in Lake Constance, Geiger counters as well as electroscopes being employed. Lake Constance is only 1,300 feet above sea-level, but the instrumental improvements more than offset the diminished effects due to atmospheric absorption, and depths of no less than 236 metres of water were attained, without the radiation being entirely absorbed. Though excessively feeble, the cosmic rays could still be

measured even at these depths. Since lead is 11·4 times as dense as water, 236 metres of water is equivalent to over 20 *metres* of lead, whereas the greatest thickness of lead—in experiments by A. S. Russell and the author—through which the  $\gamma$ -rays of radium and thorium had been studied is little more than 20 cm., or 100 times less.

Dealing first with Regener's results, the absorption curve in water is, at first, not exponential. A heterogeneity of rays of various penetrating power is indicated. But, after 80 metres of water, what is left unabsorbed appears to be homogeneous, as the curve remains exponential from this point right up to the end. For this most penetrating type, the absorption coefficient is only 1/200th of that of the  $\gamma$ -rays of radium, that is to say, these cosmical rays are 200 times more penetrating. Attention has been unduly concentrated on this, the last residual radiation, which in reality represents only a small part of the whole cosmical radiation. The softer types of rays are much more abundant, but for the softest type the penetrating power is at least five to ten times greater than that of the hardest  $\gamma$ -rays.

It has been clearly established that the rays do not come from any one point or region of space, such as from the sun or the Milky Way, but uniformly from all directions. Their total energy is by no means insignificant and is estimated to be one-tenth of the total energy of starlight. They do not appear to be affected by magnetic fields. A special expedition into the Arctic, to Churchill, Manitoba, the nearest settlement to the N. magnetic pole, has been made by Millikan to test this point. The cosmical rays were of the same intensity there as at the other places chosen for their study. Whereas, if they had been deviated by magnetic forces, or had been accompanied by high-speed electrons, it is to be expected that these would spiral round the magnetic lines of force of the earth's field, and be concentrated on the magnetic pole. Though essentially constant in intensity at all hours of the day or night, there is a small diurnal variation, of the order of only 2 per cent. in intensity, with an afternoon maximum and early morning minimum. This has been ascribed to the effect of the sun on the atmosphere, but, small as it is, it seems too great to be simply a density effect of the

air, which would be recorded by the barometer and corrected for in the ordinary way.

**Suggested Origins of the Cosmical Rays.**—Millikan lays great stress on the softer types of radiation, which he regards as a definite homogeneous type of  $\gamma$ -radiation corresponding to an energy represented by an electron falling through 25 million volts, and which has about ten times the energy of the hardest  $\gamma$ -ray. Jeans, as a supporter of the annihilation hypothesis, on the other hand, concentrates attention rather on the last and very hardest type, which may have an energy as great as that of 400 million electron-volts. Both make use of quantum considerations and somewhat doubtful extrapolations from the known relations between penetrating power and the frequency, or wave-length, the first to show that the origin of the cosmic rays is most probably due to atomic synthesis, or upbuilding of complex atoms from hydrogen, and the second that it can only be explained by the annihilation of matter into radiation. Both, since the rays are heterogeneous, may be right.

To Jeans, basing his calculations on Regener's experiments near sea-level, where the softer types will be largely absorbed, the absorption coefficients agree with wave-lengths of  $\gamma$ -rays corresponding—the hardest type to the simultaneous annihilation of four protons and four electrons, that is to say a helium atom, and the next hardest type to the annihilation of a single proton and a single electron, that is to say a hydrogen atom.

Millikan concludes that the main band, of 25 million electron-volts energy, results from the synthesis of a helium atom from four hydrogen atoms. Both sets of calculations make use of the Einstein relation between mass and energy and the departures of the atomic weights concerned from integral values to arrive at the energy of the supposed transformations. But considerable doubt still exists as to the legitimacy of the extrapolation from absorption coefficient to wave-length, partly because, to these very high-frequency rays, the nuclear electrons as well as the external electronic system may play a part in the absorption of the rays by matter.

Both speculations are of great interest. It would certainly

seem difficult to account for the energy of the very hardest type of cosmical rays by any less energetic process than by the actual annihilation of a proton and electron into radiation. At the same time, whether some of the cosmical rays may not result from such a process in the empty depths of space is, as already pointed out, a totally different question from that of the origin and maintenance of the cosmical energy of stars. For the extraordinary feature about these rays is that they come to us in their virgin condition, unaccompanied by the secondaries, with which they come into radiation equilibrium after passage through matter.

**Atomic Synthesis.**—Millikan's hypothesis, that they are due to processes of upbuilding of the heavier elements from the lighter, has from the first exercised a particular fascination on the author's mind. Ever since the discovery of the disintegration of the heaviest atoms in radioactivity, one has naturally attempted to picture in what way the original synthesis of the elements from the primordial stuff could have come about, and to ask if it is possible that such processes, complementary in their effects to radioactivity, may not also be proceeding today. The difficulty to a chemist has always appeared insurmountable. Disintegration, as we know, is a self-contained affair in which only the single atom is involved. But synthesis is what the chemist calls a reaction of higher order.

To take the simplest synthesis, that of helium from four hydrogen atoms, it is a reaction of the fourth order. This means that four atoms have to meet in the same place at the same time before it can occur at all, and chemical reactions do not and cannot occur that way. Those that appear to, almost certainly, are successive second-order reactions, in which the meeting together of only two of the combining units at a time occurs. One is, perforce, compelled to regard the complex atom synthesised as growing gradually by the accretion of hydrogen atoms, rather than in any single act, owing to the incessant jostling suffered by all molecules and atoms under the conditions we know them, as depicted by the kinetic theory of matter. This practically means that not more than two can, except by the rarest coincidence,

meet together at exactly the same place and the same time.

Now it is the peculiar feature of this cosmical radiation that it appears to originate in the spacious depths of the universe, where this jostling would not occur. The temperature is at, or near, the absolute zero, and the molecules are practically at rest. The concentration is also practically zero. Under these conditions, there would be nothing to prevent a set of atoms or molecules forming a group under their own attractions, nor anything to break them up when once formed. It is just possible that this may be the condition necessarily precedent to an atomic synthesis. The system, after a certain orientation was attained, might start to condense, slowly at first, but with increasing speed, until, finally, in a flash, the atoms coalesce to a new nucleus, and the energy of the change is radiated as a quantum of cosmic radiation. As yet we do not even know how stationary atoms and electrons would behave towards one another, and it may be that, under these conditions, either annihilation or the formation of a new nucleus might result. In this way the very unexpected production of these intensely high-frequency radiations in empty space might receive an elegant explanation.

**The Maintenance of Cosmical Energy.**—Finally, it must not be entirely overlooked that the whole of the difficulty of accounting for the maintenance of cosmical energy, and providing a sufficiently abundant source to outlast the copious outpouring of radiation from the sun and stars over almost endless periods of time, may be due to a pure assumption as to the nature of radiation, natural enough when first made, but now every day assuming a more unnatural character. Millikan has characterised the assumption, that the radiation laws which seem to hold here cannot possibly have any exception anywhere, as precisely the sort of sweeping generalisation that has led physicists into error half a dozen times in the last thirty years. But the assumption in question is, possibly, more fundamental than those which Millikan referred to.

Is radiation propagated uniformly in all directions in empty space ? On earth it appears to be, but perhaps this also is an illusion. We are surrounded on all sides by matter, and,

though above our heads it be gaseous and transparent to radiation of visible and lower frequencies, it is no less substantial than the thirty-inch layer of liquid mercury by which its weight is measured. The  $\gamma$ -radiations are completely unable to penetrate it. If the sun were made of pure radium, no detectable amount of  $\gamma$ -radiation would survive absorption at sea-level. It would be reduced to far less than a million-million-millionth of its intensity by 76 cm. of mercury or the equivalent weight of air.

It is perfectly true that, if radiation is necessarily propagated from a star uniformly in all directions, there is no known process capable of accounting for it, and no other imaginable process than the conversion of matter into energy according to the Einstein relation of equivalence. But, at the present time, when so much of our theory is merely a transitional patchwork of new ideas upon old habits of thought, rather than any consistent substitute for the old way of regarding things, surely *all* these old ideas ought to be critically examined, and, in accordance with the modern tenets, nothing allowed to be assumed which is not directly amenable to observation. We cannot, and possibly never shall be able to, observe whether light is propagated through completely empty space, and *therefore we ought not to assume that it is*. As it is, the rapidly growing superstructure of imaginative cosmogonical hypothesis, which is being reared up, threatens to obscure the foundations, so that it must be a difficult task for the younger generation to discover them at all. Mere familiarity with and reiteration of ideas is taking the place of genuine theoretical advance, amenable to scientific proof.

**Would Light go if it had Nothing to go to?**—If we could try such an experiment, it might be found that light was not propagated through space except to places containing matter—that, if we could contrive to direct it at nothing but empty space, it would not go. So long as there was an ether to vibrate there was at least something to carry it. But, in absence of the despised jellies and gyroscopes of the Victorians, we have to believe it is carried as “photons,” discrete parcels of radiation energy for which the idea of uniform propagation in all directions over a continuously in-

creasing spherical surface is more physically absurd than the idea of gyroscopic ethereal jellies. If we seek to construct our space to conform to this, that or the other geometry according as it is empty, under the influence of electromagnetic forces, or in the neighbourhood of matter (p. 201), surely we must first be able to answer the question whether or not light is really propagated as a random flight of photons in all directions or whether its world-lines, or geodesics, are not, like those of matter, produced in the space by the presence of matter. In a tentative theory of Sir Joseph Thomson, electromagnetic influences were regarded as being propagated along Faraday "tubes of force" which ended on two opposite charges. If so, one would hardly expect light to travel except in directions occupied at both ends by matter. A little more imagination might be exercised in the underlying ideas rather than in their over-elaboration.

It might be thought that the evidence of the eclipse expeditions sent out to test the predictions as to the effect of gravitation on light had settled the question as to the geodesics of light, but that is far from being the case. Science is strewn with the fatal consequences of observers being told by theorists before what they will observe. Could any more fatal handicap be imposed on an eclipse expedition than to be equipped and sent out not, primarily, for the purpose of observing the eclipse, but to look for evidence deciding between two transcendental theories, neither of them possibly within a million miles from the truth! The 1919 eclipse expeditions seemed to prefer the results done with the sun more or less obscured by clouds to other observations done under fine weather conditions "which pointed with all too good agreement" to the other value, and by condemning the latter brought in a verdict triumphantly in favour of Einstein. Later eclipses have failed to confirm this value, and have given a distinctly greater value for the deflection that any theory requires, and it is now admitted that the change of views as to the nature of light invalidates the calculations. New sources of error, such as change of focal length of the telescope by variation of temperature, have been brought into prominence. These and other errors are far greater than the minute effects being actually looked for,

and, indeed, the latter are only revealed at all after an elaborate process of "correction" has first eliminated the known errors. Under these circumstances the danger of a preconceived theory in the interpretation of the results cannot be overestimated. The best observers have made far greater blunders under not nearly as unfavourable conditions.

It would be interesting if the whole of astronomical and terrestrial phenomena were reconsidered, with the unprovable assumption, that photons are necessarily emitted uniformly in all directions like waves, eliminated, and only phenomena directly amenable to observation admitted. There are any number of still unexplained phenomena, besides the maintenance of cosmical energy, in connection, for example, with weather forecasting and the effect of planetary influences on sunspots, weather and droughts, that might take on an entirely new appearance if this were done.

If this view is taken, and the sun and stars can only propagate light and heat to distant worlds, it would completely invalidate all the estimates that have been made as to the rate at which they are radiating energy, and would reduce the amount that has to be accounted for to proportions that do not require for their provision the invention of imaginary processes. The planets, viewed from the sun, would obscure only  $1/250,000,000$ th of the celestial dome, so that a source of heat that would last only four years on the one hypothesis would last for a thousand million years on the other. In fact, between these limits, we could make it last as long as we choose by appropriate curvature of the space in which the photons travel!

## ADDENDUM

### THE ARTIFICIAL DISINTEGRATION OF LIGHT ELEMENTS BY ELECTRICAL MEANS

SINCE this book was printed, discoveries bearing on the artificial transmutation of elements were made known at the Discussion on the Structure of the Atomic Nucleus, opened by Lord Rutherford at the Royal Society meeting on April 28, 1932. We saw (pp. 102-4) that, since the  $\alpha$ - and  $\beta$ -particles may be regarded as helium ions,  $\text{He}^{++}$ , and electrons, respectively, which have acquired their velocity and kinetic energy by "falling" through a potential difference of some millions of volts, and since the former have the power of disintegrating the nuclei of the light elements in the rare encounters between nucleus and nucleus, one of the most hopeful ways of attacking the problem of artificial transmutation would be to construct transformers capable of giving potential differences of this order of magnitude, which is much greater than any yet artificially generated.

Work has begun in several different countries on these lines, and Lord Rutherford was able to announce at the meeting referred to that two investigators in the Cavendish Laboratory, J. D. Cockcroft and E. T. S. Walton, had been successful in disintegrating the nucleus of lithium and of other light elements by bombarding them with protons artificially generated by the application of high electric potentials. The most surprising feature of the work is the comparative ease with which the disintegration is effected, potential differences very much less than had been considered necessary, and little, if at all, beyond the range attainable by ordinary electrical coils and transformers, being effective in producing disintegration.

Actually the installation employed was able to give currents of the order of a milliampere at a potential difference of 800,000 volts (800 kilo-volts). This was used to accelerate

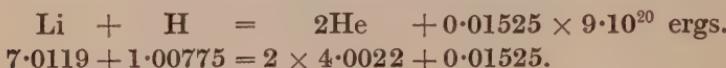
ordinary protons or hydrogen ions,  $H^+$ , produced by the electric discharge in hydrogen gas, down a long and wide highly exhausted glass tube with a very thin mica window at the end. The accelerated protons, or artificial H-rays, were able to pass through the thin mica and to produce effects outside the tube. Their velocity was estimated to be of the order of  $10^9$  cm. per second, and their range in air about 1 cm. With 710 kilo-volts, the maximum so far employed, the velocity was  $1.16 \times 10^9$  and the range 18.5 mm.

The H-rays emerging vertically from the window at the bottom end of the tube were directed on to a layer of lithium at  $45^\circ$  to the beam, and a radiation from the lithium in a horizontal direction was looked for by the scintillation method, through a mica screen of thickness equivalent to 2 cm. of air, able completely to stop the original H-rays. Surprisingly enough, with potentials as low as 125 kilo-volts, bright scintillations began to be observed. These increased very rapidly in numbers as the potential was increased, but not in brightness or range. At 400 kilo-volts several hundred scintillations a minute were counted. It was estimated that at 250 kilo-volts one scintillation resulted per  $10^9$  protons.

The scintillations observed had all the appearance of those produced by high speed  $\alpha$ -particles. The rays also produced cloud tracks in the Wilson chamber indistinguishable from those of ordinary  $\alpha$ -particles. Their range in air is about 8 cm., almost the same as for the  $\alpha$ -rays of thorium C', the velocity and energy of which would be acquired by a helium ion,  $He^{++}$ , falling through a potential of 4.38 million volts. It is to be noted that only the number, not the range or energy, of these particles increased as the potential was increased, and that their energy, assuming them really to be  $\alpha$ -particles, is over sixty times as great as that of the protons generating them. Clearly we have to do with a trigger action, in which the protons merely pull the trigger and release the store of energy in the lithium nucleus.

The following interpretation is put upon the results as probable by these investigators. It is supposed that the nucleus of the lithium isotope, of mass number 7, occasionally captures one of the protons and is so transformed into two helium nuclei, which are expelled with the energy not only

of the captured proton but of the corresponding loss in mass. We saw (p. 314) that the packing fractions of the odd and even numbered light elements lie on two different curves, and that the odd elements, as hydrogen and lithium, depart from the integral values much more than the even numbered elements, like helium. If the foregoing interpretation is correct, we may, on the Einstein principle of the equivalence of mass and energy, write the equation as follows:



The second line, giving the exact atomic masses of the elements, shows that the change is accompanied by the disappearance of 0.01525 gram per two gram-atoms of helium formed, and this by the Einstein principle is equivalent to the evolution of  $0.137 \times 10^{20}$  ergs. Weight for weight, this is about ten times as much as is given in the complete series of radioactive disintegrations of uranium, and it would give to each helium nucleus formed a kinetic energy equivalent to that acquired in falling through about 3.4 million volts. Hence the observed range of the particles corresponds fairly closely with the calculated energy of the helium nucleus produced, according to the Einstein relation. Certainly the correspondence is as accurate as could be expected, having regard to the uncertainty of some of the data.

It seems probable that the foregoing accounts for the unexpected ease with which the atom of lithium has been disintegrated. Instead of some millions of volts being necessary, the phenomena is observed at potentials almost within the range of a large induction coil. The genius of Aston in foreseeing the very great importance of the exact determination of the mass numbers of the isotopes has already borne fruit in directing attention to the light elements, and particularly those of odd atomic number, as of high energy content and, just as in the case of the heaviest radioactive elements, likely to suffer transmutation, if at all, with enormous energy evolution.

The work also furnishes yet another indirect indication of the probable accuracy of the Einstein relation.

Preliminary experiments with other elements have shown

similar results, though the particles generated were in no case of as great range as those given by lithium. Beryllium, boron, carbon, fluorine, and aluminium all appear to give particles of range between 5 and 2·5 cm., but not oxygen or copper, and in no case at such low potential as suffices for lithium. It must be remembered, of course, that the disintegrations are still on an infinitesimal scale, only one atom being disintegrated per thousand million projectiles, in the case first cited. But the rapidity with which the number increases with the potential applied makes it legitimate to believe that, with the use of sufficiently high potentials, extraordinary results may be obtained.

There can be little doubt that we are on the eve of a most remarkable development in this field. Both this and the discovery of the neutron (p. 301) pave the way for a new era of advance with regard to our knowledge of the nucleus. It should be noted that, although it has become customary to speak of the artificial disintegration of elements by bombardment with  $\alpha$ -particles, the discovery just described, if confirmed, is the first real case of an artificial transmutation. For, in these most recent experiments, the energy of the swift protons used to effect the transmutation has been artificially generated by ordinary electrical means, whereas in the case of artificial disintegration by  $\alpha$ -particles the agents owe their energy to a natural radioactive transmutation.

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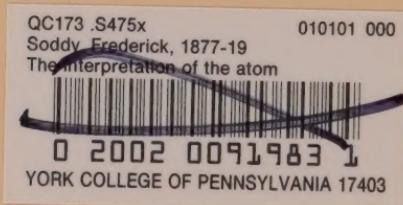
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