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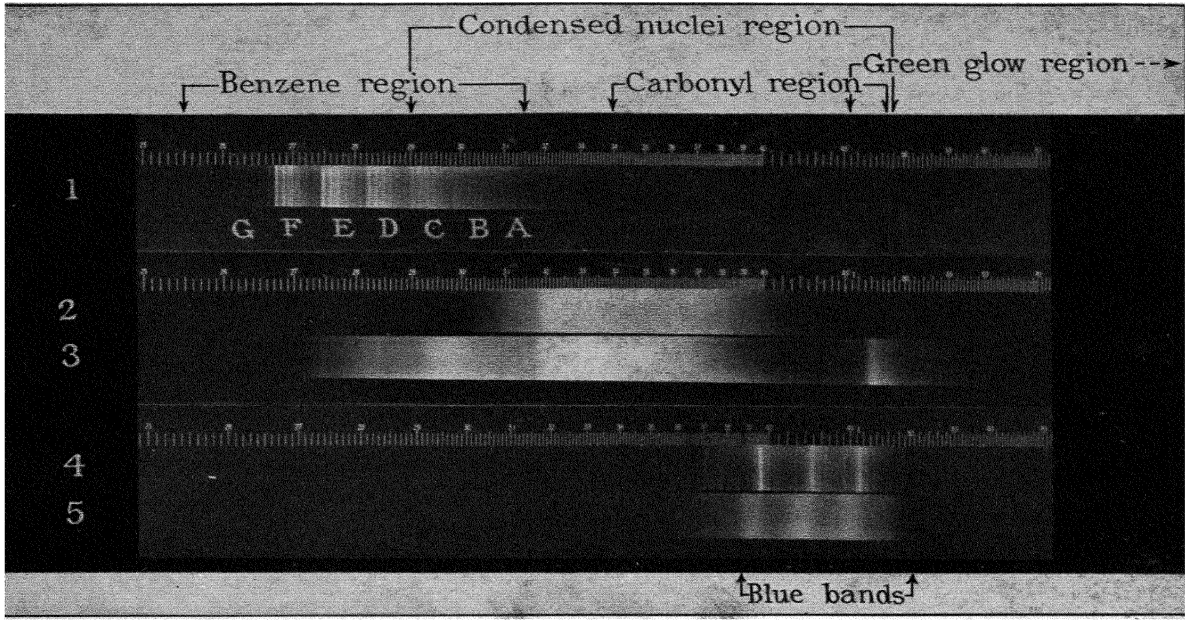
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TESLA-LUMINESCENCE SPECTRA



1. BENZENE
2. NAPHTHALENE
3. TETRAHYDRONAPHTHALENE
4. BENZALDEHYDE
5. ACETOPHENONE

The scales are approximate ones showing wave length

RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY

BY

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WITH THIRTY-SEVEN ILLUSTRATIONS

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PREFACE TO THE SIXTH EDITION

In preparing the present volume, three chapters of the last edition have been deleted to make room for fresh material; but even so, the current edition contains seventy-five pages more than its predecessor.

This expansion is due mainly to the insertion of several new chapters dealing with modern theories of line spectra, band spectra, and continuous spectra; for at the present day it is impossible to present a fair picture of the atom or of the molecule without touching upon the results of modern spectroscopic research. In preparing these chapters I have borne in mind that some at least of my readers are not professed mathematicians, and I have endeavoured to write the mathematical part of the volume so simply that no one with a schoolboy knowledge of dynamics need feel out of his depth in it. At the same time, I have included everything which seems of value to the chemist in this field. No attempt has been made to discuss recent theories of the electron, as at present their bearing upon chemistry is very slight.

Among other fresh material in the new edition will be found sections on illinium, rhenium, masurium, elements 85 and 87, the Donnan equilibrium, cosmic rays, and some flame reactions.

As in previous editions, figures indicate references to the literature, while explanatory footnotes are indicated by asterisks. The reader can thus avoid unnecessary glances at the foot of the page. The abbreviations employed are mainly those adopted by the Chemical Society.

For permission to reproduce certain figures in the book, I wish to offer my thanks to Dr. F. W. Aston, F.R.S., and Messrs. Edward Arnold and Co. for plates III. and IV., and to Sir

Ernest Rutherford, O.M., F.R.S., and the Chemical Society for Fig. 13. Figs. 3, 4, 12, 17, 22, 23 and 27 are taken by permission from *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, by Dr. J. W. Mellor, F.R.S.

I desire to acknowledge the great assistance given to me in proof-reading by Prof. D. N. M'Arthur, Dr. H. Graham, and Dr. J. K. Marsh, to all of whom I am indebted for valuable suggestions for the improvement of the text.

ALFRED W. STEWART.

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June, 1930.

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RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY

CHAPTER I

THE OLDER AND THE NEWER CHEMISTRY

THE younger generation of chemists has grown up in a science wherein X-ray spectra, atomic numbers, isotopes, nuclear charges, electrons, atomic structure, radioactivity and α-particles are taken for granted; and it is difficult for them to appreciate the vast changes in outlook which have come about within the memory of those of us whose recollections of the subject go back to the early 'nineties of last century. Chemistry is a science which, while undergoing steady progress as a whole, shows from time to time sudden accelerations in the spread of knowledge in one or other of its branches; and the last quarter of a century has been especially notable for the fundamental character of the researches which have been carried out during its span. It is safe to say that there has never been a period of equal brevity in the history of the science when so many older views have been set aside and so many new facts and fresh ideas have been brought to light to take the place of the discarded material.

These changes have widened the horizon by breaking down the artificial barrier between chemistry and physics; and it would be ungrateful to forget that a very large part of the work has been done by the physicists. The older physical chemistry, which had its day in the 'eighties and 'nineties of last century, was an attempt to create a new subject on the borderland of physics and chemistry; but this fissiparous conception has been replaced in recent years by a unifying effort so that at the present time it is hardly possible to draw a sharp line of division between physics and chemistry. Even the ordinary analytical processes are

found to have some relation to the atom of the physicist; whilst the physical model atom owes more than a little of its development to the chemical researches which produced the Periodic Classification and defined the inter-relationships of radioactive and ordinary elements.

In order to show the changes which chemistry has undergone during a single generation, it will suffice to take up in turn several of the fundamental ideas which have suffered a metamorphosis during the last quarter of a century; and to outline the differences between our present-day views and those held by ourselves and our predecessors in the last decade of the nineteenth century.

Take, first, the conception of the atom. The normal chemist of the 'nineties pictured the atom as a homogeneous, incompressible particle, probably spherical in form, and certainly indivisible into anything finer. This particle was assumed to have existed unchanged throughout the past; and it was believed that it would persist unaltered in the future. The structures produced by linking atom to atom—chemical compounds—might crumble and decay; but the atomic particles themselves were endowed with eternal stability. It was known that in the case of ionisation, these particles could acquire positive or negative electrical charges; but those charges were regarded as things which could be superimposed upon or withdrawn from the atom without altering the material particle itself. Finally, it must be borne in mind that in those days the atom was a purely hypothetical thing. No direct proof of the existence of atoms could be advanced, though the evidence in favour of the atomic theory was sufficient to convince most chemists; and even as late as 1904, Ostwald [1] was making a futile attempt to persuade us to abandon the idea of an atomic structure of matter.

When the foregoing views are contrasted with present-day knowledge, the alteration represents nothing less than a revolution in chemical thought. The old homogeneous particle has been discarded; and in its place appears a complex system of protons and electrons held together by attractions which are at present beyond the bounds even of conjecture.* Thus the dogma of the indivisible atom has vanished from science; and a new

[1] Ostwald, *J.*, 1904, **85**, 506.

* See Chapters XII and XIII.

branch of knowledge has arisen which is concerned with intra-atomic problems. With this dogma has gone another—the permanence of the atom.* There is now convincing experimental evidence that some, at any rate, of the atoms are not stable; and any one who takes an illuminated wrist-watch into a dark room can see for himself some of the effects of atomic collapse. Again, the idea that electricity was something distinct from matter has shared the usual fate of incorrect assumptions. Instead of being something superadded to the atom, electricity is found to be a vital constituent of the atomic mechanism. Finally, the existence of atoms has been placed beyond doubt by a series of investigations starting in many different fields and all converging upon a single focus.[1] Once again the "mechanical model" has proved its superiority over the "mathematical expression," as a guide to progress.

Allied to the conception of the atom is the idea of atomic weight. In the 'nineties, it was generally accepted that each atom had a definite weight and that the relative values of these weights could be determined by purely chemical methods. A vast amount of ingenuity and technique was devoted to the "exact determination of the atomic weights," and the refinements of the methods employed led at times to jests on the "chase of the fourth place of decimals." It is now known that the fractional "chemical atomic weights" correspond to nothing real.† They are merely averages—purely mathematical figments. The case of the determiners of atomic weights in the 'nineties and later is one of the most pathetic in the whole history of science; for out of that ungrudging effort towards accuracy nothing has resulted so far as real advance in knowledge is concerned. In the case of lead, no fewer than twenty-five separate determinations of the atomic weight were made; and at the end of them all, the main point had been completely missed—namely, that the chemical atomic weight of lead is not a constant of nature, but varies according to the source from which the metal is obtained.‡

The conception of chemical affinity is another of those which have undergone a considerable change during the period under review. Valency, in its essence, is of course a mere number

* See Chapter V.
† See Chapter X
[1] Perrin, *Les Atomes* (1913).
‡ See Chapter VII.

representing the relative proportions in which a given atom combines with hydrogen or oxygen; and for the most part this remains unaffected by recent advances in our knowledge. But even here the fundamental ideas have been shaken. In the 'nineties, the hydrogen atom was taken as the standard measure of monovalency, and the current information lent full support to this choice. Now, however, things are not quite so simple; for the existence of the allotropic form H_3 seems placed beyond doubt by researches in entirely different fields.* Since it is impossible to group three monovalent atoms into a triplet, the dogma of monovalent hydrogen can no longer be maintained.

Our ideas of the mechanism by means of which two or more atoms are united in a molecule have suffered more than one sea-change within the last two decades. In the 'nineties, the whole problem lacked a generalisation. On the one hand lay the metallic salts with their capacity for ionisation, which suggested an electrical conception of chemical affinity; but on the other side stood the enormous host of the carbon derivatives which showed no electrical character and which could be so easily symbolised by means of graphic formulæ. Attempts to force the carbon compounds into line with the inorganic compounds proved unsatisfactory; while the converse effort to reduce the inorganic series to a graphic formulation was equally ineffective: and towards the end of the century, the whole problem seemed beyond the power of chemists to solve upon a simple basis.

It cannot be asserted that, even at the present day, the chemical affinity problem is solved; but at least some change in outlook is obvious. It is generally agreed that chemical affinity is electrical in nature; and that polar and non-polar compounds differ from each other in degree rather than in kind. The theory of G. N. Lewis † is widely accepted as a means of formulating the machinery of chemical combination and dissociation, though at present it has hardly progressed beyond the stage of being a representation of the facts rather than an explanation. Still, even with its limitations, it furnishes the best mechanical model available to depict the union of one atom with another; and it has the decided advantage of bringing a unifying conception to bear upon the whole question.

If in the case of chemical affinity the trend of thought has been

* See Chapter XV. † See Chapter XIII.

from the complex to the simple, the converse is the state of affairs when modern developments of the idea of the element are considered; for in that field an originally simple conception has become more and more complicated with the increase in knowledge.[1]

The original definition of an element, due to Boyle,[2] was a purely empirical one. An element was something which could not be broken up by any available means. In later years, two subsidiary definitions gained a footing, one of which described an element as a material which could only gain in weight during chemical change, whilst the other limited the name "element" to substances composed entirely of identical atoms. Taking these three definitions together, we obtain a very fair idea of the views on the elements which were held by the majority of chemists in the 'nineties.

As Soddy [3] has pointed out, Boyle's definition was not permitted to remain unqualified; for two fresh assumptions crept in, though they were never explicitly stated. In the first place, the experience of chemists up to the beginning of the present century seemed to show that mixtures were easily separable into their components, whereas compounds generally demanded the use of chemical processes; and thus chemical separation came to be regarded as a more refined method than any other. Secondly, and as a sequel to this, the phrase "any available means" was translated into "any chemical method." Chemical analysis, then, became the ultimate court of appeal in the problem of the elements; and, almost unconsciously, the term "element" came to suggest a material endowed with a unique chemical character which differentiated it from all other elemental matter and permitted it to be isolated from other elements by purely chemical means.

After Dalton's time, a further idea was grafted upon this already altered stem. It was assumed that the relative weights of atoms could be determined by purely chemical methods; and hence the conception of the "chemical element" became associated with that of the "chemical atomic weight." And with the development of spectroscopic analysis, a fresh criterion —the unique spectrum—was super-added to the elemental tests.

[1] Soddy, *J.*, 1919, **115**, 1. [2] Boyle, *The Sceptical Chymist* (1661).
[3] Soddy, *J.*, 1919, **115**, 1.

Thus the original empirical definition of an element suffered marked vicissitudes even before the beginning of the present century. With the coming of Dalton's theory the atom moved into the centre of the stage and the older conception of the element was re-stated in atomic terms, whilst at the same time the idea of a "chemical element" was imperceptibly replacing the primary idea of an "element." The "chemical element" on the atomic theory could only be a material composed of atoms all of which had the same chemical character; but, again almost unconsciously, this image was chiselled until "the same chemical character" became replaced by "identical properties." Crookes [1] was the only chemist of distinction who ventured to criticise this hypothesis of elemental homogeneity; and those of us who supported Crookes' ideas at the beginning of the century must still have vivid recollections of the superior smile with which they, were dismissed by the average enthusiast for chemical dogmas.

In less than a decade and a half, the amazing results of three entirely new lines of research played havoc with all these comfortable assumptions. Radioactivity, X-ray spectra, and the analysis of positive rays, each in its own field, permitted a probing of the atomic constitution such as had been undreamed of in the 'nineties; and one by one the older dogmas collapsed under the test.

First went the idea of the permanency of the atom, which could no longer be upheld in face of the disintegration of the radio-elements; and by the same door through which it made its exit, there entered the long-discredited alchemistical dream of a transmutation of one element into another.* Next came the downfall of the "unique chemical character" dogma, which was swept away by the experimental proof that two atoms might have identical chemical character and yet differ in other properties; and this in turn led to the complete collapse of the conception of the homogeneity of the element.† Not long after this, the spectroscopic criterion was proved to be invalid as a test for atomic homogeneity. And during this period the idea that the "chemical atomic weight" was a real measure of atomic mass also passed beyond the range of acceptable

[1] Crookes, *J.*, 1888, **53**, 487; 1889, **55**, 257.

* See Chapter VI. † See Chapter VII.

ideas.* Out of the apparent chaos thus produced, there arose a single new test of elemental character—the X-ray spectrum.† But in order to appreciate the bearing of this fresh factor, it is necessary to turn to the Periodic Table and trace the development which it has undergone as a result of all these surprising discoveries.

From the time of Newlands onwards to 1913, the periodic classification of the elements rested upon the basis of the "chemical atomic weights," though a divergence from the strict numerical order had to be made in the cases of the pairs argon-potassium, iodine-tellurium, and cobalt-nickel, since in them the chemical sequence was obviously different from that inferred from the weights. On these premises, the places in the Periodic Table clearly represented a series of detached forms of matter; and Mendeléef [1] objected strongly to any graphical method of expressing the Periodic Law, on the ground that such methods did not indicate the existence of a limited and definite number of elements in each period. Thus, again by implication, there appears a fresh idea, viz. that an elementary form of matter must find a place in one or other of the spaces in the Periodic Table.

It is to Crookes [2] that we owe the first adumbration of a modification of this conception. It is true that in one half of his suggestion, Crookes was completely in error; but in the second moiety he approached very close to our modern ideas. He predicted that an "absence of absolute homogeneity may possibly yet be traced in many of the 'elements,'" so that under the name "element" it would be necessary to include a mixed material. This, as he saw, necessitated a fresh consideration of the meaning to be attached to the word "element"; and he suggested a possible modification to get round the difficulty. "For 'element' read 'elementary group,' such elementary groups taking the place of the old elements in the periodic scheme—and the difficulty falls away. In defining an element, let us not take an external boundary, but an internal type."

These views of Crookes are practically the views held to-day with regard to the Periodic Table; but it must be noted that

* See Chapters VII, VIII, and X. † See Chapter III.

[1] Mendeléef, *Principles of Chemistry*, II, 19 ff. (1897).

[2] Crookes, *J.*, 1888, **53**, 487.

with them, yet once more, a fresh implication has crept in. The "place in the Periodic Table" has taken on a different meaning from that ascribed to it by Mendeléef; for instead of the homogeneous material which he believed it to represent, it now denotes a mixture of things which are assumed to belong to the same "internal type."

The general conception of this "internal type" is simple enough; but difficulties arise when questions are put as to what constitutes the "type" and what criteria can be applied to establish whether a substance belongs to one type or another. In other words, the very definition of elementary matter becomes a difficult exercise. How complex this problem has grown may be guessed from Soddy's ironical comment [1] that the Chemical Society might safely offer a prize of a million pounds to any of its members who could shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of a first-year student of chemistry at the present time.

In 1913, a fresh line of research was opened up, which threw light upon the problem of the elements from a new angle. The investigation of the X-ray spectra of the elements by Moseley * brought out a direct relationship between this physical property and the sequence of the elements in the Periodic Arrangement; and further work proved that all forms of matter which could be represented by a single place in the Periodic Table emitted the same X-ray spectrum, although they might differ from each other in other qualities. Here, then, was a second criterion wherewith to judge the claim of a form of matter to a place in the Table; and so the X-ray spectrum and the chemical properties are now regarded as tests for membership of a given "internal type." In addition to this, the X-ray spectra furnish a roll of the different forms of elementary matter and permit the prediction of the total number of the elements between hydrogen and uranium.

It thus becomes clear that our modern ideas of defining the elements involve two things: the chemical properties on the one hand and the X-ray spectra on the other; and the irony of Soddy's suggestion about first-year students is seen to be even more keen than appears at first sight.

In the matter of the Periodic Table itself, a complete change

[1] Soddy, *J.*, 1919, **115**, 1.

* See Chapter III

in our outlook has come about within the last few years owing to the experimental advances which have been made. Not so long ago, it was accurate to describe [1] the Periodic Classification as "a completely unsolved riddle, the meaning of which seems scarcely hidden beneath the surface and yet perpetually eludes the grasp." But at the present day evidence is available which points to a simple explanation of the peculiarities of this system which for so long a time seemed a mere tantalising puzzle.* The identification of the atomic number with the surplus positive charge on the atomic nucleus has put the matter in a clearer light; and a mechanical model of the atom is now available which can be brought into harmony with the most of the Table. The rare earth class of elements is the only one which still presents difficulties; and it is merely a matter of time before some thoroughly satisfactory way of fitting them into the Table is evolved.

As a final example of the change in the chemist's outlook produced by modern investigations, Prout's Hypothesis may be considered. Little more than a century ago, Prout [2] published anonymously the suggestion that the weights of the elementary atoms were simple multiples of the weight of the hydrogen atom; and he went so far as to conjecture that hydrogen was the primitive material from which all the other elements were built up. His hypothesis had a brief popularity; but owing to the confusion of the "weight of the atom" with the "chemical atomic weight," it became discredited; since the average values so laboriously determined by the atomic weight experts, could not by any possibility be brought into harmony with his views. Not until 1919 was it possible to determine the true weights of the atoms; but when Aston's mass spectrograph † came into action, it overthrew at one stroke the whole figment of the "chemical atomic weights" and established a unitary theory of matter which corresponds very closely to the views of Prout. Aston's work, like that of Ramsay on the inert gases, stands in a place of its own in chemical history; for within an incredibly short time he determined more atomic

[1] Soddy, *Matter and Energy*, p. 70.

* See Chapters XII and XIII.

[2] Prout, *Annals of Philosophy*, 1815, **6**, 321; 1816, **7**, 113.

† See Chapters IX and X.

weights than all the other workers on the subject combined, and his measurements depend upon an entirely fresh method of approaching the subject. All that is left for future investigators in the field is the refining of his apparatus; for he has obviously exhausted the chief possibilities of this line of research.

Enough has now been said to show the nature of the revolution which has occurred in chemical science since the discovery of radioactivity. That subject, which at first seemed a mere fringe of anomalies on the outskirts of chemistry proper, has advanced until it occupies a prominent, though not predominant, position in our science; for from it have sprung some of the most important contributions to our knowledge of the atom. Other lines of research, both chemical and physical, have converged on the same focus; and at first sight it appears almost as if all the principal problems of chemistry had been solved within the last two decades. Further consideration will show, however, that many most interesting fields are still almost untouched; and the investigator of the new generation will find more than sufficient enigmas awaiting his ingenuity.

CHAPTER II

LINE SPECTRA

1. *Introductory*

ACCORDING to the conditions of experiment, a material body may either absorb or emit light; and hence spectra have been divided into two main groups: absorption spectra and emission spectra. These emission spectra in their turn are separable into three distinct classes: continuous spectra, band spectra, and line spectra. Continuous spectra and band spectra will be touched upon later in this volume. The present chapter is intended to give some account of the main points of interest suggested by line spectra.[1]

A typical spectrum of this class, produced by passing an electric discharge through a gas, consists of a number of isolated bright lines; and in order to facilitate discussion it is necessary to devise a measuring-rod by means of which the relative positions of the lines can be determined. The most obvious characteristic of a spectral line is the *wave-length* of the vibrations from which it arises. This wave-length is generally symbolised by λ. The original measure of wave-length was the *Ångström Unit* (Å. or A.U.), which was intended to equal 10^{-10} metre. Since 1907, a more accurate measurement has resulted in the introduction of the International Ångström unit, termed the I.A., which is based on the wave-length of the red cadmium line taken as $6438{\cdot}4696 \times 10^{-8}$ cm. under certain standard conditions.

The Ångström unit yields figures of a convenient magnitude in the visible and ultra-violet parts of the spectrum; but in the case of the long waves in the infra-red, the numbers tend to become unwieldy, and then it is customary to replace the Ångström unit by the *micron*, μ, which is equal to a thousandth

[1] For fuller information the reader is referred to Baly's *Spectroscopy*, Vols. II and III (1927), Sommerfeld's *Atomic Structure and Spectral Lines* (1923), and Griffith and M'Keown's *Photo Processes in Gaseous and Liquid Systems* (1929).

of a millimetre. Thus the wave-length indicated by λ=17,600 A.U. is more conveniently defined by the shorter expression λ=1·76 μ.

Though the wave-length is the most obvious characteristic of a spectral line, it is not the best one to utilise when the relationships in a series of lines have to be worked out. In this case, either of two fresh units may be employed: the oscillation-frequency or the wave-number. Of these, the *oscillation-frequency* (c/λ where c is the velocity of light) is the more fundamental, since it is unchanged from medium to medium; but in order to obtain it, an exact knowledge of the velocity of light is required. The *wave-number*, ν, on the other hand, is simply the number of waves per centimetre and its value is obtained thus:

$$\nu = \frac{10^8}{\lambda \text{ in Ångström units.}}$$

The term *frequency* is loosely used to describe both wave-numbers and oscillation-frequencies. There is no difficulty in distinguishing between them, since oscillation-frequencies are of the order of 10^{16}, whereas wave-numbers run only to ten thousands.

Before describing the relationships which have been detected in line spectra, a word of caution may not be out of place. The atoms of a rarefied gas which is emitting light under an electric discharge are by no means in the same state as the atoms of the same substance under the conditions which prevail during a chemical reaction in a test-tube. It would therefore be a mistake to assume that what holds good for the glowing gas can be transferred *en bloc* to the reacting chemical. The physicist, seeking for an hypothesis to account for radiation, has adopted a certain type of model atom which answers his requirements in this special field; but this model cannot be taken over by the chemist without modification. In chemistry we are mainly concerned with the chemical model atom, which will be described later in this volume. Doubtless in the future the physicist and the chemist together will evolve a fresh model which will answer equally well in both fields; but that stage has not yet been reached in the history of the subjects. In the meantime, however, it is necessary to keep both types of model atom in view, since each of them serves to account for certain facts which the other fails to illuminate.

2. *Balmer's Law*

Ångström introduced his wave-length scale in 1869 and thereafter came a number of attempts to trace simple relationships between the various lines which compose a spectrum. It was not until 1885, however, that any striking progress was achieved. At that date, fourteen lines had been identified as parts of the hydrogen spectrum, and the places of these had been plotted on the Ångström scale. Balmer [1] discovered that the wave-lengths of the series could be calculated from the formula:

$$\lambda = h \frac{m^2}{m^2 - n^2} \times 10^{-8} \text{ cm.}$$

wherein h is a constant for the whole hydrogen series, whilst m and n are integers.

In the case of the first four hydrogen lines, Balmer gave the following form to his expression:

$$\lambda = 3645{\cdot}6 \frac{m^2}{m^2 - 2^2}$$

wherein m has successively the values 3, 4, 5, 6 . . . and the fraction thus becomes in turn $\frac{9}{5}$, $\frac{4}{3}$, $\frac{25}{21}$, $\frac{9}{8}$. Comparing the results with Ångström's measurements for the first four lines in the hydrogen spectrum, the agreement is wonderfully close, as can be seen from Table I.

TABLE I

Line.	m	Fraction	λ calculated	λ observed
H_α	3	$\frac{9}{5}h$	6562·08	6562·10
H_β	4	$\frac{4}{3}h$	4860·80	4860·74
H_γ	5	$\frac{25}{21}h$	4340·00	4340·10
H_δ	6	$\frac{9}{8}h$	4101·30	4101·20

[1] Balmer, *Ann. Physik*, 1885, **25**, 80.

In its general form

$$\lambda = h \frac{m^2}{m^2 - n^2}$$

the Balmer Law has been found to yield accurate estimates of the positions of all the lines which have been discovered in the hydrogen spectrum up to the present; but when an attempt was made to apply it to the spectra of elements other than hydrogen, the results were less satisfactory. Nevertheless, Balmer's work marks one of the greatest advances in our knowledge of line spectra; and, with certain modifications, it underlies all the subsequent investigations in this field.

3. *The Rydberg Constant*

Inspection of the figures given in Table I will reveal a further characteristic of the hydrogen spectrum. As m increases, the differences between adjacent members of the series tend to diminish. Thus when the lines are plotted on the wave-length scale, they lie closer and closer together as we pass towards the more refrangible part of the spectrum (the ultra-violet); and eventually the series will reach a limit. When m^2 is very great and the fractional part of the expression approximates to unity, we shall have $\lambda = 3645{\cdot}6$, which will be the position of the limiting line of the series.

On plotting the wave-lengths (or the wave-numbers) of the series as abscissæ and using consecutive values of m as ordinates, Rydberg [1] found that he obtained regular curves which were much the same in shape for all the series and which resembled rectangular hyperbolas. This led him to search for a formula to express the relationships between the lines in the series; and he hit first upon this one:

$$\nu = \nu_\infty - \frac{C}{m + \mu} \qquad (1)$$

wherein ν is the wave-number of a line, m its order number, ν_∞ is the limit of the series (the value of ν when m is infinite),* and C and μ are constants special to the series in question. This expres-

[1] Rydberg, *Kongl. Svenska Vet.-Akad. Handl.*, 1890, Bandet 23, No. 11.

* Rydberg's ν_∞ obviously corresponds to Balmer's constant h.

sion proved unsuitable for general application, and Rydberg adopted instead the next simplest form :

$$\nu = \nu_\infty - \frac{R}{(m+\mu)^2} \qquad \text{(2)}$$

This proved to be a great advance, for it was found that the factor R was approximately *constant for all series*, unlike Balmer's constant h, which varied in value from series to series.

The relationship between the Balmer and Rydberg formulæ is quite simple, as can be seen from the following :

$$\lambda = h.\frac{m^2}{m^2-4} \quad \text{(Balmer's formula)}$$

So that

$$\frac{1}{\lambda} = \frac{1}{h}.\frac{m^2-4}{m^2}$$

Replacing $1/\lambda$ by ν and $1/h$ by ν_∞, the expression takes the form

$$\nu = \nu_\infty - \frac{4\nu_\infty}{m^2}$$

If for $4\nu_\infty$ we substitute R, the expression becomes

$$\nu = \nu_\infty - \frac{R}{m^2}$$

and this is obviously identical with Rydberg's expression

$$\nu = \nu_\infty - \frac{R}{(m+\mu)^2} \qquad \text{(3)}$$

for the particular case in which $\mu=0$. In other words, the Balmer formula is a special case of the more general Rydberg expression.

From the foregoing, it is obvious that R, the Rydberg constant, can be calculated from the formula

$$R = \frac{4m^2}{m^2-4}\nu \qquad \text{(4)}$$

in which the values of m and ν can be inserted to correspond with any given line in the hydrogen spectrum. As determined by Curtis [1] from the hydrogen lines, the value of Rydberg's constant

[1] Curtis, *Proc. Roy. Soc.*, 1914. (A), **90**, 605 ; 1919, (A), **96**, 147.

is 109,678·3 for wave-numbers on the international scale, corrected to vacuum.

It will be seen in a later section that the Rydberg constant R is not a true natural constant, since it can be resolved into simpler components.

4. *The Ritz Combination Principle*

In the case of the hydrogen spectrum, the Rydberg formula can be written in the following form :

$$\nu = \frac{R}{n^2} - \frac{R}{m^2}$$

Thus, Rydberg pointed out, the wave-number of any line in a spectral series can be represented as the difference between two terms ; and, as will be seen later, this has proved to be the basis of the modern physical theory of the atom.

Now it occurred to Rydberg that while the Balmer series of lines in the hydrogen spectrum was limited to the values of the above expression when $n=2$, the positions of other lines emitted by hydrogen, but not belonging to the so-called Balmer series, might be calculated by increasing n and making a corresponding increase in the values of m so as to avoid a negative result. Owing to the weakness of spectroscopic technique at the time, Rydberg was unable to do more than make the suggestion ; and it was left to Ritz [1] to bring definite proof.

If, in the expression above, the values $n=3$ and $m=4$ be inserted, a wave-number is obtained which corresponds to $\lambda=187517$. Ritz pointed out that this previously calculated value identifies the position with that occupied by the line of $\lambda=18751$, which was observed for the first time by Paschen [2] in 1908. This was obviously the first member of a series of lines in the infra-red spectrum of hydrogen (the Paschen series) ; and the remaining positions could be calculated by keeping $n=3$, and making m successively 5, 6, 7. . . .

In a similar fashion, if $n=1$, and m takes the successive values 2, 3, 4 . . . then a series of wave-numbers is obtained

[1] Ritz, *Physikal. Z.*, 1908, **9**, 521 ; *Astrophys. J.*, 1908, **28**, 237.

[2] Paschen, *Ann. Physik*, 1908, **27**, 565 ; cf. Brackett, *Astrophys. J.*, 1922, **56**, 154.

which has been found to correspond with the series of lines of extremely short wave-length which was photographed by Lyman,[1] and is known as the Lyman series.

Table II brings out the relationships between the various formulæ :

TABLE II

$\nu = \frac{R}{1^2} - \frac{R}{m^2}$ where $m = 2, 3, 4 \ldots$	Lyman Series (ultra-violet region)
$\nu = \frac{R}{2^2} - \frac{R}{m^2}$ where $m = 3, 4, 5 \ldots$	Balmer Series (visible region)
$\nu = \frac{R}{3^2} - \frac{R}{m^2}$ where $m = 4, 5, 6 \ldots$	Paschen Series (infra-red region)
$\nu = \frac{R}{4^2} - \frac{R}{m^2}$ where $m = 5, 6, 7 \ldots$	Brackett Series (infra-red region).

It is impossible to inspect this table without being struck by the combination of simplicity and regularity which it displays. The complete emission spectrum of hydrogen is a complex affair ; but the simplicity of the above formulæ inevitably suggests that the emitting mechanism cannot be a complicated one.

Latent in the above formulæ lies what is termed the Ritz *Combination Principle.* Ritz's attention was attracted by two simple regularities which he had observed in the course of his researches. First, that among the lines of a spectrum, some were found which exhibited constant differences between their wave-numbers. Thus it is possible to find lines with the wave-numbers ν_1, ν_2, ν_3, ν_4, such that $\nu_1 - \nu_2 = \nu_3 - \nu_4$. Second, that the frequency of any given line in a spectrum could be expressed as the difference between the frequencies of two other lines in the spectrum, *i.e.* for any line with wave-number ν_1, it is possible to find two other lines, with wave-numbers ν_2 and ν_3, such that $\nu_1 = \nu_2 - \nu_3$.

Very brief consideration of the nature of the formulæ will make clear what lies behind these regularities.

Table III shows some of the simpler forms taken by the Rydberg expression for the wave-number :

[1] Lyman, *Astrophys. J.*, 1906, **23**, 181 ; *Phys. Z.*, 1912, **13**, 583 ; *Spectroscopy of the Extreme Ultra-violet* (1914).

TABLE III

	Wave-number	
A.	$\left(\frac{1}{1^2}-\frac{1}{2^2}\right)R=\frac{3}{4}R$	Lyman Series (ultra-violet)
B.	$\left(\frac{1}{1^2}-\frac{1}{3^2}\right)R=\frac{8}{9}R$	
C.	$\left(\frac{1}{1^2}-\frac{1}{4^2}\right)R=\frac{15}{16}R$	
D.	$\left(\frac{1}{1^2}-\frac{1}{5^2}\right)R=\frac{24}{25}R$	
E.	$\left(\frac{1}{1^2}-\frac{1}{6^2}\right)R=\frac{35}{36}R$	
F.	$\left(\frac{1}{2^2}-\frac{1}{3^2}\right)R=\frac{5}{36}R$	Balmer Series (visible)
G.	$\left(\frac{1}{2^2}-\frac{1}{4^2}\right)R=\frac{3}{16}R$	
H.	$\left(\frac{1}{2^2}-\frac{1}{5^2}\right)R=\frac{21}{100}R$	
I.	$\left(\frac{1}{2^2}-\frac{1}{6^2}\right)R=\frac{2}{9}R$	
J.	$\left(\frac{1}{3^2}-\frac{1}{4^2}\right)R=\frac{7}{144}R$	Paschen Series (infra-red)
K.	$\left(\frac{1}{3^2}-\frac{1}{5^2}\right)R=\frac{16}{225}R$	
L.	$\left(\frac{1}{3^2}-\frac{1}{6^2}\right)R=\frac{1}{12}R$	
M.	$\left(\frac{1}{4^2}-\frac{1}{5^2}\right)R=\frac{9}{400}R$	Brackett Series (infra-red)
N.	$\left(\frac{1}{4^2}-\frac{1}{6^2}\right)R=\frac{5}{144}R$	

A little mental arithmetic will show that (B—F)=3R/4 and that the same difference is obtained in the cases of (C—G), (D—H), and (E—I). This accounts for the constant differences between the wave-numbers of pairs of lines in the hydrogen spectrum. Further, the difference 3R/4 obtained in this way is the wave-number of the first line given in the table, so that its wave-number has been expressed as the difference between the wave-numbers of two other lines.

In a similar manner, it will be found that the following relations hold:

$$B=(C-J)=(D-K)=(E-L)$$

so that the wave-number of the second line in the table can be expressed as a difference between the wave-numbers of various other pairs of lines.

These illustrations serve to make clear the statement of the Combination Principle in Ritz's original paper [1]: "By additive or subtractive combination, whether of the series formulæ themselves, or of the constants that occur in them, formulæ are formed which allow us to calculate certain newly-discovered lines from those known earlier."

The Combination Principle is one of the most important advances in spectroscopic research. It has been tested and found to hold good over the whole range of vibrations from the infra-red to the short-waved X-ray region; and it is a basal factor in the Bohr physical theory of the atom.

5. *The Bohr Theory of the Hydrogen Line Spectrum*

According to modern theory, the hydrogen atom consists of one proton and one electron. When this atom emits or absorbs light, some part of the system must be in motion; for otherwise there would be no mechanism present which could start or stop the light-vibrations. Since the proton is much more massive than the electron, it is reasonable to assume that this postulated motion is the revolution of the electron about the proton, like the movement of a planet around the sun.

If the classical mechanics be followed, the above hypothesis leads to two inferences. In the first place, the system is one in which a charged particle (the electron) is continuously accelerated towards the centre of its orbit. Such a system would radiate energy; the orbit would decrease; and eventually the electron would fall on to the proton. Obviously this mechanism would not provide the stability which is one of the main characteristics of hydrogen. In the second place, a system of this type would radiate a *continuous* spectrum, according to the classical mechanics; whereas the hydrogen spectrum is not continuous, but is composed of a series of discontinuous lines.

Thus the classical mechanics not only fails to fit the system we have postulated, but actually rules out the permanent existence of any such mechanism. If we are to find an hypothesis to

[1] Ritz, *Gesammelte Werke*, p. 162 (1911).

account for the hydrogen spectrum, we must obviously discard the classical mechanics and look elsewhere for a basis.

Planck's Quantum Theory supplies what is needed. According to Planck,[1] the exchange of energy between ether and matter takes place discontinuously in integral multiples of a small energy unit; and this exchange is brought about through some undescribed mechanism which for convenience is termed a Planck resonator. These resonators will not react with infinitely small amounts of energy. Before absorption or emission can be effected, the energy must reach a finite value (the quantum of energy, ϵ); and if greater quantities of energy are to be handled by the resonator, they must be supplied in simple multiples of the quantum.

Further, though the quantum of energy has a minimum value, it is not a constant unless we confine ourselves to a single oscillation-frequency, for Planck assumes that the quantum of energy, ϵ, and the oscillation frequency, ν, are connected by the following relation:

$$\epsilon = h\nu \quad \text{or} \quad \lambda\epsilon = h$$

wherein h is a universal constant (Planck's constant). In other words, if the energy be emitted at any wave-length, λ, then the quantum for that wave-length multiplied by the wave-length is equal to the universal constant h. Thus the quantum ϵ is small for the long infra-red waves and increases in magnitude as we pass along the spectrum towards the ultra-violet. Since ϵ is an energy factor whilst the oscillation-frequency term ν involves time, Planck's constant h represents energy$\times$time, which is an expression for action; and hence Planck's h is often spoken of as *the quantum of action.*

Here, then, in the Planck theory, the idea of discontinuous radiation comes to the front; and instead of the classical hypothesis we have now the conception of energy being radiated or absorbed under conditions which demand definite limitations, since the resonator can deal only with such quanta as are suitable for it.

Using Planck's theory as a basis, Bohr [2] evolved an explana-

[1] Planck, *Ann. Physik*, 1901, **4**, 553; *Vorlesungen uber die Theorie der Wärmestrahlung* (1906).

[2] Bohr, *Phil. Mag.*, 1913, **26**, 476, 857; 1914, **27**, 506; 1915, **30**, 394; Bohr, *The Theory of Spectra and Atomic Constitution* (1922).

tion of atomic radiation which has been extraordinarily successful in coping with the difficulties of the problem on the physical side. Departing even further than Planck from the classical mechanics, when he found it necessary, Bohr introduced three fresh ideas :

1. The number of possible orbits for an electron round an atomic nucleus is not unlimited (as in the classical dynamics), but only those orbits are permissible which fulfil certain quantum conditions. Bohr terms these " stationary orbits."
2. An electron moving in one of these stationary orbits does not radiate energy (as it would do according to the assumptions of classical dynamics).
3. An electron may leap from one orbit to another, but it may not occupy any position intermediate between two orbits ; and if this " jump " is due to the passage of the electron from an outer to an inner orbit, radiation is emitted according to certain quantum conditions.

In considering the Bohr theory it should be kept in mind that Bohr does not profess to give any picture of the actual mechanism by means of which light is emitted. Just as Planck postulated his resonators without attempting to describe them, so Bohr makes his assumption of the electronic leap from orbit to orbit without pretending to specify how this transfer gives rise to radiation.

Now consider the case of an electron, of mass m and with a negative charge e, moving in a circular orbit of radius r around a stationary proton with a positive charge e. Assume that the velocity of the electron is v and that ν is its rotational frequency. We then have the following relations :

$$\text{Electron's angular velocity } \omega = 2\pi\nu \quad . \quad . \quad (1)$$

$$\text{and } v = r\omega = 2\pi r\nu \quad . \quad . \quad (2)$$

Since the angular momentum of the electron is its mass multiplied by its velocity in its curved path, it follows that

$$\text{Electron's angular momentum} = mrv \quad . \quad . \quad (3)$$

$$= mr^2\omega \quad . \quad . \quad (4)$$

$$= 2\pi mr^2\nu \quad . \quad (5)$$

The electron is attracted toward the proton by a force e^2/r^2,

and it is also acted on by a centrifugal force $\frac{mv^2}{r}$ tending to make it leave its orbit. When these two forces are balanced, the system will be stable :

$$\frac{e^2}{r^2} = \frac{mv^2}{r} = \frac{mr^2\omega^2}{r} = mr\omega^2 \quad . \quad . \quad . \quad . \quad (6)$$

So far, we have not diverged from the classical mechanics ; and the results will hold good for any values of the various factors in the equations. Now, however, we come to Bohr's first limitation. Only those orbits are permissible for which the electron's angular momentum is equal to $nh/2\pi$, where n is a whole number and h is Planck's constant.* Bohr's condition is thus fulfilled only when

$$mvr = mr^2\omega = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By squaring both sides and transferring factors, we find

$$r^4 = \frac{n^2h^2}{4\pi^2m^2\omega^2} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

But from equation (6) we have

$$\frac{e^2}{r^2} = mr\omega^2$$

so that

$$r^3 = \frac{e^2}{m\omega^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Dividing (8) by (9), we obtain

$$\frac{r^4}{r^3} = \frac{n^2h^2}{4\pi^2m^2\omega^2} \times \frac{m\omega^2}{e^2}$$

whence

$$r = \frac{n^2h^2}{4\pi^2me^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

By making n successively equal to 1, 2, 3 . . . we get the radii of the various permissible orbits, which obviously stand in the proportion of 1^2, 2^2, 3^2, 4^2. . . . These orbits are

* Recent research has suggested an explanation of this. When an electron moves in an orbit, it is accompanied by a train of waves ; and an orbit is " permissible " only if its length is an exact multiple of the wave-length of the waves in question.

Bohr's "stationary orbits" and electrons moving in them are assumed by him to radiate no energy.

An analogous general expression for the orbital velocity of the electron is now obtained as follows.

From equation (6) we have

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

or

$$v^2 = \frac{e^2}{mr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Substituting the value for r which we found in (10), this becomes

$$v^2 = \frac{e^2}{m} \cdot \frac{4\pi^2 me^2}{n^2h^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

so that

$$v = \frac{2\pi e^2}{nh} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We now come to the phenomena of light-emission from the atom; and as a first step we must consider the change of energy in the system which is produced by an electron leaping from one orbit to another, and thus emitting radiation according to Bohr's postulate.

The total energy of the system is the algebraic sum of the potential and kinetic energies of the electron, since we have assumed that the proton is at rest. The potential energy of the electron in an orbit of radius r is given by $-e^2/r$; and its kinetic energy is $mv^2/2$. The total energy, W, is therefore expressed by

$$W = \frac{mv^2}{2} - \frac{e^2}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Replacing r and v in this by the values obtained in (10) and (13), we find

$$W = \left(\frac{m}{2} \times \frac{4\pi^2e^4}{n^2h^2}\right) - \left(\frac{e^2 \cdot 4\pi^2me^2}{n^2h^2}\right)$$

$$= -\frac{2\pi^2me^4}{n^2h^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Now imagine an electron leaping from the outer orbit for which $n=(n+1)$ to the inner orbit for which $n=n$. If the elec-

tron's energy in the first orbit is W_{n+1} and in the second orbit it is W_n, the change in energy due to the leap will be

$$W_{n+1} - W_n = -\frac{2\pi^2 me^4}{(n+1)^2h^2} + \frac{2\pi^2 me^4}{n^2h^2}$$

$$i.e.\ W_{n+1} - W_n = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right) \quad . \quad . \quad (16)$$

Since this expression within the bracket obviously has a positive value, it is evident on Bohr's assumptions that when an electron leaps from an outer orbit to an inner one, there is a liberation of energy from the system.

This brings us to another of the Bohr limitations, according to which this liberated energy appears in the form of light of a definite oscillation-frequency and amounts to exactly one quantum. Thus if an electron leaps from any orbit for which $n=n_2$ to an inner orbit for which $n=n_1$, and if in its leap energy $=(W_2-W_1)$ is emitted at an oscillation-frequency ν, then the following relations hold good :

$$\text{One quantum} = h\nu = W_2 - W_1 \quad . \quad . \quad . \quad (17)$$

$$\text{and from (16)}, \quad W_2 - W_1 = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad . \quad (18)$$

From which by inspection it is clear that

$$\text{Oscillation-frequency} = \nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \quad (19)$$

and since $\nu = c/\lambda$, where c is the velocity of light, we have this expression for the wave-number of the emitted light :

$$\text{Wave-number} = \frac{2\pi^2 me^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad . \quad . \quad (20)$$

Obviously this expression (20), which we have derived purely from the Bohr postulates, is a mere variant of the empirical Balmer-Rydberg equation for the disposition of the hydrogen lines :

$$\text{Wave-number} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

since in the Balmer-Rydberg equation n and m change their values by whole-number increments, just as n_1 and n_2 do in the Bohr expression.

Equating R against the corresponding term in the Bohr formula, we obtain

$$R=\frac{2\pi^2me^4}{ch^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

This provides a crucial test of the Bohr theory, since by substituting in equation (21) the known values for the five constants, we shall be able to calculate R and then compare it with the figure obtained experimentally. When this calculation is actually made, the results are in extraordinarily good agreement:

From experiment	$R=109678\ cm^{-1}$
From Bohr's calculation	$R=109800\ cm^{-1}$

Very few theories have, in their initial stages, provided such striking evidence in their favour as this coincidence between the calculated and observed values of the Rydberg constant.

By gathering together the results of experiment and theory which have been given above, we can obtain some ideas about the Bohr model hydrogen atom. In Fig. 1, the proton is supposed to lie at the centre, and the circles represent the various possible stationary orbits in which the electron can revolve without radiating energy. The radii of these orbits have lengths proportional to 1^2, 2^2, 3^2, 4^2 . . . When an electron jumps from an outer orbit to an inner orbit, radiation takes place from the atom. Conversely, if an electron is withdrawn from an inner orbit to an outer one, energy is absorbed by the system. If the electron is removed completely from the system, the atom is ionised.

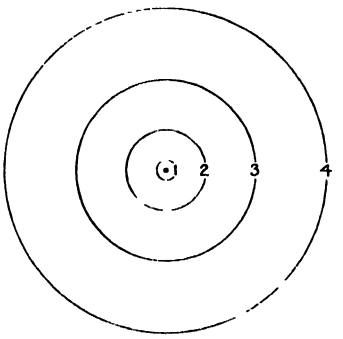


Fig. 1.

Now suppose the electron falls from Orbit 2 into Orbit 1, the Bohr theory predicts that the following relationship holds good, since it is simply equation (20) with $n_1=1$ and $n_2=2$

$$\text{Wave-number of emitted light}=\frac{2\pi^2me^4}{ch^3}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

And since the factor outside the bracket is the Rydberg constant, R, this can be written

$$\text{Wave-number} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

But this is simply the expression A in Table III (p. 18), which gives the wave-number of the first line of the Lyman series in the ultra-violet region.

If an electron falls from Orbit 3 to Orbit 1, the expression (20) will have $n_1=1$ and $n_2=3$, and this makes it identical with B in Table III.

From this it is clear that the various lines in the Lyman series are all ascribable to the leaps of electrons (from outer orbits) which come to rest in Orbit 1.

Now suppose that in equation (20) we put $n_1=2$ and $n_2=3$. This will correspond to the jump of an electron from Orbit 3 into Orbit 2. The wave-number will be given by

$$\text{Wave-number} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

and this is clearly the expression F in Table III (p. 18), which corresponds to the first line in the Balmer series. So the Balmer series, on the Bohr Theory, is produced by electrons starting from outer orbits and falling into Orbit 2.

Thus the whole known system of the hydrogen lines can be generated by one or other of the following processes :

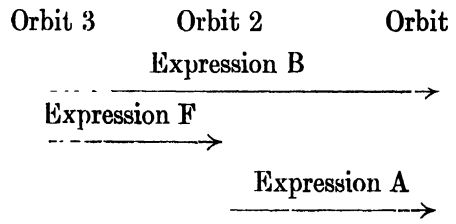
Electron starts in	Electron comes to rest in	Spectral series produced
Orbit 2, 3, 4 . . .	Orbit 1	Lyman (ultra-violet)
Orbit 3, 4, 5 . . .	Orbit 2	Balmer (visible)
Orbit 4, 5, 6 . . .	Orbit 3	Paschen (infra-red)
Orbit 5, 6, 7 . . .	Orbit 4	Brackett (infra-red)

The physical meaning of the Ritz Combination Principle can be made clear in a similar manner. We have already seen that by purely empirical means it can be proved that in Table III (p. 18)

$$A = B - F$$

Now B represents the result of an electron dropping from Orbit 3 to Orbit 1, whilst F represents the result of an electron leaping from Orbit 3 to Orbit 2. The difference between these two

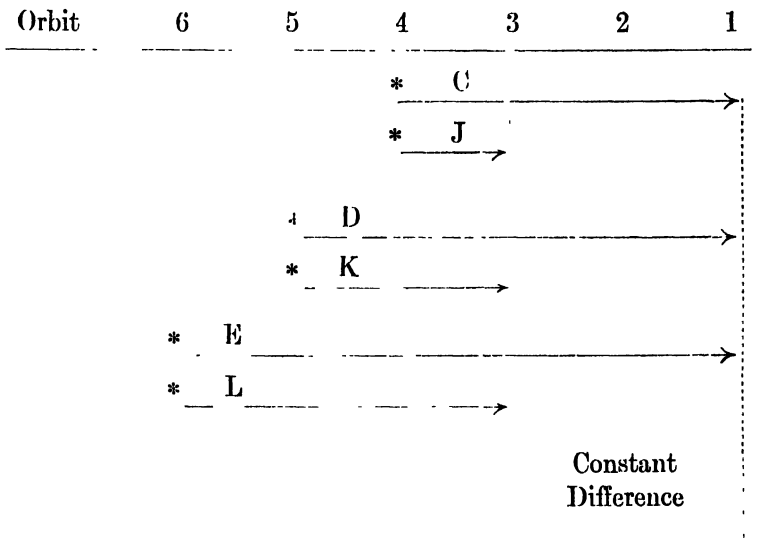
processes is simply that in the first case, B, the electron passes over the space from Orbit 3 to Orbit 2 and then goes on to Orbit 1, whereas in F the electron, also starting in Orbit 3, stops short in Orbit 2 and does not complete the course. The final leap from Orbit 2 into Orbit 1 corresponds to the expression A. The following symbols will make the matter clear.



A similar diagrammatic scheme will illustrate the second part of the Ritz Combination Principle: the constant differences observed between pairs of lines in a spectrum. It has been pointed out that in Table III (p. 18), the following constant differences have been observed between various expressions:

$$(C-J)=(D-K)=(E-L)$$

Marking the starting-orbit of the electron with a star in each case and indicating its final resting-place by means of an arrowhead, we obtain the following scheme:



Thus in each of the line-pairs (CJ, DK, and EL) the electrons generating the two lines start from the same orbit; but while one of the electrons swoops straight down to Orbit 1, the second electron of the pair stops short at Orbit 3, leaving the gap between Orbit 3 and Orbit 1 untraversed. This uncompleted part of the course, being the same in the cases J, K, and L, supplies the required constant difference.

For the sake of simplicity, we have hitherto dealt with the case of an electron rotating about a fixed proton; but obviously if we seek for a more accurate and a more general formulation of the problem, two points at once come under consideration.

In the first place, the positive charge on the nucleus of the atom may be greater than e, the charge on the electron. Taking this charge on the nucleus as E, then clearly we have to substitute Ee for e^2 wherever the latter occurs in our equations.

Again, in practice, the electron would not rotate around a *fixed* nucleus. Both electron and nucleus would move around their common centre of gravity. This entails a correction which Bohr has shown to be simple. It consists in substituting for m in our equations the fraction

$$\frac{m\mathrm{M}}{\mathrm{M}+m}$$

in which M is the mass of the nucleus and m the mass of the electron.

On inserting these corrections into the expression (21) for the Rydberg constant, the equation becomes

$$\mathrm{R}=\frac{2\pi^2\mathrm{E}^2e^2m}{ch^3}\cdot\frac{\mathrm{M}}{\mathrm{M}+m} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and it is obvious that the Rydberg constant will vary slightly according to the nuclear charge and mass of the element under consideration.

6. *The Spectrum of Ionised Helium*

As will be seen later in this volume,* the helium atom is supposed to consist of a nucleus around which circulate two electrons. A mathematical treatment of this system would

* See Chapter XIII.

involve the so-called " Problem of Three Bodies," which has not yet found a solution in our dynamics ; so that the spectrum of a neutral helium atom lies outside the bounds of calculation at the present day. If, however, one of the electrons be removed by ionisation, we are left with a nucleus and one electron ; and in this form the subject is amenable to mathematical treatment, since it is analogous to the simpler case of the hydrogen atom.

The helium nucleus is believed to carry a positive charge which is numerically equivalent to $2e$. If this be substituted for E in formula (22), it is obvious that the numerator will now contain $4e^4$ instead of the simple e^4 which we had in the hydrogen formula. Further, since the fraction $M/(M+m)$ is increased when the nuclear mass M becomes 4 instead of 1, as in hydrogen, the Rydberg constant will be considerably altered by these changes.

This is in agreement with practice. Fowler has observed that the ratio of R for ionised helium and for hydrogen is 4·001638. The units figure 4 is evidently attributable to the figure 4 introduced by making $E=2e$. The deviation from the round figure 4 is the effect of the mass factor. Now it is easy to show that the Bohr theory implies the following expression for the ratio between R for ionised helium and R for hydrogen :

$$\frac{4M_{He}(M_H+m)}{M_H(M_{He}+m)}=4{\cdot}001626$$

wherein M_{He} represents the mass of the helium nucleus, M_H the mass of the hydrogen proton, and m the mass of an electron. When the appropriate data are inserted, the result is the figure shown for the value of the fraction. Thus the Bohr theory yields a calculated ratio=4·001638, whilst the ratio determined by experiment is 4·001626. This is strong evidence in support of Bohr's views.

The spectrum of ionised helium furnishes evidence in Bohr's favour from quite another aspect. In 1896 Pickering [1] discovered in the spectrum of the star ζ Puppis a series of lines closely analogous to the known hydrogen spectrum. The resemblance was so close that the wave-lengths of the lines could

[1] Pickering, *Astrophys. J.*, 1896, **4**, 369.

be represented by means of a modification of Balmer's formula :

$$\lambda = 4650 \frac{m^2}{m^2-4} - 1032$$

A year later, Pickering [1] pointed out that both the stellar and the hydrogen spectrum could be expressed in a single formula if $n/2$ were substituted for m in the ordinary Balmer formula for hydrogen. This substitution converts the Balmer formula into

$$\lambda = 3646 \cdot 1 \frac{n^2}{n^2-16}$$

If in this formula n be given the values 6, 8, 10, 12 . . . we get the positions of the normal hydrogen lines ; whilst if n be made 11, 13, 15, 17 . . . the formula gives the wave-lengths of the stellar lines. The obvious explanation of these facts seemed to be that under stellar conditions hydrogen was capable of yielding a fresh spectrum which had not been reproduced in a laboratory.

The Bohr theory, however, furnishes a simpler solution of the matter. The wave-numbers of the lines in the spectrum of ionised helium are obtained, as we have seen, by putting $E=2e$ in the equation (22) above. The result is

$$\text{Wave-number} = \frac{mM}{M+m} \cdot \frac{2\pi^2 e^4 m}{ch^3} \cdot 4\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R \times 4\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R \times \left(\frac{1}{\left(\frac{n_1}{2}\right)^2} - \frac{1}{\left(\frac{n_2}{2}\right)^2}\right)$$

If in this expression $n_1=4$, whilst n_2 takes the successive values 5, 6, 7 . . . then the *even* values of n_2 (*i.e.* 6, 8, 10 . . .) give the Balmer series, whilst the odd values of n_2 (*i.e.* 5, 7, 9 . . .) yield the Pickering series.

Thus the Bohr theory suggests that the Pickering spectrum is emitted by ionised helium ; and, further, that ionised helium can also emit the lines of the Balmer series.

[1] Pickering, *Astrophys. J.*, 1897, **5**, 92.

Again, if we put $n_1=3$ and n_2 equal successively to 4, 5, 6 . . . the odd values for n_2 yield numbers corresponding to the positions of a series of lines observed in 1912 by Fowler [1] when a very heavy discharge was passed through a mixture of hydrogen and helium. Further experiments were made by Evans [2]; and Paschen [3] measured the Fowler lines in tubes containing helium which had been freed from all traces of hydrogen.

7. *Principal and Azimuthal Quantum Numbers*

Hitherto in this chapter we have been content to consider the case of an electron moving around an atomic nucleus in a *circular* orbit; but the astronomical analogy of the earth and the sun suggests that in reality the electronic orbits are elliptical.* Bohr's theory has been extended in this manner by Sommerfeld. For full particulars of the advances thus achieved, reference must be made to Sommerfeld's book,[4] as the space available here will permit only the merest outline sketch of the results.

In the Bohr theory, it will be remembered, the principal point was the selection of certain permissible orbits from the infinite number of possible orbits. The same problem faces us in the case of elliptical motion. Movement in an elliptical path presents a problem in two degrees of freedom, since the position of an electron in an elliptical orbit cannot be defined by less than two co-ordinates. For instance, if measurements are made from the nucleus, we shall have to define the length, r, of the radius vector and the angle, ϕ, which the radius vector makes with a fixed line. This angle is termed the azimuth.

In the case of the circular orbit, the motion of the revolving electron was defined simply by the radius of the orbit—the single factor n^2 which appeared in our equation. In elliptical orbits, however, two factors are obviously required, and n is replaced by two new variables: the *radial quantum number* n_r and the *azimuthal quantum number* n_a. The sum of these two

[1] Fowler, *Monthly Notices of the Roy. Astronomical Soc.*, 1912, 62; *Phil. Trans.*, 1914, (A), **214**, 254.

[2] Evans, *Phil. Mag.*, 1915 (6), **29**, 284.

[3] Paschen, *Ann. Physik*, 1915 (4), **50**, 901.

* Probably it would be more correct to say ellipse-like, owing to something in the atomic system akin to the precessional effect which makes its appearance in the orbit of the planet Mercury.

[4] Sommerfeld, *Atomic Structure and Spectral Lines*, p. 232 ff. (1923).

figures is termed the *total quantum number* or the *principal quantum number.*

For the sake of space, it is usual to adopt an abbreviation in expressing these values. For example, if an orbit is defined by a principal quantum number 3 and an azimuthal quantum number 2, it is generally referred to as a 3_2 orbit. An orbit defined by the principal quantum number 5 and the azimuthal quantum number 3, would be described as a 5_3 orbit.

As a result of his calculations, Sommerfeld [1] produced the following expressions :—

$$1-\epsilon^2 = \frac{n_a^2}{(n_a+n_r)^2} \quad \ldots\ldots\ldots \quad (23)$$

$$a = \frac{h^2}{4\pi^2 me\mathrm{E}}(n_a+n_r)^2 \quad \ldots\ldots\ldots \quad (24)$$

$$\mathrm{W} = -\frac{2\pi^2 me^2\mathrm{E}^2}{h^2}\cdot\frac{1}{(n_a+n_r)^2} \quad \ldots\ldots\ldots \quad (25)$$

Here ϵ is the eccentricity of the ellipse; n_a is the azimuthal quantum number; n_r is the radial quantum number; $2a$ is the major axis of the ellipse; W is energy of the system; and the other symbols have their usual meaning.

Turn now to the physical interpretation of the expressions. In the case of an electron revolving in a circular orbit around a nucleus with a charge E, the Bohr expression for the energy of the system can be written

$$\mathrm{W} = -\frac{2\pi^2 me^2\mathrm{E}^2}{n^2h^2} \quad \ldots\ldots\ldots \quad (26)$$

for this is simply the equation (15) on p. 23 with the substitution of E^2 for e^2 in the numerator to express the change in the nuclear charge. This expression (26) is of the same form as (25) and can be made identical with (25) if we choose values of the azimuthal numbers such that

$$n = n_a + n_r$$

In other words, if $n=(n_a+n_r)$, then the energy W for the *elliptical* orbit will be identical with the energy for the corresponding Bohr *circular* orbit. Further, it is evident from (25) that the energy, W, depends upon the principal quantum number$=(n_a+n_r)$.

[1] Sommerfeld, *Atomic Structure*, pp. 235–6 (1923).

The expression (24) implies that all orbits having the same principal quantum number will have equal major axes; but when (23) is taken into account, it is clear that the eccentricities of the orbits will depend upon our choice of n_a and n_r.

A concrete illustration will make this plain. Take a case in which the principal quantum number is 4. Substituting this for (n_a+n_r) in equation (24), we obtain the following:

$$\text{Semi-major axis}—a=\frac{h^2}{4\pi^2 me\mathrm{E}}\times 4^2=\frac{4h^2}{\pi^2 me\mathrm{E}} \quad . \quad (27)$$

Thus all the ellipses corresponding to the principal quantum number 4 have major axes expressed by $8h^2/\pi^2 me\mathrm{E}$.

We now turn to the calculation of the eccentricities of the various ellipses which will fulfil the quantum conditions. We have assumed that $(n_a+n_r)=4$, but this leaves us free to adjust the individual values of n_a and n_r so long as we confine ourselves to integral values for each and make the sum of the two factors $=4$.

The eccentricity, ϵ, is obtained by re-arranging equation (23) thus:

$$\epsilon=\sqrt{1-\frac{n_a^2}{(n_a+n_r)^2}} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Take the various possible values for the azimuthal and radial quantum numbers and fill them in successively in the above expression:

		Quantum Numbers n_a	Quantum Numbers n_r	Eccentricity
4_4	Orbit	4	0	$\sqrt{1-\frac{4^2}{(4+0)^2}}=0$
4_3	Orbit	3	1	$\sqrt{1-\frac{3^2}{(3+1)^2}}=\frac{\sqrt{7}}{4}$
4_2	Orbit	2	2	$\sqrt{1-\frac{2^2}{(2+2)^2}}=\frac{\sqrt{3}}{2}$
4_1	Orbit	1	3	$\sqrt{1-\frac{1^2}{(1+3)^2}}=\frac{\sqrt{15}}{4}$
4_0	Orbit	0	4	$\sqrt{1-\frac{0^2}{(0+4)^2}}=1$

Two points of interest may be noted here. In the first place, when the principal and azimuthal quantum numbers are identical, as in the case of the 4_4 orbit in the above table, the orbit in question is circular. Secondly, if the azimuthal number be reduced to zero (*i.e.* as in an orbit expressed by 4_0) the orbit is flattened out until the ellipse merges into a straight line through the nucleus, since in this case $\epsilon=1$. The electron in such an orbit would travel to and fro on a straight line through the nucleus. As in practice we have no knowledge of any such behaviour, and as all our information forbids a trans-nuclear electronic motion, this extreme case is regarded as an impossibility; and orbits of the types 4_0, 3_0, etc., are ruled out of account.

At a first glance, the Sommerfeld modification of Bohr's original scheme does not seem to bring anything fresh into the field to justify the extra complexity which it introduces. If the principal quantum number $(n_a'+n_r')$ for an elliptical orbit be the same as the quantum number of a circular orbit, then W is identical for the two orbits; and the rest of the reasoning is the same for both cases. This can be seen at once if we write down the expression for the Sommerfeld elliptical orbits side by side with the Bohr expression for circular orbits:

$$\text{Wave-number}=R\left(\frac{1}{(n_a'+n_r')^2}-\frac{1}{(n_a''+n_r'')^2}\right) \quad . \quad (29)$$

$$\text{Wave-number}=R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Since $(n_a'+n_r')=n_1$ by Sommerfeld's postulate, while $(n_a''+n_r'')=n_2$, it is self-evident that the two expressions will yield precisely the same results.

For example, suppose that an electron starts in any one of the three orbits defined by 3_3, 3_2, 3_1, and comes to rest in either of the orbits 2_2 or 2_1, there are six possible arrangements each of which involves the same energy change as any of the other five:

Electron starts in orbit.	Electron lands in orbit.
*3_3	2_2
3_2	2_2
3_1	2_2
3_3	2_1
3_2	2_1
3_1	2_1

In the example marked with a star, the electron passes from one circular orbit to another circular orbit. Here we can apply Bohr's expression (30), where $n_1=2$ and $n_2=3$, so that the equation becomes

$$\text{Wave-number}=R\left(\frac{1}{2^2}-\frac{1}{3^2}\right) \quad . \quad . \quad . \quad . \quad (31)$$

But this is precisely the same as the Sommerfeld expression for an electron passing from, say, the 3_2 orbit to the 2_1 orbit: since then for the 3_2 orbit, $n_a'=1$ and $n_r'=2$, and for the 2_1 orbit, $n_a''=1$ and $n_r''=1$, so that the expression (29) becomes

$$\text{Wave-number}=R\left(\frac{1}{(1+1)^2}-\frac{1}{(2+1)^2}\right) \quad . \quad . \quad (32)$$

which is obviously identical with (31).

When the calculation is made, the wave-number obtained is that of the first line, H_α, in the Balmer series. The physical interpretation of these results is self-apparent. An electron suffering transference from any of the orbits 3_3, 3_2, 3_1 to either of the orbits 2_2, 2_1, will generate a vibration identical with the line H_α of the Balmer series. Thus the line H_α, according to Sommerfeld, may be the result of any one of six possible changes in electronic position.

If the Bohr model hydrogen atom accounts successfully for the emission of the various hydrogen lines, why introduce the conception of radial and azimuthal quantum numbers at all? To appreciate Sommerfeld's contribution we must turn to fresh fields and deal very briefly with the Zeeman effect, the Stark effect, and fine structure of the hydrogen lines.

According to Sommerfeld,[1] when the hydrogen atom is in its natural state—*i.e.* when no external magnetic or electric field is present—the various possibilities of generation tend to produce a single line only by mere accidental coincidence. This state of affairs may be altered if the atomic system be subjected to some external agent which has the power of modifying it or if something takes place within the atom which tends to alter the elliptical orbits of the electrons in any way.

In 1896 Zeeman discovered that powerful magnetic fields have a marked influence upon spectral lines. A line which

[1] Sommerfeld, *Sitzungsber, Münchener Akad.*, 1915, p. 425; *Atomic Structure and Spectral Lines*, pp. 237, 276, 294 (1923).

normally appears single may appear as a doublet when the observed ray is in the direction of the magnetic lines of force, whilst a triplet may be seen when the observation is made at right angles to the lines of force. In the doublet, the light is circularly-polarised, whilst in the triplet two of the lines are produced by plane-polarised light and the third (in the position of the original single line) is produced by light plane-polarised parallel to the lines of magnetic force. The classical mechanics, in the hands of Lorentz, proved capable of accounting for simple cases of the Zeeman effect; but further research revealed a complexity of pattern among the Zeeman results which the classical theory failed to explain. As Sommerfeld has shown, the magnetic field disturbs the quantum orbits of the atom; the ellipses are not all similarly affected, so that alterations are produced in the energies associated with them; and the result is the series of phenomena observed in the Zeeman effect. Thus Sommerfeld's assumption of elliptical orbits has justified itself in a very complex field.

Even greater success attended it in the case of the Stark effect. If a strong electric field be applied to a luminescing gas in a highly-evacuated tube, the original spectral lines of the gas are replaced by a more intricate pattern of fresh lines. The classical electrodynamics failed completely when applied to this problem; but Sommerfeld has been able to handle the matter satisfactorily on the assumptions made in designing his model atom.

Finally, when powerful diffraction gratings or interferometers are used, certain spectral lines which appeared single with older instruments are resolved into a series of lines, so that a finer structure is revealed. For instance, the lines of the Balmer series have been experimentally resolved into doublets. Since the Bohr circular orbits lead to only single-line emission for hydrogen, the Sommerfeld elliptical orbits seemed to give a better picture of the system, provided that some intra-atomic mechanism could be provided to disturb the original ellipses.

Sommerfeld coped with this difficulty by introducing a correction based on the relativity theory. According to the Lorentz transformation, the mass of a particle will be altered if the particle is made to move with a velocity approaching that of light. Now by inserting the appropriate values in the equation

(13) on p. 23, the velocity of an electron in the innermost orbit of a hydrogen atom can be shown to be $2{\cdot}19 \times 10^8$ cms./sec. which is about 1/150 of the speed of light. This is certainly not a negligible factor in the Lorentz equation:

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

where m_0 is the normal mass of the particle, m the mass of it at velocity$=v$, and c is the speed of light.

One effect of introducing the relativity correction is to alter the character of the electronic path. Instead of imagining the electron moving round an ellipse, we have to assume further that the ellipse itself is also in motion on the pivot of one of its foci, so that there is an advance of the orbital perihelion akin to that actually observed in the movement of the planet Mercury. This distortion of the original electronic movement is the cause to which Sommerfeld ascribes the production of the fine-line structure of spectral lines; for owing to the alteration in the orbits, certain energy-changes are introduced which make the problem deviate from the simple one suggested by the Bohr circular orbits, and fresh lines are produced instead of the single one which Bohr's theory predicts.

8. *The Bohr Correspondence Principle*

Let us revert for a moment to classical dynamics and consider a particle moving with velocity v in an orbit of radius r. Then the angular velocity, ω, of the particle is expressed by

$$\text{Angular velocity } \omega = \frac{v}{r}. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and the mechanical frequency of the revolution of the electron is obviously given by dividing by 2π:

$$\text{Frequency of revolution} = \frac{\omega}{2\pi} = \frac{v}{2\pi r} \quad . \quad . \quad (34)$$

According to the old classical dynamics, this frequency of revolution corresponds to the frequency of the light emitted by the system. Let us assume that we are dealing with an electron in

one of the Bohr orbits, and see what value the classical dynamics ascribes to this frequency.

By substituting in equation (34) the values for r and v which we obtained in equations (10) and (13), on pp. 22, 23, we get:

$$\frac{\omega}{2\pi} = \frac{1}{2\pi} \times \frac{2\pi \mathrm{E}e}{nh} \times \frac{4\pi^2 m \mathrm{E}e}{n^2h^2} \quad . \quad . \quad . \quad . \quad (35)$$

wherein E is the charge on the nucleus of the atom, e the charge on the electron, m the mass of the electron, h is Planck's constant, and n is the quantum number for the orbit in question. Cancelling out, the expression takes this form:

$$\frac{\omega}{2\pi} = \frac{4\pi^2 m \mathrm{E}^2 e^2}{h^3} \cdot \frac{1}{n^3} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Inspection shows that the first term on the right-hand side is simply the expression for the Rydberg constant applicable to oscillation frequencies,* and thus the equation simplifies to

$$\text{Frequency of revolution } \omega = \frac{2\mathrm{R}}{n^3} \quad . \quad . \quad . \quad (37)$$

Next let us calculate the frequency, ν, of the vibration emitted from a Bohr atom when an electron leaps from orbit $(n+1)$ to orbit n. If in this case R represents the value of the Rydberg constant applicable to oscillation-frequencies (not to wave-numbers) we have the usual form of the equation:

$$\nu = \mathrm{R}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right)$$

and by throwing the two fractions within the bracket into one we get:

$$\nu = \mathrm{R} \cdot \frac{2n+1}{n^2(n+1)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

If, now, in the expression above, we make n very great, the expression becomes very closely approximate to

$$\nu = \frac{2\mathrm{R}}{n^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Thus from the classical dynamics we inferred (37) and from the

* If we were dealing with wave-numbers there would of course be the velocity of light factor, c, in the denominator.

Bohr postulates we arrived at (39); and in both cases the final result yields the same value for the frequency of the emission.

These two results indicate that when *the quantum numbers are great enough* there is a correspondence between the results of the classical theory and the Bohr theory; so that the two theories should give the same results among the long waves of the infra-red region of the spectrum. This is the kernel of what Bohr terms a Principle of Correspondence between the Wave Theory and the Quantum Theory, which is added to the quantum theory as something foreign to its nature. According to Bohr's view, this correspondence is not confined to the infra-red region, but can be traced over the whole spectrum. It is, as Sommerfeld flowerily terms it,[1] " a magic wand which allows us immediately to make use of the results of the classical wave theory in the quantum theory." [2]

9. *Conclusion*

In the foregoing pages, limitation of space made it difficult to deal other than briefly with even the main points of interest in the field of line spectra. Incomplete as the treatment perforce has been, it has at least served to throw into prominence the clarifying influence which Bohr's novel ideas brought in their train. As is usual in physics and chemistry, the introduction of a mechanical model has given us something definite to work upon; and though it must be confessed that the Bohr model atom breaks away from many of our preconceived ideas of dynamics, yet it is a conceivable mechanism, and it gives us some concrete picture to associate with the masses of data accumulated by much patient research.

But while this is put to its credit, we should endeavour to retain some perspective in the matter; and caution seems not out of place.

Primarily, it should be borne constantly in mind that as an actual mathematical proposition, the Bohr atom covers only two cases: hydrogen and ionised helium. Any application of it beyond these two examples is argument by analogy, since even

[1] Sommerfeld, *Atomic Structure and Spectral Lines*, p. 275 (1923).

[2] For further information about the Correspondence Principle, see Bohr, Copenhagen Ac. 1918, ff., and Sommerfeld, *Atomic Structure and Spectral Lines*, pp. 577 ff. (1923).

the case of lithium is outside the scope of mathematical treatment at the present day. Further, argument by analogy in such a field as this is more than a little venturesome, since quite obviously as we proceed to the heavier atoms we are passing into a field where the individual complexities of the systems may swamp the fundamental character of the Bohr model. Any attempt to apply the same reasoning to hydrogen and to uranium would be futile, since in the case of the latter element we have no less than ninety-two electrons circulating around the nucleus and each of them influenced by the movements and charges of its neighbours. Thus Bohr's suggestions as to the structure of the more complex atoms (with which we shall deal later in this volume *) must be regarded simply as guesses unsupported by any mathematical evidence whatever. They stand on precisely the same level as the guesses put forward by various other investigators; and from the chemical stand-point they must be scrutinised with especial care, since at its basis the Bohr theory is concerned with atoms in a luminescent state, which is quite different from the condition of the atoms in our test-tubes.

In the second place, though the Bohr atom has done magnificent service in clearing up our ideas and replacing a mass of empirical relationships by a concrete picture, it must be clearly understood that it has by no means covered the whole field of spectra. The spectrum of one of our commonest elements, iron, has not even yet been completely sifted out into an orderly grouping; and iron is only one example among many.

Lastly, the Bohr atom appears to fail in one of the simplest cases of electro-chemical action—the electrolysis of hydrochloric acid. Here, at the cathode of the apparatus, protons (hydrogen ions) are uniting with electrons to form atoms and molecules of hydrogen. Now this process, on the Bohr theory, represents the fall of an electron from outside the atom into the orbit of greatest radius †; and once it has come into the atomic system, this electron ought to fall from orbit to orbit towards the proton, and thus emit in turn the Brackett lines, the Paschen lines, the Balmer series, and the Lyman spectrum. In other words, the cathode surface should exhibit a visible glow, since some at least of the atoms will be in the Balmer stage of transition. As every one

* See Chapter XIII.

† Compare the argument in the case of continuous spectra in Chapter XXI.

knows, nothing of the sort is observed. Thus to bolster up the Bohr theory on this point, we would have to assume that in the union of an H-ion with an electron, the electron is permanently retained in the outermost orbit and does not perform any of the inter-orbital leaps which accompany emission. But if that be so how can we imagine that such leaps occur from the outermost orbit to inner ones in the normal production of the hydrogen spectrum? It is hardly possible to ascribe the difference to solution effects. This simple point is one of the weakest spots in the Bohr theory.

CHAPTER III

X-RAY SPECTRA AND ATOMIC NUMBERS

1. *The Phenomena of Crookes Tubes*

When an electric current passes through a highly evacuated tube, three types of "rays" may be produced, according to the experimental conditions: cathode rays, positive rays, and *X*-rays. As a parallel set of phenomena will be met with when we come to deal with the radioactive elements, it seems best to deal with all three classes here, though strictly the first two types lie outside the scope of the present chapter.

From the cathode of a Crookes tube, cathode rays are thrown off at right angles to the surface on the side of the plate next to the anode. They are streams of electrons travelling at very high velocities in straight lines; and are capable of penetrating thin sheets of aluminium or gold leaf. They ionise gases through which they pass; and produce an image on a photographic plate. When they impinge upon certain materials they set up fluorescence or phosphorescence; and they also heat up any substance by their impact. Finally, owing to their electrical nature, the particles which compose the stream can be deviated from their straight paths by magnetic or electric fields. Each electron represents a charge equal in quantity but opposite in sign to that carried by a hydrogen ion.

The second type of rays generated in a Crookes tube is known by various names: canal rays, Kanalstrahlen, Goldstein rays or, in recent times, positive rays. They are streams of positively charged molecules of the residual gas in the tube which are produced when the cathode is pierced with one or more apertures; and they travel in straight lines in a direction opposite to that taken by the cathode rays. They have less power of penetrating matter than cathode rays have; and they are not so susceptible to deviation by electrical or magnetic fields.

Finally come the X-rays, which are produced when cathode rays impinge upon matter. For long after their discovery, the nature of the X-rays remained in doubt; but it is now known that they are vibrations similar to light, though their wave-lengths are extremely small as compared with those of light-waves. Like light, an X-ray can be diffracted, and polarised. When passed into a solid, an X-ray pencil is "scattered" just as light is scattered in a foggy atmosphere.

If X-rays be allowed to fall upon a metallic surface, it is found that the metal is stimulated and gives off characteristic X-rays of definite wave-lengths.[1] The nature of the new radiations depends solely upon the metal from which they are generated and has no relation to the properties of the original X-ray, provided always that the parent X-ray is harder * than the characteristic radiation of the metal used. If the parent rays are too soft, no characteristic ray is excited by them. A rough rule is that the characteristic radiation of a given atom can excite the corresponding radiation of a lighter atom, but cannot produce any such effect in the case of a heavier atom.

An analogy to this phenomenon is to be found in the case of fluorescence excited by light. If white light, which is a mixture of many wave-lengths, be allowed to fall upon a solution of quinine, a blue fluorescence is produced which is characteristic of quinine. The same white light falling upon a fluorescein solution generates a green fluorescence, which is characteristic of fluorescein.

It has been shown that some elements give out several kinds of characteristic radiations, and these types are known as the *K*, *L*, etc., series. The *K* radiation is about three hundred times more penetrating than the *L* type. Both of these radiations conform to an empirical relation known as Owen's Fifth-power Law, which connects quality of the radiation with the atomic weight of the metal emitting it. This law states that the penetrating power of the radiation is roughly proportional to the fifth

[1] Barkla and Sadler, *Phil. Mag.*, 1908, **16**, 550; Kaye, *Phil. Trans.*, 1909, A, **209**, 123.

* The terms "hard" and "soft" applied to X-rays indicate the penetrative power of the rays, hard rays being more penetrating than soft ones. The hard rays are of shorter wave-length than the soft ones.

power of the atomic weight of the metal from which the rays are generated.[1]

These characteristic X-rays are governed entirely by atomic factors and are not affected by molecular conditions; for an element has been shown to give exactly the same quantity of characteristic rays whether it exists in the free state or in combination as a salt.[2] For example, Fe, Fe_2O_3, Fe_3O_4, $FeSO_4$, and $K_4Fe(CN)_6$ all emitted the characteristic X-rays of iron.[3]

It has been found that strong characteristic radiations may be obtained in the following manner.[2] The cathode stream of a Crookes tube is allowed to fall upon an anti-cathode of the metal whose characteristic radiation it is desired to produce. Screens of the same metal are then placed in the path of the X-rays generated at the anti-cathode; and in this way any non-characteristic radiations are converted into those characteristic of the metal under examination.

2. *The Method of Measuring X-ray Spectra*

The work of W. H. and W. L. Bragg[4] provided a means of determining the wave-length of any particular X-ray, and thus opened the way to an examination of the X-ray spectrum emitted when a given substance is excited by the ordinary methods. The investigations of Moseley[5] in this field resulted in the discovery of a new atomic relation of fundamental importance; and their extension by other workers[6] has thrown light upon a number of points of great interest.

The method employed by Moseley was as follows. The stream of electrons from the cathode of an X-ray tube was concentrated upon a small area of an anti-cathode composed

[1] Owen, *Proc. Roy. Soc.*, 1912, A, **86**, 426.

[2] Kaye, *Phil. Trans.*, 1908, A, **209**, 123; Chapman, *Phil. Mag.*, 1911, **21**, 446.

[3] Glasson, *Proc. Camb. Phil. Soc.*, 1910, **15**, 437.

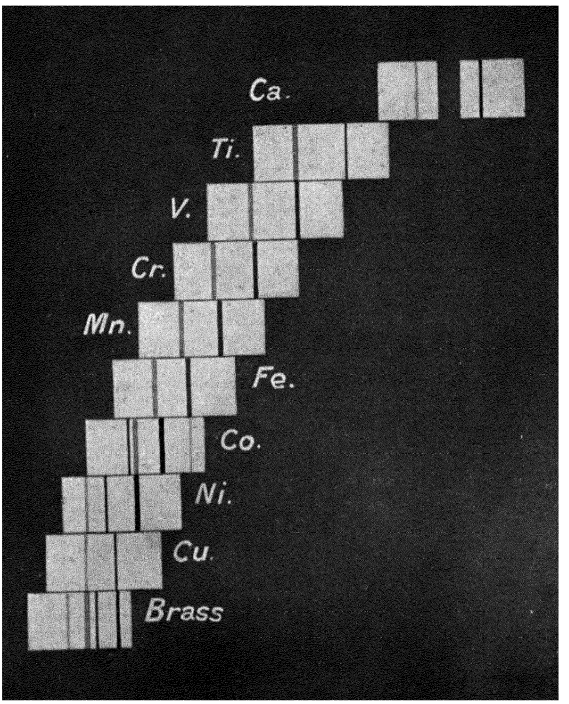
[4] See W. H. Bragg, *X-Rays and Crystal Structure.*

[5] Moseley, *Phil. Mag.*, 1913, **26**, 1024; 1914, **27**, 703. Lieutenant Moseley was killed during the Dardenelles campaign, 1915.

[6] See, *inter alia*, de Broglie, *Compt. rend.*, 1913, **156**, 1153; 1916, **165**, 87, 352; de Broglie and Lindemann, *ibid.*, 1913, **156**, 1461; Herweg, *Verh. deut. phys. Ges.*, 1914, **16**, 73; Siegbahn and Friman, *Physikal. Z.*, 1916, **17**, 17, 48, 61; Siegbahn and Stenström, *ibid.*, 318; Siegbahn, *Ber. deut. phys. Ges.*, 1916, **18**, 39, 150, 278; Siegbahn and Friman, *Phil. Mag.*, 1916, **31**, 403; Friman, *ibid.*, 1916, **32**, 497; *cf.* Rutherford and Andrade, *ibid.*, 1914, **28**, 854.

PLATE II.

SOME X-RAY SPECTRA



→ Increasing Wave Length.
(*From Kaye's "X-Rays."*)

Moseley's photographs of the X-ray or high-frequency spectra of a number of metallic anticathodes. The spectra, which are the third order, are placed approximately in register in the figure. For each metal, the more intense line, with the longer wave-length, is the K characteristic radiation. The brass shows the Zn and Cu lines ; the cobalt contained both nickel and iron as impurities.

of the element whose high-frequency spectrum it was desired to examine. The characteristic rays thus set up were allowed to pass through a slit in a platinum plate, after which they emerged from the X-ray tube through an aluminium window. In their path, inclined at a certain angle, was placed the cleavage face of a crystal of potassium ferrocyanide which analysed the X-ray beam. After being diffracted by the crystal, the rays were allowed to fall upon a photographic plate; and in this way photographs of the X-ray spectrum were obtained. Owing to the weakness of certain of the radiations, the spectrometer was constructed so as to be capable of evacuation; and it thus became possible to photograph even those X-rays which would have been intercepted by a layer of air.

From the photographs thus obtained, the wave-lengths (or the frequencies) of the X-rays emitted by the anti-cathode could be conveniently measured.

3. *The Nature of the X-ray Spectra*

It will be remembered that the characteristic rays emitted by various elements fall into series which are termed the *K*, *L*, *M*, and *N* series.* Moseley showed that the *K* spectrum of all the elements contains two strong lines; and an examination of Plate II will show that a certain regularity can be traced as we pass from element to element. The strongest line in the spectrum is termed the α-line and the weaker one is named the β-line. Inspection of the figure shows that in the case of the cobalt spectrum the original specimen has been contaminated with nickel and iron (since the spectrum contains weak lines characteristic of these elements); whilst the nickel spectrum contains traces of the copper spectrum also.

Later work has shown that the spectra are not quite so simple as they were at first supposed to be; for more lines have been detected which were missed by Moseley. The spectra obtained when X-rays of the *L* series are used instead of the *K* series are still less simple. But even the most complex X-ray spectra are simplicity itself compared with ordinary light spectra.

* The *N* series was detected in the case of the heavy elements, *e.g.* uranium, thorium, and bismuth (Dolejsek, *Z. Physik*, 1922, **10**, 129).

In the case of gaseous elements such as chlorine, it might be supposed that experimental difficulties would hinder the determination of the X-ray spectrum; but it has been found that such elements can be dealt with by utilising a compound instead of the element itself. Potassium chloride, for example, shows the line spectrum of potassium, and in addition it exhibits certain non-potassium lines which are evidently due to the chlorine atom in the molecule. In this way it is possible to establish the high-frequency spectra of gaseous and liquid elements; though of course the method breaks down in the case of the inert gases which form no compounds.

The problem presented by the wave-number of the α-lines in the spectra of various elements must now be examined. If for each element the factor Q be calculated from the equation—

$$Q = \sqrt{\frac{\nu}{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)R}} = \sqrt{\frac{\nu}{\frac{3}{4}R}} \quad . \quad . \quad . \quad . \quad (1)$$

in which ν is the wave-number of the α-line in the X-ray spectrum of the element in question, whilst R is the Rydberg constant,* there is obviously a certain regularity in the results—

	Q.	Atomic Weight.	Atomic Number.
Titanium . . .	20·99	48·1	22
Vanadium. . .	21·96	51·06	23
Chromium . .	22·98	52·0	24
Manganese .	23·99	54·93	25
Iron	24·99	55·84	26

Examination of the figures shows that there is no direct relation between the factor Q and the atomic weight for any given element. At the same time, there is a certain regularity in the values for Q; for each of them differs approximately by one unit from its neighbours above and below. Further, the elements when arranged in order of their Q values, lie in the order which is suggested by their chemical properties.

* It may be noted in passing that Moseley used Rydberg's earlier result (R=109,720) instead of the more recent value R=109,675, but the difference between the two is slight.

If we now turn to the Periodic Table and, beginning with hydrogen as No. 1, count along the Table until we arrive at titanium, we shall find that it is the twenty-second element in the series; vanadium is the twenty-third; chromium is the twenty-fourth, and so on. Here also we have a series of figures each differing from its neighbours by unity; and the arrangement of the elements in each of the two series is the same. The numbers obtained by counting along the Table from hydrogen are termed Atomic Numbers.[1] Inspection will show that for any element in the above series the factor Q and the atomic number N are approximately related thus—

$$N-1=Q$$

Moseley [1] suggested that the integer N was identifiable with the number of free positive units of electricity contained in the atomic nucleus, which brought his work into line with the earlier view of Soddy *: that the chemical nature of an element depends, not on its atomic weight, but upon its electrical character.[2]

The denominator of the fraction in equation (1) is obviously one of the expressions with which we became familiar in Chapter II; and by squaring both sides, substituting (N−1) for Q, and rearranging the terms, we can bring this new expression into parallelism with those which were found applicable to optical spectra. The equations below serve to bring out this parallelism and also to show how the wave-numbers of the α-lines of the *K*, *L*, *M*, and *N* series of X-ray spectra are related to each other.

K-Series Wave-number of α-line $=(N-1)^2 . R\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$ (2)

L-Series " " " $=(N-1)^2 . R\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$ (3)

M-Series " " " $=(N-1)^2 . R\left(\frac{1}{3^2}-\frac{1}{4^2}\right)$ (4)

N-Series " " " $=(N-1)^2 . R\left(\frac{1}{4^2}-\frac{1}{5^2}\right)$ (5)

[1] Moseley, *Nature*, January 5th, 1914.

* See Chapter VII.

[2] Soddy, *Jahrb. Radioaktiv. Elektron*, 1913, **10**, 193; *Nature*, December 4th and 18th, 1913; *Chemistry of the Radio-elements*, II, 6, (1914)

The general equation for the whole of the lines is

$$\text{Wave-number} = (N-b)^2 R \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad . \quad . \quad (6)$$

in which N is the atomic number of the element under examination, b is a constant with which we shall deal later, and R is the Rydberg constant. The factor $n_1=1$ for the *K*-series, 2 for the *L*-series, 3 for the *M*-series, and 4 for the *N*-series; and the factor n_2 represents a series of whole numbers starting with (n_1+1).

Inspection reveals at once that this general expression for the X-ray spectra differs from the general expression for the hydrogen lines only by the introduction of the factor $(N-b)$; and if $N=1$ and b be negligibly small, the two expressions become identical. On the other hand, if N be large (and with uranium it reaches a value of 92) then the wave-number is increased almost ten thousand times and consequently the wave-length is shortened in the same ratio. From this, we should expect to find that the heavier atoms would yield shorter and more penetrating waves, which is exactly in accordance with experimental results. The characteristic X-rays of tungsten (atomic number 74) are much shorter in wave-length and much more penetrating ("harder") than those emitted by aluminium (atomic number 13) or titanium (atomic number 22).*

From the close parallelism between the general formulæ for optical and X-ray spectra, it is a fairly obvious inference that the Ritz Combination Principle will hold good in the field of the X-rays. This has been tested and found to be the case.

We must now try to get some idea of how these characteristic X-rays are generated within the atom; and our conception of the process must take into account two main points in the experimental evidence:

1. That the oscillation-frequency of the X-rays is much greater than that of the rays we encounter in optical spectra;
2. That in order to excite a characteristic X-ray in an element of atomic number N, we must either (*a*) bombard the element with the high-velocity electrons of a cathode

* A practical application of this is found in the choice of tungsten as an anti-cathode or target in X-ray tubes when high penetrative power is desired.

ray; or (*b*) subject the element to the characteristic X-ray of another element having an atomic number (N+1) or greater.

Now consider the theoretical side. If Planck's theory be adopted, the quantum of energy, $h\nu$, increases in value with the oscillation-frequency; so that in the case of the X-rays, owing to their high oscillation-frequency, the quanta must attain much greater magnitudes than among optical spectra. Such quanta could be furnished by high-velocity electrons which were suddenly stopped in full career by entering an atomic system. But if the energy is supplied in the form of the characteristic X-ray from another element there are certain limitations involved, of which the most important are the magnitudes of the two quanta concerned in the operation.

From what has been said above, it is evident that the oscillation-frequency of the α-line in the *K*-series of any element can be expressed by

$$\nu = \tfrac{3}{4}\mathrm{R}c(\mathrm{N}-1)^2$$

where c is the velocity of light.

The quantum of energy for this frequency is obviously

$$h\nu = \tfrac{3}{4}\mathrm{R}hc\,.\,(\mathrm{N}-1)^2$$

and it is clear that if we have two elements of atomic numbers N and (N+1), the former's quantum of energy will be less than that of the latter. But the Planck resonator of the second element will not work at all unless it receives, as a minimum, its own energy-quantum. This it could get from an element of higher atomic number, but evidently not from an element of lower atomic number. Hence the theory suggests that the radiation from one atom, A, can excite X-rays from another atom, B, only if the atomic number of atom A is greater than that of atom B—which accords with the experimental results.

Now apply Bohr's ideas to the problem.[1] On this basis we must evidently assume a series of orbits of which the innermost is very close to the nucleus of the atom. This follows from the equation which we used before

$$\mathrm{W}_2 - \mathrm{W}_1 = h\nu$$

[1] Compare Kossel, *Verh. deut. physikal. Ges.*, 1914, **16**, 899, 953; 1916, **18**, 339; *Ann. Physik*, 1916, **49**, 229; *Z. Physik*, 1920, **1**, 119; **2**, 170; *Valenzkräfte und Rontgenspektren* (1921).

which represents the quantum of energy as the difference between two energy-levels in the atom. Since we have found that a large value for ν corresponds to the fall of an electron into the innermost orbit of an atom, and since the quantum in the case of the X-rays is very great, the assumption of a very small radius for the innermost orbit is the simplest we can make. We thus obtain a picture of the mechanism which is something like the following.

By the inrush of a cathode ray electron from outside the atom, one of the innermost electrons in the atomic system is displaced and driven upward into one of the larger orbits (or shells, if Kossel's phraseology be used). To replace it, another electron drops down from an outer orbit; and in falling towards the nucleus, this electron gives out the energy which appears as a quantum of energy radiated at X-ray frequency.

The constant b which appears in the equation (6) is termed the *screen-constant* or the *shielding-constant* on account of its nature. Suppose that the innermost shell of the atom (the K-shell) contains a certain number of electrons. The presence of this electronic "screen" will have the effect of diminishing the influence of the nuclear charge upon any electron placed in the outer shells (the L-, M-, and N-shells). Further, if an electron occupies a place on one of the atomic shells, it is not only attracted by the nucleus of the atom, but simultaneously it is repelled by all the other electrons which have places in that shell. This tends to reduce the value of the nuclear attraction by the amount * expressed in the formula

$$S_n = \frac{1}{4} \sum_{k=1}^{k=n-1} \operatorname{cosec} \frac{\pi k}{n}$$

wherein S_n is the constant for an electron in a shell containing n electrons.

Since the screen-constant is the result of a very complex play of forces, its magnitude cannot be calculated with any degree of accuracy; and the factor b which represents it in equation (6) is inferred purely empirically from the experimental data.

* The reasoning on this point is to be found in Sommerfeld: *Atomic Structure and Spectral Lines*, pp. 72 ff. (1923).

4. *The Gaps in the Periodic Table*

It is clear that if the atomic numbers of any two elements be determined from their X-rays spectra, we are in a position to state the number of the other elements which are interposed between them in the atomic order. For example, in the table given on p. 46, titanium is the twenty-second element and iron is the twenty-sixth ; from which, without any further knowledge, we could state that between titanium and iron there must be three elements corresponding to the atomic numbers: 23, 24, and 25. These elements are, of course, vanadium, chromium, and manganese.

The atomic number of uranium has been found to be 92, so that between it and hydrogen there is room for only ninety elements. At the time of Moseley's discovery of the relationship between the X-ray spectra and the order of the elements, eighty-four elements had been proved to exist, which left six forms of matter still to be accounted for if the list was to be completed. The numbers attached to these were 43, 61, 72, 75, 85, and 87. Numbers 43 and 75 are congeners of manganese which have now been detected and christened respectively masurium and rhenium; Number 72 has been isolated and named hafnium ; whilst Number 61 is the rare earth element illinium. This leaves still the two elements corresponding to 85 and 87 : the one a member of the halogen family, and the other the heaviest of the alkali metals.

The importance of Moseley's work in this field can hardly be over-estimated. The rare earth group of elements had long been one of the puzzles of chemistry; and the definite proof of the exact number of elements in this class has removed the possibility that much time and labour might be wasted in seeking for fresh members of the group after the roll was actually complete. The rare earth group stands apart from the rest of the Periodic Table, and contains within itself no indication of the number of elements which it includes ; so that without Moseley's " key " we might have seen many fruitless efforts to discover " missing " members long after the whole flock was actually gathered together in the fold. With the help of Moseley's results, we are able to feel certain that the discovery of illinium has completed the rare earth series, so that there is no need to look for other elements in this class.

It is, of course, possible that the atomic models of Langmuir and Bury * might eventually have given us a clue to the number of elements in the rare earth group; but these models themselves owe much to Moseley's work and would, without it, be unsupported by any experimental evidence.

5. *The Anomalies of the Periodic Table*

It is well known that the Periodic Table, on the original basis of the atomic weights, is not free from blemishes in its arrangement. Argon and potassium do not follow one another in the order of their atomic weight; nor is the chemical sequence of iron, cobalt, and nickel the same as the order of increasing atomic weight. Iodine and tellurium are also inverted in the usual form of the Table.

Moseley's work has shown that the atomic numbers run parallel to the chemical sequence of the elements and not to their order of atomic weights. For example, the X-ray spectra show that the value of N for potassium is 19, which brings it into Group I as usual, instead of placing it in Group O as the atomic weight sequence does. Also, the atomic order of the iron group is: iron (26); cobalt (27); and nickel (28): which agrees with the chemical behaviour and not with their arrangement by increasing atomic weight. Tellurium and iodine also fall into their chemical order. This supports what has already been said with regard to the importance of the atomic numbers from the chemical standpoint.

A crucial test of the correctness of Moseley's atomic numbers was furnished by the case of the isotopes.† These are elements having different atomic weights, but possessing properties so similar on the chemical side that they are believed to be inseparable from one another by any reactions. If the atomic number is a function of that portion of the atomic structure which manifests itself in chemical properties, then clearly the spectra of two isotopes ought to be identical. The matter has been put to the test by Rutherford and Andrade.[1] Lead and radium-B are chemically inseparable from one another; and when their X-ray spectra were compared, it was found that

* See Chapter XIII. † See Chapter VII.

[1] Rutherford and Andrade, *Phil. Mag.*, 1914, **27**, 854; see also *ibid.*, 1916, **32**, 49.

they were identical. Thus each group of chemically inseparable atoms has a single atomic number covering the whole group; and the individual isotopes are not entitled to separate enumeration.

6. *The X-ray Spectrum of Hydrogen*

A point of some interest comes to light when an attempt is made to calculate the probable positions of lines in the X-ray spectrum of hydrogen.

Since the hydrogen atom contains only a single electron, the screen-constant, b, should disappear from the equation; while for hydrogen $N=1$; so the Moseley expression for the α-line of the hydrogen K-series—

$$\text{Wave-number}=(N-b).R\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

becomes simply $3R/4$. This, it will be remembered, is the value for the first line in the Lyman ultra-violet spectrum of hydrogen.*

From this it follows that owing to hydrogen's unique place in the system of the elements, its extreme ultra-violet spectrum and its X-ray spectrum are identical.

7. *Conclusion*

Moseley's work upon X-ray spectra and atomic numbers ranks as one of the great achievements of science. Before his investigations were made, the Periodic Table stood upon a purely chemical basis, part of which seemed not altogether beyond criticism; and the closest known connection between elemental sequence and physical properties was represented by the atomic volume curve of Lothar Meyer. Moseley's researches threw light upon the problem from a fresh angle. Here, in the examination of a single physical property of the elements, there came to view a step-by-step change as element succeeded element in the series; vexed questions such as the relative atomic weights of argon and potassium ceased to give trouble, since the atomic numbers ran in the true chemical order; and, most important of all from the chemist's standpoint, Moseley's determinations settled definitely the total number of elements lying between the

* See p. 18.

two known extremes, hydrogen and uranium. It is now known that there are only ninety-two types of terrestrial matter each of which is characterised by specific chemical properties of its own.

Turning to the meaning of the atomic numbers, a clue is to be found in the speculations of van den Broek.[1] As will be seen later in this volume, the modern theory of the atom assumes a system consisting of a positively charged nucleus surrounded by zones of electrons ; and according to van den Broek the atomic number of any given atom may be considered to represent the number of net positive charges in the nucleus or (which comes to the same thing) the number of electrons in the outer region of the atom. Thus by coupling together the speculations of van den Broek and the experimental work of Moseley, we obtain an adumbration of atomic structure which will grow more definite as we consider the further evidence which has been pouring upon us in recent years with such surprising rapidity.

In conclusion, it seems well to emphasise the fact that the atomic numbers determined by Moseley have completely supplanted the old atomic weights as a means of elemental classification. Soddy, as will be seen later,* had overthrown the atomic weights as aids to classifying the elements ; and Moseley's discoveries came in the nick of time to permit a new system to be erected over the ruins of the older one.

[1] Van den Broek, *Physikal. Z.*, 1913, **14**, 33 ; *Nature*, 1913, **93**, 373, 476 ; Soddy, *ibid.*, 399, 452 ; Rutherford, *ibid.*, 423 ; Bohr, *Phil. Mag.*, 1913, **26**, 1.

* See Chapter VII.

CHAPTER IV

THE PHENOMENA OF RADIOACTIVITY

1. *Historical*

In 1895 Röntgen showed that when cathode rays impinged upon the end of a vacuum tube they gave rise to a green luminescent patch, from which was projected a series of rays—the X-rays. From the phosphorescence of the Crookes tube to the green phosphorescence of certain minerals is only a short step, and in 1896 Becquerel began an investigation of the latter phenomenon. He found that crystals of potassium uranium sulphate had the property of affecting a sensitive photographic plate (wrapped in black paper) in exactly the same way as it would have been affected by an X-ray discharge. The experiment led to the discovery of what are now called the Becquerel rays.

These radiations are invisible to the eye, just as the X-rays are. They are given off by metallic uranium, and also by uranium salts. Like the X-rays they can pass through thin sheets of glass or metal; and a further resemblance is to be found in the fact that neither set of rays can be refracted by ordinary means. Again, the Röntgen rays have the property of ionising gases through which they are passed; and it has been found that in this instance, also, the Becquerel rays resemble the others, though their action is much more feeble. The charged leaves of a well-insulated electroscope will remain separated for a very considerable time, owing to the fact that ordinary dry air is a poor conductor of electricity; but if a piece of uranium be brough tnear the electroscope, the Becquerel rays which are given off from the metal at once ionise the air, making it a better conductor of electricity, and thus the leaves of the electroscope fall together much more rapidly than they did before the uranium was brought near them. This furnishes a method of determining the activity of any particular sample of

uranium; for it is only necessary to measure the rapidity with which an electroscope is discharged when the sample is placed in its vicinity. If the uranium is sending out many Becquerel rays, the electroscope leaves will soon fall together; if the Becquerel rays are few, the instrument will be discharged very slowly.

It would naturally be concluded, from the above evidence, that the Becquerel rays and the Röntgen rays were identical. As a matter of fact, however, they are not so. It is not necessary to go into details here, as the matter will be dealt with in a later section.

Soon after Becquerel's work on uranium and its salts, Schmidt discovered that thorium also had radioactive properties; and since that time various other elements have been described which belong to the same class. Of these the most important is radium.

2. *Radium*

In this and the succeeding sections only an outline of the properties of the various radioactive substances can be given. To enter fully into the physical side of the question is impossible within the limits of the present volume: so the subject will be treated mainly from the point of view of chemistry, and the physical evidence will be dealt with only in so far as it aids the comprehension of the purely chemical side.[1] The properties of radium and its derivatives will be taken as typical and described at some length, while the allied substances will be treated more briefly.

In the introductory section of this chapter, attention was called to the fact that uranium salts throw off radiations which affect photographic plates just as the X-rays do. Now, uranium compounds are found naturally in the mineral pitchblende, which occurs usually (like the rare earths) in igneous rocks such as granite. Madame Curie,[2] in the course of an examina-

[1] For an account of the practical methods employed in radioactivity measurements the reader is referred to Makower and Geiger's *Practical Measurements in Radioactivity*. A full account of commercial process of extracting radioactive materials is given in Henrich's *Chemie u. Chemische Technologie radioaktiver Stoffe* (1918).

[2] Thesis presented to the Faculté des Sciences, Paris; see *Chem. News*, 1903, **88**, 85, 97, 134, 145, 159, 169, 175, 187, 199, 211, 223, 235, 247, 259, 271.

tion of a great number of naturally occurring substances, discovered that in some cases the natural ore was much more radioactive than the amount of uranium salt contained in it would lead us to expect. For example, pitchblendes are about four times as active as metallic uranium; chalcolite (a double phosphate of uranium and copper) is twice as active as uranium. Further, when Madame Curie prepared artificial chalcolite, she found that instead of being more active than metallic uranium, it was two and a half times less active. This proved conclusively that the activity of the natural chalcolite was not due entirely to the uranium contained in it, but must be attributed to the presence in the natural ore of some substance not found in the synthetic product.

The presence of this new body in pitchblende and other minerals having been established, the question of extraction then arose. It was easy to carry out an ordinary analysis, and to determine by measurements with an electroscope whether the activity was a property of the filtrate or of the precipitate. The details of the method of analysis employed can be found in the original papers.[1] A long series of operations must be gone through before a mixture consisting of radium bromide and barium bromide is obtained.

After the isolation of the bromides of radium and barium from the mixture has been accomplished, it is necessary to separate them from each other. This is done by fractional crystallisation, either from aqueous solution or from a solution of the salts in water acidified with hydrobromic acid. The latter is the better method of the two. It is possible to employ the method of fractional precipitation instead of crystallisation, the mixed salts being thrown down from an aqueous solution by means of alcohol. In either case, the radium bromide is less soluble than the barium salt.

The radium salts which are obtained in this way resemble the corresponding barium compounds in many respects. Radium chloride is isomorphous with barium chloride; and the two salts, when they are freshly prepared, are similar to each other in appearance. It has been found that if the radium salt stands for a time it gradually becomes coloured, the tint ranging from

[1] Ebler and Bender, *Z. anorg. Chem.*, 1914, **88**, 255; *U.S.A. Bureau of Mines, Bulletin* **104** (1915); Schlundt, *J. Physical Chem.*, 1916, **20**, 485.

yellow to rose-pink. The coloration becomes much more marked if a trace of impurity (such as a barium salt) be present in the crystals.

Another property which noticeably altered by lapse of time is the blue luminescence exhibited by freshly prepared radium salts or their solutions. The presence of barium salts in this case also appears to have some influence, for the blue light is more strongly exhibited by an impure sample of radium salt than it is by a pure one.

An aqueous solution of a radium salt has been found to evolve a mixture of oxygen and hydrogen, and there appears to be no cessation of this process, which offers such a peculiar parallel to electrolytic action.[1] A still more extraordinary property of these salts, however, remains to be described. Curie and Laborde[2] observed that the temperature of a radium salt is always a little higher than the temperature of the air about it; in other words, the radium salts are continually giving out heat. Curie and Laborde showed that the quantity of heat disengaged in one hour by one gramme of pure radium would amount to about a hundred gramme-calories. The *increase* in the heating effect of radium preparations[3] over a period of sixteen years has been measured * and shown to amount to 11 per cent.

When a radium salt is placed in the flame of a Bunsen burner it gives rise to an intense carmine-red coloration, which is very characteristic. The spectrum of the element has been examined by several workers, and found to be quite different from any known spectrum.

The atomic weight of radium was at one time the subject of considerable controversy,[4] but it is now taken as 226·0. This value places radium below barium in the alkaline earth column of the Periodic Table; and the resemblance between the two elements fully justifies the position.

[1] See also Ramsay, *Monatsh.*, 1908, **29**, 1013.

[2] Curie and Laborde, *Compt. rend.*, 1903, **136**, 673.

[3] Mme. M. Curie and Yovanovitch, *J. Phys. Radium*, 1925, **6**, 33.

* These results agree with the theory based on atomic disintegration very closely.

[4] Madame Curie, *Chem. News*, 1903, **88**, 159; *Compt. rend.*, 1907, **145**, 422; Runge and Precht, *Physikal. Z.*, 1908, **4**, 285; Watts, *Phil. Mag.*, 1903, **6**, 64; Thorpe, *Proc. Roy. Soc.*, 1908, A, **80**, 298; Hönigschmid, *Monatsh.*, 1912, **33**, 253; Whytlaw-Gray and Ramsay, *Proc. Roy. Soc.*, 1912, A, **86**, 270.

Metallic radium has been isolated by Madame Curie and Debierne.[1] A solution containing about a decigramme of radium chloride was electrolysed, the cathode being mercury and the anode being platinum-iridium. After the electrolysis was completed, the amalgam of radium at the cathode was placed in an iron boat and heated in a current of hydrogen which had previously been purified by passage through the walls of a platinum tube heated in an electric furnace. At approximately 700° C., the mercury had all been driven off and the boat contained a brilliant white metal which fused sharply in the neighbourhood of 700° C. and began to attack the quartz tube in which the experiment was carried out. On exposure to air, a black film formed upon the metal, this being probably radium nitride. Radium attacks water violently, forming a soluble oxide. A trace of the metal having fallen upon a sheet of paper, it was found that the paper was blackened and apparently carbonised. It appears that metallic radium is more volatile than barium.

3. *The Becquerel Rays*

Mention has already been made of the fact that the salts of radium and other radioactive elements emit a series of radiations which have been termed the Becquerel rays, from the name of their discoverer. Since a very considerable part of the peculiar activity of radioactive bodies is closely connected with these rays, it is necessary at this point to enter into some consideration of the question. The first problem which presents itself is that of the nature of the rays in question. Are they homogeneous or not?

To settle this point, two methods are available. In the first place, we may interpose in the path of the rays some sort of filter which will separate one component from the rest; or, secondly, we may pass the rays through a magnetic field, and determine whether they are uniformly deflected as a whole or whether they can be resolved into a series of vibrations having different deflections.

With regard to the first of these methods, an experiment mentioned by Strutt[2] will make the application clear. Suppose

[1] Madame Curie and Debierne, *Compt. rend.*, 1910, **151**, 523.

[2] Strutt, *The Becquerel Rays and the Properties of Radium*, 1904, p. 51.

that an electroscope be charged so that the leaves of it diverge from one another. If a small quantity of a radium salt is placed near the electroscope the leaves fall together, say, in ten seconds. If the radium salt be wrapped in a sheet of tin-foil and again placed in position near the electroscope, the leaves take longer to fall, say, a hundred seconds. We have thus filtered off some part of the rays. Now, if all the rays were of the same type, we should expect to increase the time of discharge to a thousand seconds by doubling the sheet of tin-foil. This, however, is not found to be the case; but, instead, the rate of discharge hardly falls at all with the superposition of the second thickness of tin-foil. It is thus made clear that we have practically intercepted one set of rays by means of the tin-foil, but that there still remain other rays which the tin-foil sheets do not arrest. Obviously the Becquerel rays contain at least two constituents, one of which is stopped by tin-foil, the second not. We have now to discover whether or not we can sift further the rays to which tin-foil is transparent. To do this, a thin casing of lead is placed behind the tin-foil, and here we find a similar behaviour. The addition of one sheet of lead causes a perceptible lengthening of the period of the electroscope's discharge; but the interposition of a second slip of lead does not diminish further the velocity of the discharge to any marked extent. Thus again we have reached a border-line between two sets of rays, one of which will pass through the lead, while the other cannot do so.

The second method, in which a magnetic field is used, must now be mentioned. The actual details of the experimental methods employed need not be described in this place,[1] but the results which have been obtained by the application of the electro-magnet to the problem are important.

Suppose that a magnetic field is applied at right angles to the plane of the paper and directed towards the paper; the state of affairs [2] may be represented by Fig. 2.

Here L is a piece of lead in which a hollow has been drilled. At the bottom of the hollow is placed some radium salt, R. Under the influence of the magnetic field, the radiations from the radium salt are split up into three groups, which have

[1] See Rutherford, *Radioactivity*, 1905, chaps. iv. and v.

[2] Madame Curie, *Chem. News*, 1903, **88**, 169.

been termed by Rutherford the α-, β-, and γ-rays.* The γ-rays are not deflected by the magnetic field, and are thus comparable to ordinary X-rays; but their penetrating power is very much greater than that of the X-rays. The β-rays resemble the cathode rays of a high-vacuum tube; and like these they are deflected by the magnetic field in the manner shown in the figure. They appear to be streams of particles carrying a negative electric charge. If a sensitive photographic plate,

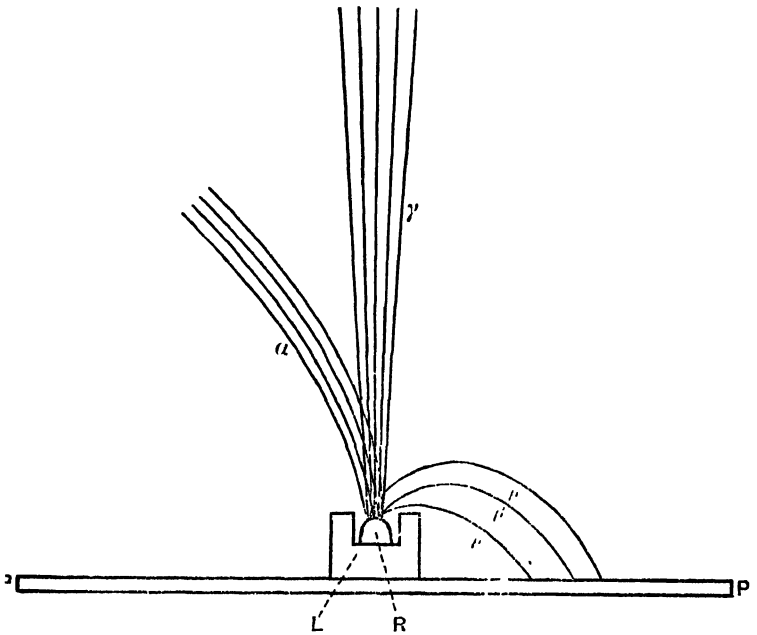


FIG. 2.

PP, is placed under the leaden cell containing the radium salt, the sensitive film is affected at the spot where the β-rays fall. Finally, we come to the third set of components of the Becquerel rays. These, the α-rays, are deflected from the straight path of the discharge by the electric field; but instead of being bent in the same way as the β-rays, they are curved in the opposite direction, as can be seen by their track on the photographic film. They are therefore positively charged particles; and are

* As will be seen later, the β-rays do not arise from radium itself but come from certain other substances which appear in specimens of radium salts after standing.

now known to be helium atoms. We must now discuss the properties of these different rays in turn.

The γ-rays, as already mentioned, are not deflected to any extent by a magnetic field, even when this is very powerful. Their penetrating power also is very marked. For instance, Strutt [1] has observed that even 8 centimetres of sheet lead will not suffice to arrest these radiations. With regard to the origin of γ-rays, Rutherford has put forward certain suggestions which can best be dealt with later in connection with the structure of the atomic nucleus.*

The nature of the β-rays also is beyond doubt. They are electrical particles projected from the surface of the radioactive salt, just as particles are driven out from the cathode of a high vacuum tube. Naturally, they do not all travel with the same velocity; some sets of particles move more slowly than others, and it has been found possible to analyse the swarm of electrons by deflecting them in magnetic fields. It has been found that the slowest-moving electrons are most deflected—as can be foreseen—and it has been proved, further, that the β-rays as a whole are less deflected than the cathode rays from Crookes tubes. Hence it is clear that the electrons forming the β-rays of radium are moving at a much higher velocity than those which are shot out by the cathodes of vacuum tubes. It has been estimated that the velocities of light, the β-ray electrons, and the electrons of ordinary cathode rays are approximately the following:—

Light	30×10^4	kilometres per second
β-rays	(6×10^4) to (28×10^4)	,, ,,
Cathode rays .	(2×10^4) to (10×10^4)	,, ,,

It appears, then, that the velocity of the electrons in the β-rays is greater than that of any other known natural body. From the fact that the radioactive bodies are losing negative electricity at a considerable rate owing to the departure of the electrons of the β-rays, it is clear that the remaining portion of the salt must gradually acquire a positive charge, and that if loss of this charge be prevented by insulation it will eventually become quite measurable. In point of fact, one experimenter [2] noticed

[1] Strutt, *The Becquerel Rays*, p. 83.

* See p. 171.

[2] Dorn, *Physikal. Zeitsch.*, 1903, **4**, 507.

that when a sealed glass tube containing radium was opened after several months, a bright electric spark was produced.

The nature of the α-rays has been placed beyond doubt in the following manner.[1] When the radioactive gas radon is introduced into a thin-walled glass tube surrounded by a jacket (see Fig. 3), the α-rays traverse the thin-walled container and accumulate in the space between it and the jacket. By raising the left-hand mercury reservoir, the collected material is forced up into the small spectrum tube shown at the top of the apparatus. Examination showed that the helium spectrum was visible after a time, which proves that the material part of the α-particles is helium.

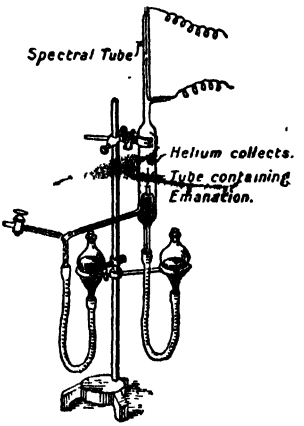


FIG. 3

The number of α-particles ejected per minute by a radioactive source was determined by Rutherford and Geiger[2] by means of the apparatus shown in Fig. 4. The apparatus consists of two sections, (*a*) the so-called firing chamber on the left of the diagram and (*b*) the detecting chamber on the right,

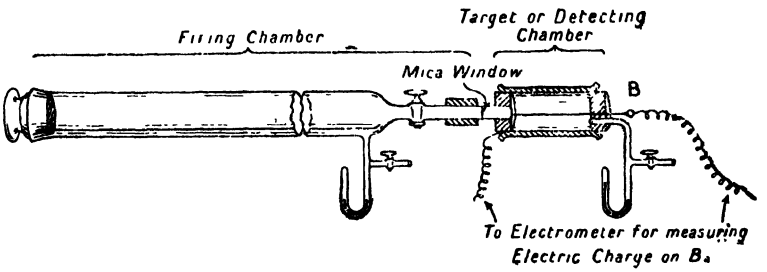


FIG. 4.

which are connected by a channel through a stop-cock as shown. The detecting chamber is a brass cylinder with ebonite ends, and is fitted with a central charged and insulated wire, B, one end of which is led to an electrometer. The brass cylinder is

[1] Rutherford and Royds, *Phil. Mag.*, 1909, **17**, 281.
[2] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 141.

connected to the other terminal of the electrometer. X-rays are now projected on the gas in the interior of the detecting chamber, so as to ionise it. In the firing chamber, a radioactive substance is spread out in a thin film of small surface area on a support which can be moved up and down the chamber by means of an external magnet; and the firing chamber is then exhausted. The mica window shown in the diagram allows this to be done without affecting the gas pressure in the detecting chamber.

When an α-particle finds its way from the firing chamber into the detecting chamber, it raises the ionisation of the gas there and produces a sharp deflection of the electrometer needle. Thus the number of particles traversing the mica window per second can be determined. Since the distance, d, of the window from the source is known, and also the area of the window, it is obvious that the total number of particles ejected by the source per second can be easily calculated, by multiplying the number of particles traversing the window by the factor

$$\frac{\text{area of sphere of radius } d}{\text{area of window}}.$$

By means of another apparatus [1] the total charge on a number of α-particles was determined, the number of particles having been estimated by the method described above. Simple division then gives the charge per particle, which was found to be two unit positive charges.

The α-rays are, therefore, streams of helium atoms each carrying two positive charges; and thus they form a parallel to the positive rays observed in the Crookes tube. The speed of the α-particle (about one-tenth that of light) is much higher than any velocity which can be produced in a positive ray tube. It seems probable that part at least of the heat generated by radioactive materials is due to the α-particle impacts. Crookes devised an instrument, the spinthariscope, by means of which the effects of the collision between α-particles and ordinary matter can actually be observed. The spinthariscope consists of a zinc sulphide screen, above which a tiny fragment of a radioactive substance is suspended on the end of a steel pointer. When the screen is examined through a lens, it is found to be sprinkled with tiny points of light which appear and vanish

[1] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 162.

almost at once. These light-spots are apparently due to the phenomenon known as triboluminescence, in which the breaking of a crystal causes a flash of light; and it is supposed that the flashes in the spinthariscope are caused by the fracture of the zinc sulphide crystals under the impact of helium atoms discharged from the radioactive substance on the pointer. The triboluminescence phenomena on a larger scale can be observed by any one who rubs two pieces of sugar together in the dark.

In the foregoing paragraphs the properties of the α-, β-, and γ-rays have been discussed *seriatim*; but it must be remembered that the effects produced by radioactive substances in general are not caused by the separate action of each type or ray, but are really due to the united action of all three kinds. A few instances may now be given of the changes which radium produces upon various substances when it is placed in their vicinity.

The first effects which are recognisable are those due to fluorescence or luminescence of one kind or another. Suppose that an X-ray fluorescent screen is brought near a radium compound; the screen will become strongly lit up, just as it is when acted upon by the Röntgen rays. Bary [1] found that many of the alkali metals and alkaline earths are also fluorescent when brought into the neighbourhood of a radium preparation. The minerals willemite and kunzite shine with special brilliance under Becquerel rays. Madame Curie [2] showed that paper, cotton, and other substances could exhibit the same phenomenon. Becquerel [3] observed that while a ruby will fluoresce under the action of light-rays, it remains inert with regard to radium. Again, a diamond which shines in presence of the rays from radium does not light up when X-rays are thrown upon it. Many other instances of this action of the Becquerel rays might be quoted.

If a fluorescent substance of the type mentioned above is exposed to the continued action of the radium rays, it is found that the power of shining which it possesses does not remain constant, but slowly diminishes, while at the same time the physical appearance of the fluorescent body changes. Barium platinocyanide on long exposure to the rays grows darker in

[1] Bary, *Compt. rend.*, 1900, **130**, 776.
[2] Madame Curie, *Chem. News*, 1903, **88**, 212.
[3] Becquerel, *Compt. rend.*, 1899, **129**, 912.

colour, finally becoming quite brown ; its luminescence also dies away gradually. Both the original colour and the power of fluorescing can be regenerated by exposing the salt to light for a time.

When some varieties of glass are exposed to the action of the Becquerel rays they show fluorescence, and at the same time become tinted brown or violet according to the alkali metal contained in them. If the glass is warmed, after the process has gone on for a time, it loses its tint and becomes again transparent, regaining at the same time its original power of fluorescence. During the heating it phosphoresces spontaneously. The same is true for such minerals as fluorspar.[1]

The Becquerel rays have the power of ionising gases, just as the X-rays do. It is obvious that the electroscopic method of determining activity depends upon this property.

In many cases the action of the Becquerel rays upon ordinary chemical elements or compounds is well marked. For instance, the Curies have shown that by their influence oxygen can be converted into ozone.[2] Again, if yellow phosphorus be subjected to the action of the radiations, it becomes changed into the red allotropic modification.[3] On the other hand, it has been shown by Sudborough[4] that the presence of radium salts has no influence upon some geometrically isomeric substances which are transmuted into the stable form by the action of light. If the Becquerel rays act upon a solution of iodoform in chloroform, it becomes purple owing to the separation of iodine.[5] Ammonia[6] is decomposed by the Becquerel rays ; and water[7] is broken up, yielding oxygen and hydrogen along with a certain proportion of hydrogen peroxide.[8] If a mixture of *dry* oxygen and hydrogen[9] be allowed to remain in contact with radium bromide, however, no combination results. Hydrogen sulphide and sulphur dioxide[9]

[1] Lind, *J. physical Chem.*, 1920, **24**, 437 ; Henrich, *Z. angew. Chem.*, 1920, **33**, 5, 13, 20.

[2] Curie, *Compt. rend.*, 1899, **129**, 823.

[3] Becquerel, *Compt. rend.*, 1901, **133**, 709.

[4] Sudborough, *Proc.*, 1904, **20**, 166

[5] Hardy and Willcock, *Proc. Roy. Soc.*, 1903, **72**, 200.

[6] Perman, *J.*, 1911, **99**, 132.

[7] Usher, *Jahrb. Radioaktiv. Elektronik*, 1911, **8**, 323.

[8] Sabot, *Arch. Sci. phys. nat.*, 1916, **42**, 391 ; Choudhari, *Chem. News*, 1917, **116**, 25.

[9] Baker, Royal Institution Lecture, March 11, 1911.

are both decomposed by the rays. When air is left in contact with a radium salt over mercury, nitrous oxide is produced in comparatively large amounts.[1] The action of the Becquerel rays upon hydrogen peroxide has been studied ;[2] but in this case it is difficult to know exactly how much must be ascribed to the direct action of the rays and how much to the influence of alterations in the glass of the containing vessel, which, in turn, will affect the rate of decomposition of the peroxide. Other examples[3] of the chemical effects of the Becquerel rays have been observed, but it is not necessary to deal with them here.

The physiological effects of the radium radiations are very striking. If a radium salt be allowed to remain in contact with the skin for even a few minutes, it is apt to produce extremely painful eruptions; and these are the more troublesome owing to the fact that they take some weeks to make their appearance. Thus even by bringing radium near the skin, without actual contact, we may produce very deep-seated changes in the tissues without having any outward sign that we have injured them. The action of the radiations upon the tissues is apparently due to the break-down of lecithin, which makes up a considerable part of the epidermis. This destructive character of the radium salts, however, is not without its uses, for in cases of rodent ulcer it has been successfully employed to cure the disease ; and at the present time we seem to be on the verge of considerable advances in this direction. Hardy[4] has found that the coagulation of globulin may be brought about by the influence of the Becquerel rays, and in this case the action appears to be due to the positive charge carried by the α-particles.

The Becquerel rays have a destructive effect on colouring materials such as indigo and chlorophyll, which become bleached when exposed to the action of radioactive substances.

Of considerable interest is the influence exerted by the Becquerel rays upon colloidal solutions.[5] Under the conditions

[1] Soddy, *Annual Reports*, 1911, **8**, 299.

[2] Körösy, *Pfluger's Archiv.*, 1910, **137**, 123 ; Kailan, *Monatsh.*, 1911, **32**, 1019.

[3] Lind, *Monatsh.*, 1912, **33**, 295 ; Kailan, *ibid.*, 71 ; *Sitzungsber., K. Akad. Wiss. Wien*, 1912, **121**, 1329.

[4] Hardy, *Proc. Physiol. Soc.*, 1908, XXIX.

[5] See F. Sekera, *Kolloid Z.*, 1920, **27**, 145, for a summary of this work.

of the experiments, it was mainly the β-rays which came into action, which corresponds to bombarding the solutions with electrons; and, as might be anticipated, the discharge precipitates positively charged colloids but is without effect on negatively charged colloidal particles. Ferric hydroxide sols, for example, are precipitated, whereas the electronegative sols of gold or of molybdenum and vanadium hydroxides are unchanged.

The β-rays seem also to have an influence in the initial stages of crystallisation, since a supercooled specimen of sulphur develops more crystallisation centres in a given area when it is exposed to the rays than when it is not treated.

For further information on the effects produced by α-rays, β-rays, and γ-rays, reference must be made to the original papers.[1]

[1] Lind and Bardwell, *J. Amer. Chem. Soc.*, 1924, **46**, 2003; 1925, **47**, 2675; 1926, **48**, 2335; Errera and Henri, *J Phys. Radium*, 1926, **7**, 225.

CHAPTER V

THE DISINTEGRATION THEORY AND THE RADIOACTIVE SERIES

1. *The Disintegration Theory*

At the time of their discovery, the radioactive properties of the radio-elements seemed capable of explanation on either of two lines. According to purely physical ideas, radium might be regarded as a kind of transformer which took up energy from its surroundings and subsequently emitted the same energy in other forms, just as a fluorescent substance absorbs certain wave-lengths of light and emits the energy thus acquired in the form of a characteristic fluorescence. This hypothesis has now been shown to be invalid. The second view assumes that radium is an unstable material which undergoes decomposition; and that this decomposition is accompanied by the emission of matter and energy.[1]

The disintegration theory, as it is termed, assumes that the radio-elements are unstable and spontaneously undergo change. During the change, Becquerel rays are emitted and the original radioactive atom is converted into a new atom with a nature different from the parent. This new atom may in its turn be radioactive and emit rays, changing in the process into a third atom, different from its two predecessors. Thus radium emits an α-particle and changes to the inert gas radon; radon in its turn emits a new α-particle and becomes converted into radium-A; the expulsion of yet another α-particle from radium-A leads to the production of radium-B; and after this a β-ray is emitted and the radium-B changes into radium-C, and so on.

Thus the ejection of an α- or of a β-ray from a radioactive element leads to the disintegration of the original element and the formation of a new element which may or may not have radioactive properties.

[1] Rutherford and Soddy, *Phil. Mag.*, 1903, **5**, 576.

This theory can be established by evidence of the following nature. Suppose that we have a radioactive element A, which disintegrates into a second element B by radioactive change. In any ordinary specimen we shall have a mixture of A and B, since A is always producing B. Now let us suppose that A and B can be separated by chemical means. If we remove all traces of B, then we shall have a pure specimen of A; but after this has stood for a time it will become contaminated by traces of B, which will be formed by the disintegration of A. It was an actual experiment of this type which led to the enunciation of the disintegration theory.

Crookes,[1] in the course of an investigation of the properties of uranium, found that if a uranium salt was precipitated by means of ammonium carbonate and the precipitate treated with excess of the reagent, the precipitate almost entirely redissolved, leaving behind it only a very slight residue. The redissolved uranium was found to be radioactively inert, while all the original radioactivity appeared to be concentrated in the small residue. The residue Crookes termed uranium-X. So far, there was nothing out of the common; it appeared that the activity of uranium was really due to the presence in it of this trace of uranium-X. A much more important result was obtained later, however, when it was found that the inactive uranium, after standing for some months, became once more radioactive.*

About the same time, Becquerel[2] separated uranium and uranium-X in another way. He mixed solutions of uranium and barium salts, and then, on precipitating the barium as sulphate, he found that the barium had acquired radioactive properties, while the uranium had lost them. After standing for a year, the two products were re-examined, and it was found that by that time the barium had lost its activity, while the uranium was again as radioactive as it was at the beginning of the experiments.

The only possible conclusion which can be drawn from these results is that the activity of uranium is due to some substance which is produced spontaneously by uranium.

[1] Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409.

* The activity determinations were made photographically, and are thus concerned only with the β-rays; had the α-rays been used as a test, the uranium would not have appeared to lose much activity.

[2] Becquerel, *Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977.

Rutherford and Soddy [1] found a similar series of phenomena in the case of thorium, and they proceeded to investigate quantitatively the rate at which thorium-X lost its activity. They found that, starting with inactive thorium and active thorium-X, after four days the thorium had regained half its original activity, while in the same time the thorium-X had lost half its radioactive powers. The date of decay and recovery can be expressed in both cases by exponential equations—

$$\text{For the decay of Th X,} \qquad I_t = I_0 \times e^{-\lambda t}$$
$$\text{For the recovery of Th activity,} \quad I_t = I_0(1 - e^{-\lambda t})$$

in which I_0 represents the initial activity of the thorium or the thorium-X, I_t the activity after a time t has elapsed, and e the base of the Napierian logarithms. The factor λ, it is found, is the same for both decay and recovery. Similar results were obtained with uranium and uranium-X, except that in this case the period during which the uranium-X lost half its activity was about twenty-two days, instead of four as in the case of thorium.

The most striking peculiarity of this decay and regeneration is the fact that it is totally unaffected by changes of temperature, even a white heat appearing to have no accelerating influence. This differentiates it from ordinary chemical reactions, which are all more or less susceptible to changes of temperature.

There is one other point which must be mentioned. It has been shown that the degree of activity of any salt is directly proportional to the amount of the radioactive element in the salt, and has no connection with the acidic part of the molecule. The activity of radium bromide is different from that of radium carbonate, and depends purely, in each case, upon the percentage of radium metal in the salt.

From the foregoing evidence, certain conclusions can be drawn. In the first place, the fact that the percentage of radioactive element present in a salt is the measure of its activity proves conclusively that radioactivity is a property of the atom, and not of the molecule. Secondly, the fact that radioactive change is independent of temperature proves that the reaction is not an ordinary molecular decomposition. We must therefore have to do with some new atomic property. Finally, since

[1] Rutherford and Soddy, *J.*, 1901, **81**, 321, 837.

the α-particles which are driven out in the Becquerel rays are material bodies, it is obvious that some material system is breaking down; and from what has gone before it is clear that this system cannot be a molecular one. It must therefore be atomic.

Another matter may conveniently be mentioned at this point. Let us assume that we have a radioactive substance X which is disintegrating and yielding a second element Y; and that this element in its turn is disintegrating into a third one Z. If we start with a pure specimen of X, we shall soon find it contaminated with a certain amount of Y; and the quantity of Y present would gradually increase, provided no further change were to take place. Actually, however, Y in its turn is breaking down; so that obviously a time will come when X is producing Y at the same rate as Y is decomposing. The ratio of the amounts of X and Y then present will remain constant after this point has been reached; and X and Y are then said to be in *radioactive equilibrium.*

Certain constants used in connection with the radioactive series may be mentioned here. If Q_0 be the initial quantity of a radio-element present, and Q be the quantity remaining after t seconds have elapsed, then the *radioactive constant* of the element, $\lambda(\text{sec})^{-1}$, can be found from the equation—

$$Q=Q_0e^{-\lambda t}$$

wherein e is the base of the Napierian logarithms. The factor λ represents the fraction of the element transformed, reduced to the unit of time. The reciprocal of λ is termed the *average life* of the radioactive atoms belonging to the element under consideration. The *period*, T, is obtained from the equation: $\lambda T=-\log_e 0{\cdot}5$. It represents the time in which the quantity of the radio-element is reduced to one half. The *range* in cms. of an α-particle through air at 0° C. and 760 mm. pressure is designated by a_0.

2. *Multiple Disintegration*

It will be recalled that the α-rays of radioactive elements are made up of positively charged helium atoms, whilst the β-rays are streams of electrons. If an atom emits an α-ray, its disintegration involves a loss of matter in the form of a

helium atom; and consequently its disintegration product must have an atomic weight four units lower than that of the parent substance. On the other hand, the β-ray change involves only the displacement of an electrical charge and entails no loss of matter; so that the product will have the same atomic weight as the parent.

From this it follows that if a radioactive element is susceptible to disintegration along both lines simultaneously it is possible that it may give rise to two different products,* one of which will have the same atomic weight as the parent (β-ray change), whilst the second product has an atomic weight four units lower than that of the parent (α-ray change).

Several cases of this type have been observed among the radioactive elements. In such cases it is usually found that one mode of disintegration predominates over the other.

3. *The Radioactive Series*

From what has already been said it will be clear that certain family relationships can be traced among the radio-elements. A given radio-element disintegrates and gives rise to a product; this in its turn produces a third substance, and so on. All these elements stand in a genetic relation to one another and may be regarded as a *radioactive series.*

In the earlier days of radioactive research three of these series were recognised and were named, after their parent substances, the uranium, thorium, and actinium series. It is now believed that the uranium series includes as one of its branches the actinium series also; so that at the present time there are supposed to be only two series: the uranium series and the thorium series.

To avoid cumbrousness, however, it will be convenient to treat the material in the older form, indicating merely the point of junction of the uranium and actinium series.

The thorium series is the simplest. In the following table the main facts are given as to the atomic weight, average life, type of rays emitted by the element, and also its atomic number and the group in the Periodic Table in which its properties enable it to be placed.

* See Chapter VII, p. 114.

THE THORIUM SERIES

Element.	Atomic Weight.	Average Life.	Rays.	Group	Atomic Number.
Thorium . . .	232	$1{\cdot}89 \times 10^{10}$ years	α	IVa	90
↓					
Mesothorium-1 .	228	9·67 years	β*	IIa	88
↓					
Mesothorium-2 .	228	8·9 hours	β	IIIa	89
↓					
Radiothorium .	228	2·91 years	α	IVa	90
↓					
Thorium-X . .	224	5·25 days	α	IIa	88
↓					
Thoron . . .	220	78 seconds	α	0	86
↓					
Thorium-A . .	216	0·2 second	α	VIb	84
↓					
Thorium-B . .	212	15·3 hours	β	IVb	82
↓					
Thorium-C . .	212	87 minutes	α and β	Vb	83

At thorium-C multiple disintegration occurs, and it is found that thorium-C gives rise to two disintegration products. One of these, thorium-C′, is the product of a β-ray change. Its atomic weight is therefore the same as that of its parent, viz. 212. The second disintegration product of thorium-C is termed thorium-C″. It results from an α-ray change in thorium-C, and its atomic weight is therefore 208. The disintegration of thorium-C results in the change of 65 per cent. of it into thorium-C′ and 35 per cent. of it into thorium-C″. Both thorium-C′ and thorium-C″ break down to end-products, thorium Ω' and thorium Ω'', having the atomic weight 208. The constants for the two substances may be given here.

	Atomic Weight.	Average Life.	Rays.	Group.	Atomic Number
Thorium-C′ . .	212	10^{-11} seconds	α	VIb	84
Thorium-C″ . .	208	4·5 minutes	β	IIIb	81
Thorium Ω' and Ω''	208	—	—	IVb	82

* This radiation is so soft that it has not yet been experimentally detected. Its existence, however, can be deduced from the Group Displacement Law (see Chapter VII).

We must now turn to the uranium series and, leaving out of account for the present the branching in the chain which introduces the actinium series, deal simply with the successive disintegrations which give rise to the radium group.

THE URANIUM-RADIUM SERIES

Element.	Atomic Weight.	Average Life.	Rays.	Group.	Atomic Number.
Uranium-I	238	$6{\cdot}75 \times 10^9$ years	α	VIa	92
↓					
Uranium-X_1	234	35·5 days	β	IVa	90
↓					
Uranium-X_2	234	1·65 minutes	β	Va	91
↓					
Uranium-II	234	3×10^6 years	α	VIa	92
↓					
Ionium	230	10^5 years	α	IVa	90
↓					
Radium	226	2440 years	α	IIa	88
↓					
Radon	222	5·55 days	α	0	86
↓					
Radium-A	218	43·2 minutes	α	VIb	84
↓					
Radium-B	214	38·7 minutes	β	IVb	82
↓					
Radium-C	214	28·1 minutes	α and β	Vb	83

At this point, as in the case of the thorium series, a branched chain begins. Radium-C disintegrates simultaneously into radium-C′ and radium-C″. We may take the further disintegration of these in succession.

Element.	Atomic Weight.	Average Life.	Rays.	Group.	Atomic Number.
Radium-C′	214	10^{-6} seconds	α	VIb	84
↓					
Radium-D.	210	23·8 years	β	IVb	82
↓					
Radium-E	210	7·20 days	β	Vb	83
↓					
Radium-F.	210	196 days	α	VIb	84
↓					
Radium Ω′	206	—	—	IVb	82

Radium-C″ yields the end-product of its series directly —

Element.	Atomic Weight.	Average Life.	Rays.	Group.	Atomic Number.
Radium-C″	210	2·0 minutes	β	III*b*	81
↓					
Radium-Ω″	210	—	—	IV*b*	82

The actinium series presents a problem which is not yet absolutely settled. Boltwood [1] showed that there is a constant relationship between the quantities of uranium and actinium found in the older minerals, which suggests that actinium may be a descendant of uranium. If this be true, the actinium series must be regarded as a subsidiary branch of the uranium disintegration products, since from ascertained values it appears that at one stage in the disintegration (assuming it to take place) 97 per cent. of the product belongs to the main chain of descent and only 3 per cent. to the actinium series.

Four views have been suggested to account for the origin of the actinium series; and all agree in tracing the actinium family back to the element uranium-Y. The first hypothesis, now discredited, regarded uranium-Y as a product of uranium-I. The other three suggestions are shown diagrammatically below:

$$\text{U-I} \xrightarrow{\alpha} \text{UX}_1 \xrightarrow{\beta} \text{UX}_2 \xrightarrow{\beta} \text{U-II} \xrightarrow{\alpha} \text{Io} \xrightarrow{\alpha} \text{Radium Series}$$
$$\text{UX}_2 \xrightarrow{\beta} \text{U-Y} \xrightarrow{\beta} \text{Pa} \xrightarrow{\alpha} \text{Actinium Series}$$

$$\text{U-I} \xrightarrow{\alpha} \text{UX}_1 \begin{cases} \xrightarrow{\beta} \text{UX}_2 \\ \xrightarrow{\beta} \text{UZ} \end{cases} \begin{matrix} \xrightarrow{\beta} \text{U-II} \\ \xrightarrow{\beta} \end{matrix} \begin{cases} \xrightarrow{\alpha} \text{Io} \xrightarrow{\alpha} \text{Radium Series} \\ \xrightarrow{\alpha} \text{UY} \xrightarrow{\beta} \text{Pa} \xrightarrow{\alpha} \text{Actinium Series} \end{cases}$$

$$\text{U-III} \xrightarrow{\alpha} \text{UZ}_1 \xrightarrow{\beta} \text{UZ}_2 \xrightarrow{\beta} \text{U-IV} \xrightarrow{\alpha} \text{UY} \xrightarrow{\beta} \text{Pa} \xrightarrow{\alpha} \text{Actinium Series}$$

The first of these seems to leave no place for the element uranium-Z, which was discovered by Hahn.[2] The second scheme postulates that UX_1 can eject a β-ray electron in two different ways, leading to two products UX_2 and UZ; and that

[1] Boltwood, *Amer. J. Sci.*, 1908 (iv), **25**, 269; compare Meyer and Hess, *Sitzungsber. Akad. Wiss. Wien*, 1919, **127**, (IIa), 909; Meyer, *ibid.*, 1920, **129** (IIa), 483; Kirsch, *ibid.*, 309; Hahn and Meitner, *Z. Physik*, 1921, **8**, 202; Widdowson and Russell, *Phil. Mag.*, 1924 (vi), **46**, 642.

[2] Hahn, *Ber.*, 1921, **54** (B), 1131; *Z. physikal. Chem.*, 1923, **103**, 4[illegible]

uranium-II can disintegrate by α-ray change in two different manners, giving rise to two individual products, ionium and uranium-Y. Nothing like this has been observed in any other radioactive change. The third hypothesis assumes the existence of an undiscovered isotope of uranium (designated uranium-III) which is assumed to disintegrate on lines parallel to those followed by uranium itself. For details of the arguments in favour of these schemes, the original literature must be consulted.[1] A discussion of the whole problem of the radioactive series is given in two papers by Russell and Widdowson.[2]

THE ACTINIUM SERIES

Element.	Average Life.	Rays.	Group.	Atomic Number.
Protoactinium . .	$1{\cdot}7\times10^{4}$ years	α	Va	91
Actinium . .	28·8 years	β	IIIa	89
Radioactinium . .	28·1 days	α	IVa	90
Actinium-X . .	16·4 days	α	IIa	88
Actinon	5·6 seconds	α	0	86
Actinium-A . . .	$2{\cdot}9\times10^{-3}$ seconds	α	VIb	84
Actinium-B . . .	52·1 minutes	β	IVb	82
Actinium-C . . .	3·10 minutes	α	Vb	83
Actinium-C″ .	6·83 minutes	β	IIIb	81
Actinium Ω″ . .	(hypothetical)	—	IVb	82

4. *Potassium and Rubidium*

A most curious case of radioactivity is that discovered by Campbell and Wood,[3] who observed a very feeble β-ray activity in potassium and rubidium. It is remarkable to find radioactive powers in elements so low in atomic weight and so far removed from the normal group of radioactive materials in the

[1] Soddy and Cranston, *Proc. Roy. Soc.*, 1918, A, **94**, 384; Hahn and Meitner, *Physikal. Z.*, 1918, **19**, 208; Hahn, *Ber.*, 1921, **54** (B), 1131; Neuburger, *Naturwiss.*, 1921, **9**, 235; Hahn, *ibid.*, 236; *Z. physikal. Chem.*, 1923, **103**, 461; Russell, *Nature*, 1921, **111**, 703; Piccard, *Arch. Sci. phys. nat. Genève*, 1917, **44**, 161; Johnstone and Boltwood, *Phil. Mag.*, 1920 (vi), **40**, 50; Joly, *Nature*, 1922, **109**, 480; Neuburger, *Ahrens Sammlung*, 1920–22, **26**, 315.

[2] Russell, *Phil. Mag.*, 1924 (vi), **46**, 642; Widdowson and Russell, *ibid.*, **48**, 293. See also Imori and Yoshimura, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 11; Russell, *Nature*, 1927, **120**, 545.

[3] Campbell and Wood, *Proc. Camb. Phil. Soc.*, 1907, **14**, 15; Campbell, 1909, **15**, 11.

Periodic Table, the more so since the radioactive alkali metal No. 87 has been sought for in vain. The results of Campbell and Wood have been confirmed by numerous later workers.[1]

Potassium sends out more penetrating β-rays than rubidium; but when the two elements are in equal quantity the activity of rubidium is greater than that of potassium. The rubidium rays can be cut down to half by interposing an aluminium screen of 0·02 mm. thickness; which implies that the rays are slightly more penetrating than those of uranium-X; whereas the potassium rays have thirteen times as great a power of penetration. The ratio of $\beta\gamma$-activity of potassium to that of uranium has been estimated as 1 : 460.

Further information on this subject will be found later in this book, where the evidence can be brought into better perspective.*

5. *Radioactive Recoil*

When an α-ray change takes place, a helium atom is ejected by the disintegrating atom. Now since action and reaction are equal, it is clear that the residue of the original atom—the disintegration product—will move in a direction opposite to that taken by the helium atom, as a rifle recoils when the bullet is fired from it. And just as in the case of the rifle, the momentum of the helium atom and the momentum of the disintegration product will be equal to one another.

It may be well to choose a concrete case so that the matter may be readily grasped. When radium-A disintegrates, it gives rise to a helium atom with atomic weight 4 and an atom of radium-B with an atomic weight 214. The helium atom is ejected with a velocity of $1{\cdot}77\times10^9$ cm. per second, so that its momentum is $4\times1{\cdot}77\times10^9$ in atomic units. The momentum of the atom of radium-B is clearly $214\times v$, where v is the velocity

[1] McLennan and Kennedy, *Phil. Mag.*, (1908) (vi), **16**, 377; Levin and Ruer, *Physikal. Z.*, 1908, **9**, 248; Strong, *Physical Review*, 1909, **29**, 170; Henriot, *Compt. rend.*, 1909, **148**, 910; Henriot and Vavon, *ibid.*, **149**, 30; Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 154; Campbell, *Proc. Camb. Phil. Soc.*, 1909, **15**, 11; Ebler, *Chem. Ztg.*, 1908, **32**, 812; Hahn and Rothenbach, *Physikal. Z.*, 1919, **20**, 194; Hoffmann, *ibid.*, 1923, **24**, 475; *Z. Physik*, 1924, **25**, 117; Harkins and Guy, *Proc. Nat. Acad. Sci.*, 1925, **11**, 628.

* See pp. 149–50.

of that atom. Whence we have, since the two momenta are equal in numerical value—

$$v = \frac{4 \times 1{\cdot}77 \times 10^9}{214} = 3{\cdot}3 \times 10^7 \text{ cm. per sec.}$$

The atom of radium-B formed during the disintegration will thus be moving at a velocity of $3{\cdot}3 \times 10^7$ cm. per second; and this velocity may be quite sufficient to carry it away from the mass of radium-A in which it was formed. This phenomenon is termed *radioactive recoil;* and in some cases it forms a means of separating a disintegration product from its parent element, *e.g.* radium-B and radium-A.

Now if the original radium-A be deposited in a thin layer upon the surface of a plate, it will be evident that, since recoils will be taking place in all directions, half of the freshly-formed radium-B will recoil into contact with the plate, whilst the remainder will fly upwards and escape from the plate's surface. In actual practice, some of the particles, even when they are ejected in an upward direction, fail to get clear of the plate. The ratio of the number of atoms of radium-B actually escaping from the plate to the number of atoms which theoretically should escape is termed the *efficiency of the recoil.*

CHAPTER VI

RADON, THORON, AND ACTINON

1. *The Emanations of Thorium and Actinium*

In a volume of this size, no attempt can be made to deal in detail with the properties of the thirty and more radio-elements; and for a full account of these reference must be made to special monographs.[1] Radon,* however, has played such a distinctive part in the history of the subject that it deserves description in some detail; and the present chapter will therefore be devoted to an account of the three radioactive gases: thoron, actinon, and radon.

In 1899 Owens[2] was engaged in an examination of the radiation effects of various thorium derivatives, and in the course of the work he observed that the radiations were by no means constant when measured electrically. Further investigation showed that the inconstancy was due to air-currents about the apparatus; for when the experiments were carried out in closed vessels, the ionisation of the air reached a maximum and then remained constant. Now, if radioactive effects can be influenced simply by passing air across the radioactive substance which forms the subject of the experiment, it seems probable that part, at least, of the radioactive influence is due to some material which can be mechanically blown away by the current of air. This material might be either a gas or a cloud of tiny particles of thorium, which had been loosened from the main body of the radioactive mass.

[1] Soddy, *Chemistry of the Radio-elements*; Henrich, *Chemie und Chemische Technologie Radioaktiver Stoffe* (1918); Russell, *Chemistry of the Radioactive Substances* (1922); Hevesy and Paneth, *Lehrbuch der Radioaktivität*, (1923).

* Radium emanation was christened Niton by Ramsay and Gray, but has been renamed Radon in parallel with thoron (thorium emanation) and actinon (actinium emanation).

[2] Owens, *Phil. Mag.* 1899, (vi), **48**, 360

Rutherford [1] pursued this line of research, and was able to prove that thorium did actually liberate something which we may term an emanation, and that this emanation had radioactive properties. He showed that the properties of the emanation very closely approximated to those of a gas. For instance, it can be blown about by air-currents; it can be bubbled through liquids; a mica stopper will prevent it escaping; and, finally, it causes no deposition of water-globules in the dust-counter. This last experiment proves that the emanation is not a cloud of thorium particles, for these would of course form nuclei for the condensation of water; while the molecules of a gas are too small to produce this effect. The gas has been named Thoron.

The activity of thoron was found to decay very rapidly. To measure this decrease in activity, a very ingenious method was employed, the outline of which is as follows. Pure air was blown across some thorium salt, and in this way became mixed with the emanation from the thorium; the mixed gases were then passed into a long brass cylinder through whose walls projected three insulated electrodes. The brass cylinder was insulated and connected with a battery; and the current through the gas was measured by means of an electrometer in the usual way. It was found that the current diminished progressively along the cylinder; and by passing the stream of mixed gases at different rates through the tube, it was possible to determine the rate of decay of the thoron. Le Rossignol and Gimingham [2] found that the activity of thoron fell to half value in fifty-one seconds. Thoron condenses at —120° C., and the process, which is gradual, is complete at —155° C.

In the light of this work, it seemed probable that the other radioactive elements also might give off analogous emanations. Debierne [3] showed that this was true in the case of actinium, which gives off a gas, actinon, having properties similar to those of thoron, though its time of decay is very much shorter—about four seconds. It condenses between —100° C. and —143° C. This substance does not call for detailed treatment, as the general properties of thoron and actinon resemble those of radon, which are described in some detail in the next section.

[1] Rutherford, *Phil. Mag.*, 1900, (6), **49**, 1.
[2] Le Rossignol and Gimingham, *Phil. Mag.*, 1904, (6), **8**, 107.
[3] Debierne, *Compt. rend.*, 1903, **136**, 146.

2. *Radon*

The discovery of thoron speedily led to that of the emanation from radium, which was detected in 1900 by Dorn.[1] It resembles the thorium derivative in most respects, but is much more durable.

When we consider the amount of radon which is evolved from a given quantity of radium, the first thing which forces itself upon our notice is the difficulty which would be experienced in handling the minute quantity of gas which can be obtained. It has been found that the amount of radon from 1 gramme of radium in radioactive equilibrium has a volume of about one-tenth of a cubic millimetre.[2] Now, the usual quantity of radium salt used by experimenters varies from 20 to 60 milligrammes, and it must be remembered that only a part of this salt is radium. From these figures it will be seen that the volume of radon obtainable at any time will be very minute. Consequently, it is necessary to devise some method by means of which we can transfer these tiny bubbles of gas from one vessel to another. It has been found that this is best accomplished by mixing the radon with a large quantity of neutral gas. The mixed gases can then be transferred from vessel to vessel without any appreciable loss of radon. One of the simplest ways of obtaining the mixture is to pump off the gas from a solution of radium bromide in water. Pure radon can then be obtained by exploding the mixture of hydrogen and oxygen thus produced along with the radon, condensing the radon by cooling with liquid air, and pumping off any excess hydrogen and residual helium.

Radon behaves as an ordinary gas. It obeys Boyle's Law,[3] and diffuses like other gases when placed in a vessel. Experiments have been made by various workers,[4] with a view to determine the molecular weight of radon from its rate of diffusion, but the results are, of course, extremely inaccurate. It must be borne in mind that in these diffusion experiments we are

[1] Dorn, *Abh. d. Naturforscher Gesellsch. Halle*, 1900.

[2] Gray and Ramsay, *J.*, 1909, **95**, 1073.

[3] Ramsay, *Compt. rend.*, 1904, **138**, 1388.

[4] Rutherford and Brooks, *Trans. Roy. Soc. Can.* (2), 1902, **7**, 21; *Chem. News*, 1902, **85**, 196; Curie and Danne, *Compt. rend.*, 1903, **136**, 1314; Bumstead and Wheeler, *Amer. J. Sci.* (4), 1904, **17**, 97; Makower, *Phil. Mag.* (6), 1905, **9**, 56.

dealing with a very minute quantity of radon mixed with a very large volume of some indifferent gas, so that the results are affected by many factors which do not come into view in ordinary diffusion experiments. All that could safely be inferred from these investigations was that the molecular weight of radon must be high, probably over a hundred. As will be seen later, this estimate is under the mark.

Radon has been liquefied and its critical constants have been determined by Ramsay and Gray.[1] The liquid emanation is colourless and transparent by transmitted light. It is phosphorescent and shines with a colour which varies with the nature of the glass of the tube in which it is enclosed, the usual tints being green to lilac. When highly compressed, the tint resembles that of a cyanogen flame, being slightly bluish-pink. The solid emanation is not transparent. It melts at —71° C. Like the liquid, the solid phase of the emanation is phosphorescent; but the colour of the phosphorescence is much more brilliant, and varies with the temperature. On cooling below the melting-point, the tint of the emitted light is steel-blue; further cooling changes it to yellow, and it finally becomes orange-red. On warming the tube containing it, the colours reappear in inverted sequence. The red phosphorescence disappears at —118° C., while at —59° C. or —60° C. the liquid is dull bluish-green. The critical temperature is 377·5° absolute, and the vapour-pressure at this temperature is 47,450 mm.

The atomic weight of radon was determined by Gray and Ramsay,[2] whose method consisted in weighing a given volume of the gas. When it is remembered that the total volume which they were able to obtain at any one time was less than 0·1 c.mm., some idea of the difficulties of the research will be obtained.

Evidence described later in this chapter proves conclusively that radon belongs to the inactive gas group of elements; and making the usual assumptions with regard to the periodic arrangement of the elements, it can be predicted that radon will lie somewhere above xenon in the series. Its atomic weight might therefore be either 176 or 222 approximately, as the following figures show, since the difference between two successive

[1] Gray and Ramsay, *J.*, 1909, **95**, 1073.

[2] Gray and Ramsay, *Proc. Roy. Soc.*, 1911, A, **84**, 536.

atomic weights in the lower section of this group is generally about 45:

Helium.	Neon.	Argon.	Krypton.	Xenon.	I.	II.
4	20	40	83	130	176	222

If the figure 222 were correct, then 0·1 c.mm. of radon would weigh less than 1/1400 milligramme; and in order to weigh this small mass with sufficient accuracy it was necessary to devise a balance which would turn with a load of not more than a hundred-thousandth of a milligramme. The production of this balance is certainly the high-water mark of modern physico-chemical technique.[1] The beam of the balance is formed from threads of quartz fibre, and carries a small mirror of platinised silica. Instead of weights, a counterpoise is used which consists of a small quantity of air sealed up in a quartz bulb. The whole balance is surrounded by an air-tight case in which the pressure can be varied by means of a pump. When the air-pressure in the balance is the same as that in the bulb, the apparent weight of the bulb's contents is nil. In a vacuum, the sealed-up air exerts its full weight, as it is not counterpoised by the buoyancy of the air in the case. At any pressure intermediate between ordinary pressure and a vacuum, the apparent weight of the air in the bulb can be calculated. In this way, by varying the pressure of air in the case, we can bring the balance into equipoise; and this can be determined by throwing a beam of light from the platinised mirror on to a scale some feet away from the apparatus. Many corrections are necessary in the course of a weighing, but for an account of these the reader is referred to the original paper. The results obtained by Ramsay and Gray give a mean atomic weight of radon equal to 223; so that radon should lie two places above xenon in the Periodic Table.

The spectrum of radon has been examined by Ramsay and Collie,[2] who have found that it closely resembles in general characteristics the spectra of the inactive gases. The spectrum fades very soon, and is replaced by the hydrogen spectrum. There is one bright line at 5595; Ramsay and Collie suggest that this may be identical with the line in the spectrum of

[1] Steele and Grant, *Proc. Roy. Soc.*, 1909, A, **82**, 580.

[2] Ramsay and Collie, *Proc. Roy. Soc.*, 1904, A, **73**, 470; Rutherford and Royds, *Phil. Mag.*, 1908, (vi), **16**, 313; Watson, *Proc. Roy. Soc.*, 1909, A, **83**, 50.

lightning [1] which does not seem to have been identified with that given by any known gas.

Like radium itself, radium emanation spontaneously gives out a very considerable quantity of heat. The maximum value of heat liberated per hour from the emanation generated by one gramme of radium is given by Rutherford [2] as 75 calories; this includes the heat emitted by the disintegration products of the emanation. Radon gives out only α-rays.[3]

It has been shown by Curie and Debierne [4] that the amount of radon evolved by radium is independent of the pressure to which the radium is subjected; and it has been found that changes of temperature also appear to be without influence upon the rate of formation.

As regards the chemical nature of radon, it has been shown by Rutherford and Soddy [5] that the emanations of thorium and of radium both manifest an extraordinary inertness even when submitted to the action of strong chemical reagents. For example, no change could be detected in the gases after passing them over red-hot platinum black, or finely divided palladium, lead chromate, magnesium powder, or zinc dust. Such inertness can be paralleled only by the elements of the argon group; and it seems evident that radon must be reckoned as belonging to that class of bodies. Ramsay and Soddy [6] made even more stringent tests, by sparking radon with oxygen in presence of alkali—a process which brings even nitrogen into combination—as well as by passing a mixture of air and radon over a highly heated mixture of magnesium powder and lime. In the latter case the mixture of gases was passed for three hours across the magnesium-lime mixture, which was heated to a bright redness; the measurements of the radioactivity of the radon made before and after the experiment gave exactly the same result. In the course of these experiments it was found, further, that radon is unattacked even by phosphorus burning in oxygen.

On the basis of the foregoing results, a place in the Periodic

[1] Pickering, *Astrophys. J.*, 1901, **14**, 368.
[2] Rutherford, *Radioactivity*, p. 431 (1913).
[3] Rutherford and Soddy, *Phil. Mag.*, 1903, (6), **5**, 445.
[4] Curie and Debierne, *Compt. rend.*, 1901, **133**, 931.
[5] Rutherford and Soddy, *Phil. Mag.*, (6), 1902, **4**, 580; 1903, **6**, 457.
[6] Ramsay and Soddy, *Proc. Roy. Soc.*, 1902, **72**, 204.

System can now be assigned to radon. From the chemical evidence, it is clear that radon is one of the inactive gases; and the evidence of its physical constants makes it practically certain that it must lie below xenon in the Table.

If radon *per se* is inert, it displays a very great influence when brought into contact with other substances. This influence has nothing whatever to do with the chemical reactivity of the gas, but is due purely to its radioactive powers. We must now mention one or two experiments which have been carried out in this field.

Giesel [1] noticed that when a solution of radium bromide was allowed to stand, it evolved some gas which investigation showed to be chiefly hydrogen. Ramsay and Soddy [2] found that the gas mixture contained 29 per cent. of oxygen, the rest being hydrogen. The slight excess of hydrogen they ascribed to contact between the gas mixture and the grease of a tap, which would remove some of the oxygen.

Ramsay [3] carried out a further series of experiments upon the action of radon on water, and found that there was a mean excess of 5·51 per cent. of hydrogen over and above the quantity required to form water with the oxygen liberated. When the gases were stored over mercury, the percentage of hydrogen was still greater, owing to some of the oxygen being used up in oxidation of the mercury. When mercury is not present, various causes of the presence of the excess of hydrogen might be suggested. It was shown that the corresponding amount of oxygen was not lost by oxidation of the radium bromide to bromate, nor was there any formation of ozone or hydrogen peroxide; no bromine is liberated from the radium bromide. In all cases care was taken to prevent the gases coming in contact with tap-grease. Ramsay showed, further, that the action of radon is a reversible one; for while, on the one hand, it decomposes water to produce electrolytic gas, it also has the faculty of recombining oxygen and hydrogen to form water again. In later experiments it was found that traces of hydrogen peroxide may be formed by the action of radon upon water.

[1] Giesel, *Ber.*, 1902, **35**, 3605.

[2] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 294.

[3] Ramsay, *J.*, 1907, **91**, 931; Cameron and Ramsay, *ibid.*, 1908, **93**, 966, 992.

Enough has been said to show that radon possesses simultaneously two sets of properties which, before its discovery, it would have been hard to believe capable of co-existence. On the one hand, it is itself chemically inert; but, on the other hand, it can influence the chemical properties of other substances to a very marked extent. There is one other property which it exhibits, and this is perhaps the most extraordinary of all. Spontaneously, it disintegrates and yields another element, helium.

Before dealing with the disintegration of radon, however, it will be well to mention some experiments which throw some light upon the earlier stages of the decompositions which it undergoes. Ramsay and Soddy [1] made an investigation of the volume of the emanation, with a view to determining whether or not the substance remained constant. The results which they obtained are given in the following table:

Time in days.	Volume in c.c.
Start	0·124
1	0·027
3	0·011
4	0·0095
6	0·0063
7	0·0050
9	0·0041
11	0·0020
12	0·0011
28	0·0004

The first number seems very large in comparison with the others; this may possibly be due to an uncondensable gas being present and forced into the walls of the tube.

From these results it is clear that the radon is gradually disappearing. Now, we need not suppose that matter is being destroyed, but rather that something akin to the condensation of a gas to the liquid state is taking place, which will, of course, be accompanied by a contraction in volume. The simplest hypothesis is that the gaseous emanation which was derived from solid radium is undergoing a further change which is reconverting it into a solid substance.

Here we touch another line of evidence tending to prove the same point, and we must turn aside to consider the phenomena which are classed under the heading *excited activity*.

[1] Ramsay and Soddy, *Z. physikal. Chem.*, 1904, **48**, 691.

It was shown by M. and Mme. Curie [1] in the case of radium, and by Rutherford independently [2] in the case of thorium, that these substances have the faculty, when placed near other bodies, of communicating to the latter the power of exhibiting the phenomena of radioactivity. Debierne [3] later observed that actinium had a similar property.

It is found that the strength of the excited activity depends, not upon the nature of the object upon which it is located, but purely upon the strength of the activity of the exciting radioactive preparation, and the length of time that it was left in the neighbourhood of the excited object. After the radioactive substance has been removed from the neighbourhood of the excited object, the latter begins to lose its radioactive properties, and the decay of these follows an exponential curve. Further research proved that the excited activity is proportional to the amount of emanation present.

Now, Rutherford [4] has shown that if a platinum wire is exposed to thoron it becomes endowed with excited activity. If a wire so treated be immersed in hot water, very little change can be detected in the activity when it is withdrawn and dried; but if the wire be immersed in concentrated hydrochloric acid, it is found that the activity is lost by the wire, but is acquired by the solution; and, further, if the solution be evaporated to dryness, the activity has been transferred to the dish. This active matter can be removed from the wire or the dish by simple scraping.

All this goes to show that we are dealing now with a solid substance, and not with a gas. But a solid substance might be supposed to be a compound of thoron with the platinum of the wire. This view is quite untenable, when it is proved that red-hot platinum black will not attack thoron; so the alternative view must be adopted, viz. that the emanation has deposited the solid substance upon the platinum.

Thus the results of measurements of diminution in the volume of the emanation, as well as those phenomena which have just been described, point alike to the view that thoron

[1] M. and Mme. Curie, *Compt. rend.*, 1899, **129**, 714.
[2] Rutherford, *Radioactivity*, p. 295.
[3] Debierne, *Compt. rend.*, 1904, **139**, 411.
[4] Rutherford, *Phil. Mag.* (6), 1900, **49**, 188.

and radon are continually being transformed into solid substances.

Further investigation of the rate of decay in the case of excited activity showed that this solid *active deposit* (as Rutherford terms it) was not a permanent substance, but was one which rapidly passed through a series of changes. Instead of the decay being expressible by the usual exponential equation—

$$I_t = I_0 \times e^{-\lambda t}$$

it is found that though it follows the exponential law, the total decay series is made up of different factors. The first decay period has one value for λ, the second has another value for λ, and the third yet another. This proves, of course, that the primary radioactive deposit is first converted into a second one, having a different radioactive capacity; and that this second one is in turn changed into a third substance which has a decay constant different from that of its predecessors.

In this way the existence of the radium derivatives A, B, C, D, E, and F has been established, and it has been possible to compare them with other bodies by determining the decay constants of the substances under examination. The chief point of interest in these substances lies in the fact that radium D, E, and F are found in radio-lead, which appears to owe its activity to their presence, while polonium appears to have constants agreeing with those of radium F.

3. *The Production of Helium*

Though the measurements of radioactive decay mentioned in the last section were sufficient to show that radon was capable of undergoing transformation into other forms of matter, the results were not quite convincing, for, to some extent, the proof depended upon certain theoretical assumptions which were incapable of rigid demonstration. The quantities of the transformation products were extremely small; and no chemical or spectroscopic experiments could be made which threw much light upon the differences between the various substances. It was not until Ramsay and Soddy [1] began their work upon radon that a product was actually observed whose chemical individuality was beyond doubt.

[1] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, A, **72**, 206; 1904, **73**, 346.

Rutherford and Soddy,[1] after finding that radon was an inert gas, put forward the view that it belonged to the argon family; and they further pointed out the fact that helium is always found in minerals which contain uranium or thorium. The question as to whether this association of helium with the radioactive minerals had any connection with their activity was thus opened.

Ramsay and Soddy dissolved in water 20 mg. of radium bromide which had been prepared three months previous to their experiments, and they collected the gas which was evolved from the solution. This gas was for the most part electrolytic gas, which had been produced by the action of the radium and radon upon the water; but it also contained some radon. To separate the latter from the other gases, the mixture was passed over a red-hot, partly oxidised copper spiral, and the water so formed was removed by means of phosphorus pentoxide. After this the gas was passed into a tiny vacuum tube, in which the spectrum was examined and carbon dioxide detected. This gas was eliminated by means of liquid air, and a re-examination of the spectrum in the small vacuum tube showed the presence of helium, the D_3 line being visible. Further experiments were made, and practically all the lines in the helium spectrum were found. This work has been confirmed by several workers,[2] and it has been shown that actinium also gives rise to helium.[3]

In this way, it was proved conclusively that radon actually gives rise to helium. The objection might be made that the helium is present throughout the course of the experiments; but this is shown to be untenable by the fact that the helium spectrum is not visible at first. When an exammination is made at the beginning of the process, it is found that a new spectrum is visible which does not contain the helium lines: the latter develop slowly and are visible only some days after the radon has been brought into the vacuum tube. For instance, in one experiment radon was led into the vacuum tube on July 17th; the new spectrum—that of radon—was then observed, which contained no helium lines. After standing until the 21st, the

[1] Rutherford and Soddy, *Phil. Mag.*, 1902, (vi), **4**, 581.

[2] Dewar and Curie, *Compt. rend.*, 1904, **138**, 190; Meyer and Himstedt, *Ann. Physik.*, 1904, **15**, 184.

[3] Debierne, *Compt. rend.*, 1905, **141**, 383; Giesel, *Ber.*, 1907, **40**, 3011.

helium spectrum was observed, and compared with that of a helium vacuum tube.

It is thus shown that the helium is not present in the earlier part of the experiments, nor is it in any way connected with the presence of the radium salt in the solution: it is derived from radon alone. In this way the disintegration hypothesis has obtained its strongest support. Previous to the work of Ramsay and Soddy, the evidence in favour of this hypothesis depended, to a great extent, upon postulates which could not be experimentally tested; but by the production of helium from radon, the break-down of one radioactive substance into a non-active body was conclusively demonstrated.*

These experiments throw light upon another point. It has been found that helium exists in many minerals, as well as in the waters of several mineral springs; and for a considerable time the presence of this very rare gas under such conditions was inexplicable. Ramsay and Soddy's researches have cleared up this question also; for it has been shown that both minerals and mineral waters which contain helium have also more or less well-marked radioactive properties. They are therefore certain to contain a small proportion of radioactive emanations, and it is doubtless from this source that helium is derived.

4. *The Disintegration Theory and the Age of Minerals*

If a mass of uranium were placed in a hermetically sealed vessel and allowed to disintegrate under these conditions, it is evident that either the quantity of helium or the amount of lead which collected in the vessel would give a measure of the period during which the uranium has been enclosed. Calculation shows that one gramme of uranium in radioactive equilibrium with all its disintegration products will give rise to about 11×10^{-5} cubic millimetres of helium; so that from the ratio of the quantities of helium and uranium present we can readily ascertain how long the process has been going on. A similar calculation will be possible with regard to the uranium-lead ratio.

Now in certain minerals uranium is present; and the helium given off by it and its disintegration products remains occluded

* Compare the later investigation by Rutherford and his collaborators on the α-particle (see p. 63).

in the solid material instead of being lost to the air. By breaking up the mineral, liberating and estimating the helium and comparing its mass with that of the uranium present, we can arrive at a rough estimate of the period during which the uranium has been confined in the rock under these conditions—in other words, since the rock solidified. Strutt [1] has investigated the matter and has been able to put forward estimates of the duration of the geological periods based on his results. It must be borne in mind that these estimates are minimum ones, since it is most improbable that *all* the helium generated is retained by the rocks.

The uranium-lead ratio in minerals is also open to criticism when it is taken as a guide to geological age. It can be calculated that one gramme of uranium produces per annum of lead $1{\cdot}21 \times 10^{-10}$ grammes; but this is a very rough approximation. Further, the value of the method depends upon the assumption that during that time no lead has been introduced into the mineral from external sources, which can never be certainly established.

It will be seen that both methods can lead only to approximations to the truth; but they are none the less valuable, in that they give us definite evidence on a period which has hitherto been even more vaguely calculated. The following table [2] gives some of the main results obtained. The figures represent millions of years which have elapsed since the strata were laid down. Under the heading He/U are given the results derived from the helium-uranium ratios; while the column headed Pb/U shows the figures deduced from the lead-uranium ratio in minerals. The numbers in the case of the helium ratios show the minimum possible age of the rocks; but the real age is probably much greater.

Strata.	He/U.	Pb/U.
Miocene	6·3	30
Eocene	31	70
Carboniferous	146	330
Devonian	145	390 ?
Archæan	405–715	940–1580

[1] Strutt, *Proc. Roy. Soc.*, A, 1908, **81**, 272; 1910, **83**, 298; 1911, **84**, 379.

[2] A fuller table is given by Holmes, *Discovery*, 1920, **1**, 108; see also Holmes, *The Age of the Earth* (1913); Holmes, *Proc. Roy. Soc.*, 1911, **A, 85**, 248; Holmes and Lawson, *Phil. Mag.*, 1914 (vi), **28**, 833; Boltwood, *Amer. J. Sci.*, 1907, [4], **23**, 77; Lawson, *Naturwiss.*, 1917, **5**, 429, 452, 610, 709; Gleditsch, *Arch. Math. og Naturwiss.*, 1919, **36**, 73.

It will be seen that the values differ considerably among themselves, as is only to be expected in view of the difficulties of the problem; but they provide us with a much more accurate gauge than do the previous estimates based on time required for the deposition of the strata.

Another means of attacking the same problem is found in pleochroic haloes. In some specimens of certain minerals such as tourmaline and mica, spots have been observed which have diameters of 0·01–0·02 mm., and which contain a central nucleus surrounded by concentric coloured spheres. The nucleus is believed to contain a minute speck of radioactive material; and the discoloration is supposed to be caused by the ejection of α-particles from the speck, which tint the mineral just as glass is tinted when subjected to the α-rays of radon. Since each disintegration product will eject α-particles having a different range from those of all its congeners (assuming that it ejects α-rays at all), the radius of each sphere of colour represents the extreme range of one set of α-particles in mica; and by making certain assumptions it is possible to estimate the approximate age of the mineral containing the halo. The results thus obtained agree approximately with those derived from the uranium-lead ratio or the uranium-helium ratio.[1] One minute halo observed in Arendal mica was found to correspond to the hypothetical action of an α-ray having a range of about 1·5 cm. in air; and Joly [2] suggests that this may be due either to an element which has completely decayed and disappeared or else to an existing element having a radioactivity so feeble that it cannot be detected by normal methods.

[1] Joly, *Phil. Mag.*, 1907 (vi), **13**, 381; 1910, **19**, 327; Joly and Rutherford, *ibid.*, 1913 (vi), **25**, 644; Joly, *Phil. Trans.*, 1917, A, **217**, 51; *Proc. Roy. Soc.*, 1923, A, **102**, 682; *Nature*, 1922, **109**, 480; Holmes, *Age of the Earth* (1913).

[2] Joly, *Nature*, 1922, **109**, 517, 578; *J.*, 1924, **125**, 897; compare Imori and Yoshimura, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 11; Russell, *Nature*, 1927, **120**, 545.

CHAPTER VII

THE ISOTOPES

1. *The Recognition of Isotopy*

In 1910, Soddy [1] called attention to the fact that the evidence then accumulated proved that certain members of the radioactive group of elements exhibited a complete identity of chemical behaviour. Thus thorium-X, actinium-X, and radium had been found to be chemically indistinguishable from one another; ionium, radiothorium, radioactinium, and thorium were also endowed with identical properties so far as chemical reactions went; and the three emanations could not be distinguished from each other by any chemical means.

As Soddy indicated, there are here three groups of substances in which each element is readily distinguishable from the rest by means of its radioactive constants, but in which no member of a group can be isolated from its neighbours by the employment of purely chemical methods of separation.

When the atomic weights of these substances are compared, it is found that they are not identical. That of ionium is 230, of thorium 232, and of radiothorium 228. It thus became clear that there could exist two or more elements with different radioactive constants and different atomic weights but with identical chemical properties. Soddy hazarded the conjecture—which has since proved well founded—that these phenomena would prove to be the beginning of some embracing generalisation which would throw light, not only on radioactive processes, but on the elements in general and the Periodic Law.

In 1911, Soddy carried his views to a further stage. Chemical analysis, as consideration will show, is not necessarily a method of separating matter into homogeneous elements; but is,

[1] Soddy, *Chemical Society's Annual Reports*, 1910, **7**, 285; see also Soddy, *The Chemistry of the Radio-elements*, 1st edition, I, 29 (1911).

instead, a mode of isolating from each other certain types of matter which differ in behaviour when treated with a given reagent. Hitherto it has been assumed that, when chemical analysis has done its best, the resulting substances are entirely homogeneous or, as we say, elemental forms of matter. But is this conclusion justified? No chemical process with which we are acquainted at present will separate thorium and ionium from one another; yet when we apply to a mixture of these elements a totally new method of analysis – radioactive analysis —we find that we are not dealing with one substance but with two.

Chemical analysis, then, can separate matter into a number of "types" which are *homogeneous in chemical behaviour*. Each "type" is recognisably different from other "types" by means of its chemical reactions; but it may or may not be homogeneous as regards other properties such as atomic weight or stability.

To express this idea, Soddy coined the word *isotopes*. A group of two or more elements occupying the same place in the Periodic Table and being chemically identical and non-separable is defined as a group of isotopes; and within a group * the separate members are said to be isotopic with one another. Thus ionium, thorium, and radiothorium are isotopes; the three emanations are isotopic with one another; and mesothorium-1 is an isotope of radium.

It has been convenient to deal with the problem of isotopy from the standpoint of the radio-elements; but it must not be supposed that isotopic forms belong exclusively to this class. The work of Aston, which will be dealt with in a later chapter,† has established that isotopy can be detected in the case of many of the non-radioactive elements. As a matter of fact, the first discovery of isotopes was made by means of positive ray analysis in the case of the two forms of neon,[1] though until the theory of isotopy had been developed, the meaning of the experimental result was not fully grasped.

* Fajans suggested the name "*pleiad*" for the group, but this term has not been generally adopted.

† See Chapters IX and X.

[1] Thomson, *Rays of Positive Electricity*, p. 112 (1913).

2. *The α-Ray Change*

To Soddy we owe also the next step in advance in our knowledge of the rationale of radioactive change,[1] his publication on the subject dating from 1911.

When a helium atom is expelled by a radioactive element, it carries with it two positive charges; and the disintegration product is therefore characterised by an electrical charge two units less positive—or more negative—then the original element. At the same time, owing to the loss of four units of matter in the form of the helium atom, the atomic weight of the disintegration product is four units less than that of the parent substance.

Now the loss of one positive charge by an atom may be regarded as equivalent to a disappearance of one positive valency of that atom; which is the same as a shift of one column to the left in the Periodic Table. The loss of two positive charges would therefore correspond to shifting an element into the second column to the left in the Table, or, in modern parlance, lowering the atomic number by two units.

Taking the two changes together, Soddy enunciated the rule that the expulsion of an α-ray by an element results in the formation of a new element which has an atomic weight four units less than that of its parent and which is situated two columns to the left in the Periodic Arrangement.

For example, radium has an atomic weight of 226 and it lies in Group II of the Table. As a result of the α-ray change it passes into radon, which has an atomic weight of 222 and which lies in Group 0—two columns to the left of Group II. Again, radon in its turn ejects an α-particle and becomes converted into radium-A, which has an atomic weight of 218 and which occupies a position in Group VI * of the Periodic Arrangement. This last change may be rather difficult to grasp, but possibly the following reasoning may make it clearer. Radon loses two positive charges (which are equivalent to two positive valencies) during the α-ray change. But radon starts by having no valency at all. The loss of two positive valencies is therefore simply

[1] Soddy, *Chemistry of the Radio-elements*, Part I, p. 30 (1911).

* This example has been chosen to illustrate a particular point; but it must be understood that our knowledge of the chemical character of radium-A came at a later date from Fleck's investigations, of which an account is given in the next section.

equivalent to the gain of two negative valencies; so that the new element is characterised by two negative valencies; and this brings it into the oxygen column of the Table.

Consideration of the atomic numbers will show that each α-ray change lowers the atomic number by two units, since the atomic numbers of the three elements mentioned are: radium =88; radon=86; radium-A=84.

3. *Fleck's Investigation of the Chemistry of the Radio-elements*

The next advance in our knowledge of the subject was due to the work of Fleck [1] which was carried out at the suggestion of Soddy. The object of the investigation was to find the common element which each radio-element most resembled, and then to see whether, after the two had been mixed, any separation of the constituents was possible by chemical means. At the time when this investigation was begun, very little was known about the chemistry of the "active deposit" group; but Fleck's researches established the relationships between some sixteen radio-elements and also showed their kinship with certain non-radioactive elements.

The difficulties of the research can hardly be over-estimated. In the first place, some of the substances examined could be obtained only in minute traces. Secondly, the average life of the elements was, in some cases, extremely brief. Thirdly, owing to the rapidity with which the substances became contaminated with disintegration products, radioactivity measurements were complicated by subsidiary factors.

It is impossible to give here a detailed account of all the various examinations made by Fleck; but for the present purpose it will be sufficient to describe a single example, which will give some idea of the difficulties which had to be overcome. The case of thorium-B and thorium-C may be chosen.

Thorium-B emits only β-rays, whilst thorium-C yields α-rays. If a complete separation of the two compounds is effected, then the thorium-B will be inactive at first as far as α-ray measurements go, but will show a gradually increasing α-radiation owing to the formation of thorium-C by disintegration.

[1] Fleck, *J.*, 1913, **103**, 391, 1052.

On the other hand, thorium-C will show a gradual falling off in α-radiation owing to its disintegration.

Fleck found that when a small quantity of a lead salt was added to a solution containing thorium-B and thorium-C in radioactive equilibrium, complete precipitation of the lead as sulphide carried down both of the radio-elements with it. Incomplete precipitation led to a preponderance of thorium-C in the sulphide precipitate. When, in addition to the lead, another metal was present which gave a sulphide soluble in ammonium sulphide, no activity was found in the ammonium sulphide solution. This proves that neither thorium-B nor thorium-C is allied to the noble metals.

A mixture of the two radioactive materials with salts of lead and copper was then tested. It was found that when the solution of the mixture was precipitated with sodium carbonate and the precipitate was digested with potassium cyanide solution, no activity was found in the solution. This demonstrates that the radio-elements in question must be akin to either lead or bismuth, since these are the only two metals of the second analytical group which behave in this manner.

A mixture of lead and bismuth salts with salts of the two radio-elements was then treated with sulphuric acid and alcohol. The precipitated sulphate was removed and the bismuth was precipitated by means of sulphuretted hydrogen. Radio-activity measurements proved that the lead sulphate precipitate contained thorium-B, whilst the bismuth sulphide precipitate contained the thorium-C sulphide. This established the resemblance between thorium-B and lead on the one hand and between thorium-C and bismuth on the other.

Many other methods were tested in the attempt to separate thorium-B from admixed lead, and thorium-C from admixed bismuth; and all led to the same conclusion. Among them may be mentioned the following: (1) Precipitation of lead as sulphate and of bismuth as sulphide; (2) Precipitation of lead as sulphate and of bismuth as hydroxide; (3) Precipitation of lead as chloride; (4) Precipitation of lead as sulphide and of bismuth as oxychloride; (5) Precipitation of lead as lead hydroxide and of bismuth by means of *m*-nitrobenzoic acid; (6) Precipitation of bismuth with alcohol; (7) Electrolytic

separation; (8) Fractionation of lead by means of sulphuric acid and alcohol.

It will be seen that these reactions prove conclusively that no separation of lead from thorium-B, or of bismuth from thorium-C, can be attained by the ordinary methods.

This series of investigations by Fleck established the correctness of Soddy's α-ray rule; and also led on to the further generalisation which will be described later in this chapter.

4. *The β-Ray Change*

The credit of throwing light upon the effect of β-ray changes is shared by no less than four investigators who almost simultaneously and, possibly, independently had arrived at solutions of the problem.[1] It was pointed out by them that the expulsion of a β-ray * from a radioactive element resulted in the formation of a disintegration product with a chemical character which placed it in the column to the right of that which is occupied by the parent substance; or, to use the modern terminology, increased its atomic number by one unit.

For instance, uranium-X_2, which belongs to Group V, ejects a β-ray and is converted into uranium-2, which falls into Group VI; radium-B, in Group IV, throws off a β-ray and yields radium-C, which belongs to Group V.

5. *The Group Displacement Law* †

It is now possible to fit together into a connected whole the three main facts with regard to the relations between the Periodic

[1] Von Hevesy, *Physikal. Z.*, 1913, **14**, 49 (January 15); Russell, *Chem. News*, 1913, **107**, 49 (January 31); Soddy, *ibid.*, 97 (February 28); *Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 188; Fajans, *Physikal. Z.*, 1913, **14**, 131, 136 (February 15). Of the four, only Soddy and Fajans produced correct results. See footnote † below.

* "Rayless" changes are probably actually β-ray changes in which the β-ray is of a penetrating power so feeble as to defy identification at present.

† The main credit in the discovery of this law is due to Soddy, who first grasped the meaning of the isotopes and the α-ray change. To him also is due the initiation of Fleck's researches which definitely established the validity of the law. Russell, when enunciating the rule for the β-ray change, combined it with Soddy's previous α-ray rule; but owing to the fact that he failed to regard the Periodic Table as continuous from Group 1 through Group 0 to Group VII, his statement of the law was somewhat imperfect. Soddy and Fajans practically simultaneously published the complete generalisation; but from the foregoing

System and the course of disintegration of the radioactive elements.

The Law of Group Displacement may be stated as follows: When a radio-element expels an α-particle, the disintegration product has an atomic weight four units less than that of its parent and an atomic number two units less than that of the parent element. In a β-ray change, the disintegration product has the same weight as the parent atom, but its atomic number is aun it higher than the atomic number of the parent element.

The application of this rule to the Periodic Table leads to the conclusion that if a parent radio-element in Group M suffers an α-ray change, the disintegration product will fall into place in Group (M—2); whilst in the case of the β-ray change a parent in Group M will yield a disintegration product belonging to Group (M+1). In the case of the radioactive emanations belonging to the Zero Group, the disintegration products from the α-ray change fall into Group VIB, since they have the atomic number 84 corresponding to that position. It should be remembered that the Periodic Table is really cylindrical and that the ordinary flat picture of it is merely a kind of Mercator's projection of the true arrangement. A glance at the chart at the end of this volume will show the true continuity from the alkali metals of Group I, through the Zero Group, and into Group VII.

It is evident that the combined effect of an α-ray change and two β-ray changes, in any order, will be to yield a final disintegration product having an atomic number identical with that of the original parent. Fig. 5 will make the matter clear. The atomic weight and atomic numbers shown are merely illustrative and do not correspond to any known cases.

In 1913, Soddy [1] published a diagram showing the results of all the radioactive changes known at that date and elucidating the positions in the Periodic Table occupied by various radio-elements. A more complete scheme [2] was published in 1919, which showed the linking of the uranium and actinium series of

it will be seen that the lion's share of the credit belongs to the former investigator. Fleck's results, though unpublished, seem to have been known to those interested in the subject at the time.

[1] Soddy, *British Association Report*, 1913, p. 445.

[2] Soddy, *J.*, 1919, **115**, 16.

disintegration products. It is noteworthy that in his original scheme of 1913, Soddy graphically expressed the fact that there is a unit difference of nuclear charge between successive places in the Table, thus anticipating Moseley's independent inference drawn from the X-ray spectra.

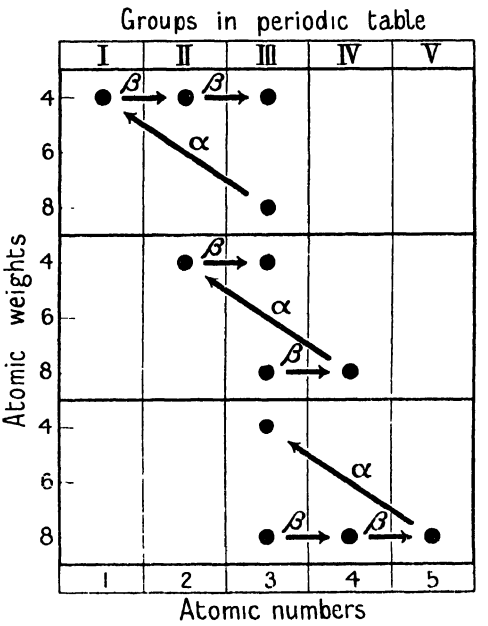


FIG. 5.

The chart at the end of this volume embodies some of the information given by Soddy in his diagrams. It is intentionally incomplete so far as the chain of descent of actinium is concerned; for, as has been pointed out, the disintegration series from uranium to actinium is still a subject of discussion. It seemed better to start the actinium series with uranium - Y, from which point onwards it is firmly established, and to admit no contentious matter into the chart.

With the chart before him, the reader will be able to follow out the exact results obtained where a radio-element undergoes one α-ray change and two β-ray changes. Thus, for example, uranium lies in Group VI. It throws off an α-particle, producing X_1, which belongs to Group IV. A β-ray change yields uranium-X_2, a Group V element; and a further β-ray change gives rise to uranium-II, which belongs to Group VI. Thus, starting with an element in Group VI, we have ended with a new element in the same Group, though with an atomic weight four units less than that of the original uranium. Again, take the case of actinium-B. This element lies in the lead Group. It ejects a β-particle and yields actinium-C, which belongs to the bismuth Group. Actinium-C now expels an α-particle and pro-

duces actinium-D, an element in the thallium Group. Finally, actinium-D throws out a β-particle and passes into the end-product of the series. This end-product lies in the lead Group from which we started.

Inspection of the chart will show that in certain columns two or more elements are to be found. For example, at the right-hand side in Group VIA, uranium-I and uranium-II are marked; whilst in some of the other columns the numbers of elements are even greater, reaching a maximum in Group IVB. The result of Fleck's investigations proved conclusively that elements which occupy the same place in the Periodic Table cannot be separated from one another by ordinary chemical means. This holds good whether these elements belong to the same radioactive series or not. For example, radio-actinium, thorium, and ionium, though each belongs to a different series, are chemically inseparable from one another. They belong, as has already been indicated, to the class named by Soddy the isotopes. If thorium and ionium are mixed together they cannot be separated again by any process of ordinary chemical analysis, though by applying radioactivity tests it can be proved that more than one element is present.

Soddy [1] has drawn attention to some of the consequences which follow from the recognition of isotopy. In the first place, the position occupied by an atom in the Periodic Table is not a mere function of its mass, but depends mainly upon the electrical content of the atom and is only to a subsidiary extent influenced by atomic mass. From this it follows that a chemical element is not necessarily homogeneous but may be, as Crookes [2] suggested as far back at 1888, composed of atoms of different atomic weights; and what we term the "atomic weight" may be merely an average value and not a true physical constant.

Secondly, Soddy pointed out that further up the Table in the vertical columns lie the ordinary families of elements, in which the differences in mass between similar elements are much greater than in the case of the isotopes; and instead of identity we get analogy in chemical character between them. From this

[1] Soddy, *Chemistry of the Radio-elements*, Part II, 6 (1914).

[2] Crookes, *J.*, 1888, **53**, 487; see also *J.*, 1889, **55**, 257. The reader is advised to consult these papers.

comparison, Soddy drew the conclusion that the chemical nature of matter is a function of two variables: mass and electrical character. The electrical content is the essential variable in the horizontal rows: whilst in the vertical columns the mass plays the preponderant part. Mass also enters into the problem of the stability of elements, and it may in some cases play a preponderant part from this standpoint.

6. *The Atomic Weight of Lead*

An inspection of the chart at the end of this volume will show that the end-products of the radioactive series, marked as black circles, all fall into Group IVB of the Periodic System; and, since they only occupy one space in that Group, they are isotopic with one another. Closer inspection will reveal a still more interesting fact.

If the atomic weight of radium be taken as 226, then the atomic weight of the product of radioactive change (passing through radium-F) will be 206, since this series of changes involves the expulsion of five α-particles each of which has an atomic weight of four units. The end-product, radium-Ω'', in the branch through radium-C$''$ will have an atomic weight of 210, since only four α-particles are expelled during the changes.

Again, starting with thorium, which has an atomic weight of 232·4, there is a succession of six α-ray changes in both branches of the chain, so that in each case the atomic weight of the end-product should be 208·4.

With regard to actinium we are not on quite such sure ground; but the atomic weight of the end-product here must be either 208 or 212.

Now the atomic weight of lead itself, as given at that time in the International Table of Atomic Weights, was 207·1; and the question at once arises: Is ordinary lead a homogeneous element or is it a mixture of two isotopes? A mixture of the end-products from uranium (through radium-F) and from thorium in equal proportions would have exactly the atomic weight which is required; and since the material is not radioactive and as its two constituents would be inseparable from each other by chemical means, the results of atomic weight determination would work out exactly as in practice.

Soddy [1] threw out a hint that the examination of the atomic weight of lead derived from minerals containing uranium and no thorium might differ from the atomic weight of lead found in other minerals containing thorium but no uranium; though he was careful to point out that the results might be obscured by other factors.

This line of research was taken up by several investigators. The first results were published by Soddy and Hyman,[2] who examined the lead derived from Ceylon thorite, a mineral containing 55 per cent. of thorium and 1 to 2 per cent. of uranium. The percentage of lead in the mineral is so small (0·4 per cent.) that it may be entirely of radioactive origin. Since the rate of change of uranium is two-and-a-half to three times that of thorium, the lead, if derived from both sources, should contain about ten parts of thorium-lead to one part of uranium-lead. On this calculation the atomic weight of lead from thorite ought to be rather higher than that of ordinary lead; and when the atomic weight was actually determined, it was found to be 207·694 * as compared with 207·2 for ordinary lead.[3] Photographs of the spectra of the two varieties of lead were found to be identical with the exception of one line, 4760·1, which was much stronger in the spectrum of ordinary lead than in that of thorite lead.[4]

Richards and Lembert [5] then published a series of determinations of the atomic weights of lead from five different radioactive minerals and from two commercial, non-radioactive specimens of lead. They found that lead occurring in uraninite derived from North Carolina had an atomic weight of 206·40, whilst common lead had an atomic weight of 207·15. The leads from other minerals took up positions intermediate between these extremes. Richards and Wadsworth obtained the value of 206·08 for radioactive lead from Norwegian clèveite.

[1] Soddy, *Annual Reports*, 1913, **10**, 269–70.

[2] Soddy and Hyman, *J.*, 1914, **105**, 1402.

* This is the corrected figure; see Soddy, *Annual Reports*, 1916, **13**, 247.

[3] Baxter and Grover, *J. Amer. Chem. Soc.*, 1915, **36**, 356.

[4] See also Hönigschmid and Horovitz, *Monatsh.*, 1915, **35**, 353; Merton, *Proc. Roy. Soc.*, 1915, A, **91**, 198; Siegbahn and Stenström, *Compt. rend.*, 1917, **165**, 428; Haskins and Aronberg, *Proc. Nat. Acad. Sci.*, 1918, **3**, 710, for other data with regard to the identity of the spectra of isotopes.

[5] Richards and Lembert, *J. Amer. Chem. Soc.*, 1914, **36**, 1329; see also Richards and Wadsworth, *J. Amer. Chem. Soc.*, 1916, **38**, 2613.

Another series of determinations is due to M. Curie.[1] Lead from carnotite was found to have an atomic weight of 206·36, whilst the metal from galena gave an atomic weight of 207·01.

Finally, Hönigschmid[2] determined the atomic weight of lead from Joachimsthal pitchblende and found it to be 206·405.

Taking the whole of the results,[3] it will be seen that the lowest figure is 206·08 and the highest is 207·694, common lead being 207·2. Since some of the results were obtained by investigators who have specialised in atomic weight determinations, no doubt can be entertained as to their accuracy; and it must be taken as proved that the "atomic weight of lead" is not a physical constant, but differs according to the specimen chosen for examination.

From measurements with the mass-spectrograph, Aston[4] found three different masses (206, 207, 208) for lead atoms. The atoms of mass 207 may be regarded as disintegration products of the actinium series.

The importance of the foregoing results requires but little emphasis. Clearly they struck at the very root of the chemical conceptions which were current at that time; and, since they were found in the case of non-radioactive materials, they could not be brushed aside as forming part of the abnormalities which characterise the radio-elements. They formed the most conclusive evidence of the correctness of Soddy's theory of the isotopes from the purely chemical side, as the proof of the existence of different forms of lead can now be based entirely upon chemical investigation, independent entirely of radioactivity measurements; and with this advance we enter upon the field of the normal elements themselves.

Some recent work on the atomic weight of boron is of special interest in this connection, since boron, unlike lead, has no apparent relationship with any members of the radioactive

[1] Maurice Curie, *Compt. rend.*, 1914, **158**, 1676.

[2] Hönigschmid and Mlle. Horovitz, *Compt. rend.*, 1914, **158**, 1796; *Monatsh.*, 1915, **36**, 353.

[3] See also Soddy, *Nature*, 1915, **94**, 615; *Engineering*, 1915, May 28 and October 1; Richards and Wadsworth, *J. Amer. Chem. Soc.*, 1916, **38**, 221, 1658, 2613; Fajans, *Z. Elektrochem.*, 1918, **24**, 163; Hönigschmid, *ibid.*, 1919, **25**, 91; Davis, *J. Physical Chem.*, 1918, **22**, 631; Richards and Sameshima, *J. Amer. Chem. Soc.*, 1920, **42**, 928.

[4] Aston, *Nature*, 1929, **123**, 313; compare Rutherford, *ibid.*

series. Briscoe and his collaborators [1] have examined samples of boron from California, Tuscany, and Asia Minor. Three different methods of estimation were employed: (1) analysis; (2) measurement of the density of boron oxide; and (3) determination of the density of boron trichloride. The atomic weights obtained in each case are given in the following table.

Samples from	California	Tuscany	Asia Minor.
By analysis	10·841	10·825	10·818
From boron oxide . .	10·847	10·823	10·818
From boron chloride .	10·830	10·825	10·817

Confirmation of this result is furnished by Hönigschmid,[2] who gives 10·840, 10·825, and 10·818 as the atomic weights yielded by three different samples of boron of unknown origin.

7. *The Properties of Isotopes*

When two isotopic forms of matter are compared, it is found that they are indistinguishable from each other so far as certain properties are concerned; whilst in other qualities they exhibit marked differences. It will be convenient to deal with these in turn, beginning with the properties wherein differences have been detected.

Atomic Weight.—This has been treated in the foregoing section in the case of the isotopic forms of lead, so one other example will suffice here. The element uranium-1 has an atomic weight of 238. It undergoes the α-ray change, loses a helium nucleus, and yields uranium-X_1, which must therefore have an atomic weight of 234. Now uranium-X_1 is isotopic with thorium, which has an atomic weight of 232; so that in this case the two isotopes differ from each other by two units of atomic weight.

Radioactivity.—The average life of the atom in uranium-X_1 is 35·5 days; whereas the average life of the thorium atom is $1{\cdot}89\times10^{10}$ years. Further, uranium-X_1 emits β-rays, whereas thorium ejects α-particles. Thus the two elements differ from each other both in atomic stability and in the manner of their disintegration. Again, radium-B, with an average life of

[1] Briscoe and Robinson, *J.*, 1925, **127**, 696; Briscoe, Robinson, and Stephenson, *J.*, 1926, 70; Briscoe, Robinson, and Smith, *J.*, 1927, 282.

[2] Private communication to Aston, see *Ann. Reports*, 1926, **23**, 283.

38·7 minutes, is isotopic with ordinary lead, which is quite inactive.

Density.—Soddy and Hyman,[1] working with thorite lead, found the density to be $D_4^{20} = 11{\cdot}376$, whereas the value for ordinary lead is 11·3415. Richards and Wadsworth [2] found the density of lead from Norwegian clèveite to be 11·273. Other results were obtained by the same investigators. On calculating the atomic volumes for the various isotopic forms of lead from these measurements, it was found that all the isotopes had the same atomic volume.

The list of properties in which isotopes show identity is much longer.

Atomic Number and X-ray Spectrum.—Rutherford and Andrade[3] examined the self-excited X-ray spectrum of radium-B, which is produced by the impact of the β-ray discharge upon the surrounding atoms of the element; and they found that the wave-length of the L-radiation coincided with that which is to be expected from lead or any other element with atomic number 82. From this result it must be inferred that two isotopes have the same atomic number and emit identical characteristic X-rays.

Atomic Volume.—It has already been pointed out that the atomic volumes of the various forms of lead are identical, although the atomic weights are different. This seems to prove that the atomic volume of an element is a true physical constant. It must be borne in mind, however, that up to the present no attempt has been made to compare the atomic volumes of all the elements at corresponding temperatures and pressures, so that the existent data are probably not comparable over the whole elemental range.

Melting-points.—These appear to be identical for the isotopic forms of lead.[4]

Molecular Solubility of Salts.—These have been found to coincide within experimental error, as the following figures show.[5] The refractive indices of the solid salts are also equal within experimental error.

[1] Soddy and Hyman, *J.*, 1914, **105**, 1402; Soddy, *Nature*, 1915, **94**, 615.

[2] Richards and Wadsworth, *J. Amer. Chem. Soc.*, 1916, **38**, 221, 1658.

[3] Rutherford and Andrade, *Phil. Mag.*, 1914, **27**, 854.

[4] Lembert, *Z. Elektrochem.*, 1920, **26**, 59.

[5] Fajans and Lembert, *Z. anorg. Chem.*, 1916, **95**, 297; compare Richards and Schumb, *J. Amer. Chem. Soc.*, 1918, **40**, 1403.

SATURATED SOLUTIONS OF LEAD NITRATES

Material.	Molar Concentration.	Refractive Index of Solid Salts.
Nitrate of ordinary lead	1·7993	1·7815
Nitrate of lead from uranium ore . .	1·7991	1·7814

A corollary to this result is that equal volumes of two solutions saturated respectively with different isotopes will have different weights, and therefore different densities; and, further, the solubilities of the two materials will be different if they are expressed as grammes per litre and not as molar concentrations.

Electrical Properties.—No difference has been detected in practice between two isotopes so far as electrochemical potential is concerned. Paneth and Hevesy [1] showed that the decomposition potential at which radium-E is deposited on the cathode is altered in the same direction and to the same extent by the addition of the isotopic element bismuth as it would be by the addition of the same number of ions of radium-E. Similar results were obtained in the case of thorium-B and its isotope, lead. In the second place, in the deposition of radium-E and of thorium-B at potentials below the decomposition voltage, the addition of isotopic elements prevents this decomposition though other elements are without influence. Finally,[2] when a galvanic chain was formed in which radium-D was one of the members, the potential of the chain was found to be practically the same as that of a similar chain wherein ordinary lead was substituted for the radium-D. The voltage in the former cases was —0·884 volt; whilst in the latter it was —0·888 volt.

Examinations of electrical conductivity and electromagnetic properties revealed no differences between isotopic materials.[3]

Optical Spectra.—The earliest work in this field was carried out by Russell and Rossi,[4] who were unable to detect any difference between the arc spectrum of pure thorium oxide and the arc spectrum of thorium oxide containing 20 per cent. of ionium oxide. A negative result was also obtained by Exner

[1] Paneth and Hevesy, *Physikal Z.*, 1914, **15**, 797.

[2] See also Klemensiswicz, *Compt. rend.*, 1914, **158**, 1889.

[3] Lachs, Nadratowska, and Wertenstein, *Ber. Warschauer wiss. Ges.*, 1916, **9**, 652; Bridgman, *Proc. Nat. Acad. Sci. Amer.*, 1919, **5**, 351.

[4] Russell and Rossi, *Proc. Roy. Soc.*, 1912, A, **87**, 478.

and Haschek.[1] Soddy and Hyman,[2] on examining the spectra of ordinary lead and thorite lead, found them in complete agreement both as regards wave-lengths and intensity of the lines, with the exception of a line at 4760·1 A.U., which was much stronger in the ordinary lead spectrum than in the photographs of the thorite lead spectrum. Hönigschmid and Horovitz[3] as well as Merton[4] also found the spectra of common lead and lead from radioactive sources to be identical within the limits of experimental error.

These results seemed to establish the spectral identity of isotopes; and they certainly prove that so far as general character is concerned, two isotopic elements emit the same kind of spectrum. Recent work with instruments of higher dispersive power has, however, led to another conclusion. Aronberg,[5] using a Michelson 10-inch grating, observed in the sixth order spectrum a difference between the spectrum of ordinary lead (atomic weight=207·20) and that of lead from radioactive sources (atomic weight=206·318). The line which in the ordinary lead spectrum occurs at 4058 A.U. is found to be shifted by 0·0044 A.U. in the specimen from radioactive sources. This result has been confirmed by Merton,[6] using a Fabry and Perot etalon for increasing the dispersion.

Other evidence has been brought forward to prove that the optical spectra of isotopes are not necessarily identical; but the discussion of it is too lengthy for this place; and the original papers must be consulted for further information.[7]

In the band spectra of common lead and lead from uranium ore, Grebe and Konen[8] have detected a systematic deviation

[1] Exner and Haschek, *Sitzungsber, K. Akad. Wiss. Wien*, 1912, **121**, IIa, 1075.

[2] Soddy and Hyman, *J.*, 1914, **105**, 1042.

[3] Hönigschmid and Horovitz, *Monatsh.*, 1915, **36**, 355.

[4] Merton, *Proc. Roy. Soc.*, 1915, A, **91**, 198; Richards and Wadsworth, *J. Amer. Chem. Soc.*, 1916, **38**, 2613.

[5] Aronberg, *Astrophys. J.*, 1918, **47**, 96; see also Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, 1917, **3**, 710.

[6] Merton, *Proc. Roy. Soc.*, 1920, **96**, A, 388; 1921, **100**, A, 84.

[7] Merton, *Proc. Roy. Soc.*, 1921, **99**, A, 87; McLennan and Ainslie, *Proc. Roy. Soc.*, 1922, **102**, A, 342; McLennan, Ainslie, and Cale, *ibid.*, **102**, 33; Merton, *Nature*, 1922, **110**, 632; Ehrenfest, *ibid.*, **109**, 745; Bohr, *ibid.*, 746; Nicholson, *ibid.*, 1922, **110**, 37; Nagaoka, Sugiura, and Mishima, *ibid.*, 1924, **113**, 459; Nagaoka and Sugiura, *ibid.*, 534; Perrette, *Compt. rend.*, 1925, **180**, 1589; Jenkins, *Nature*, 1926, **117**, 893.

[8] Grebe and Konen, *Physikal. Z.*, 1921, **22**, 546.

between the positions of certain lines lying between 4257·690 A.U. and 4251·458 A.U. In the case of eighteen lines, it was found that the wave-length for ordinary lead was longer by 0·055 A.U. than that of the corresponding line in the spectrum of uranium lead. It is suggested that the band spectrum takes its rise in diatomic molecules of lead; and the figures calculated on this assumption belong to the same order as those actually observed. The band spectrum of boron oxide has been found by Mulliken [1] to be complex, being built up by the superposition of two different spectra each of which is attributed to one of the boron isotopes. Further details are given in Chapter XX.

Infra-red Spectra.—Imes [2] observed that the infra-red band of hydrogen chloride which appears at 1·76 is attended by satellites; and it has been suggested by Loomis [3] that these satellites could be attributed to isotopy in chlorine.

8. *Radioactive Indicators*

When a minute trace of a radioactive material is added to some of its non-active isotope, the mixture behaves experimentally in all respects as though it were homogeneous. Thereafter, no normal physical or chemical process is capable of altering the composition of the mixture; and whatever fate befalls the inactive isotope will overtake also the radioactive constituent. Now radioactive analysis can detect traces of active elements which are millions of times too small to be discovered by any other method; and by using the electroscope, the presence of the active material can always be proved. But this implies that a corresponding quantity of the inactive isotope must also be there, even though its concentration is far too small to allow it to be detected by any of the usual tests. The radioactive material thus acts as an indicator to show that some of the inactive isotope is present; and if the relative proportions of active and inactive material in the original mixture are known, the electroscopic estimation of the radioactive substance gives at once the quantity of the non-radioactive isotope which is present in the specimen examined. One or two examples

[1] Mulliken, *Nature*, 1924, **113**, 423, 489.

[2] Imes, *Astrophys. J.*, 1919, **50**, 251.

[3] Loomis, *Nature*, 1920, **106**, 179; *Astrophys. J.*, 1920, **52**, 248; Kratzer, *Z. Physik*, 1920, **3**, 460.

of the employment of this method [1] in practice may be given here.

Solubility Determination.—By mixing lead with radium-D, the solubility of lead salts was estimated in some cases by evaporating the solution to dryness and determining the activity of the residue. In this way the solubility of lead chromate in water at 25° C. was found to be 0·012 mgr. per litre; and of lead sulphide 0·3 mgr. per litre.[2]

Diffusion.—The rate of diffusion of lead at 340° C. was determined by mixing it with thorium-B and allowing the mixture to diffuse into a mass of inactive lead.[3]

Phenomena at Boundary Surfaces.—According to current theories, when a solid is placed in contact with its saturated solution, a continual exchange of molecules takes place between liquid and solid all along the boundary surface. This phenomenon has been brought within the scope of experimental investigation by the use of a radioactive indicator.[4] Crystals of lead chloride were impregnated with thorium-B and placed in contact with a saturated solution of ordinary lead chloride. From an estimation of the radioactivity of the solution at fixed intervals, it was possible to measure the rate at which lead was passing from the solid to the liquid; and thus the rate of exchange is experimentally determined. The phenomena of dissolution of solids in liquids when the solid layer is of molecular dimensions have also been investigated by analogous methods.[5]

Intramolecular Exchanges.—The difference between ionic and non-ionic phenomena has been demonstrated in the following way.[6] When activated lead nitrate and normal lead chloride are dissolved in molecular proportions in boiling pyridine, the lead in the lead chloride which crystallises out is found to be half as active as the activated lead of the original lead nitrate. This proves that in the case of these ionisable salts, there is an

[1] For a general survey of the field, see Paneth, *Z. angew. Chem.*, 1922, **35**, 549; *Radio-elements as Indicators*, (1928).

[2] Paneth and Hevesy, *Monatsh.*, 1913, **34**, 1393.

[3] Groh and Hevesy, *Ann. Physik*, 1920 (IV), **63**, 85; 1921, **65**, 216; see also Hevesy, *Z. Physik*, 1920, **2**, 148.

[4] Hevesy, *Physikal. Z.*, 1915, **16**, 52.

[5] Hevesy and Rona, *Z. Physikal. Chem.*, 1915, **89**, 294.

[6] Hevesy and Zechmeister, *Ber.*, 1920, **53** (B), 410; *Z. Elektrochem.*, 1920, 26, 151.

exchange of lead atoms in solution. But when the activated lead nitrate is mixed with non-ionising organic lead derivatives such as lead tetraphenyl, no such exchange of lead atoms is observed.

An interesting point arises in connection with lead ions of different valency. When acetates of inactive divalent and activated quadrivalent lead were crystallised together from glacial acetic acid, it was found that the activity distributes itself between the two salts. Since the ions differ from each other only in that the quadrivalent ion has two more electrons than the divalent one, this result points to a free exchange of electrons in the solution.

Adsorption Phenomena.—By means of radioactive indicators it is possible to measure the area of the adsorbing surfaces of powdered crystals.[1]

The Detection of Unweighable Quantities.—By mixing an active element with its inactive isotope unweighably minute quantities of the inactive material can be detected by using the electroscope to trace the active constituent of the mixture.[2]

The Discovery of New Compounds.—The possibility of obtaining bismuth hydride was first established by the preparation * of minute traces of the radioactive hydride of the isotopic thorium-C, which was then detected by means of the electroscope. Polonium † hydride is known only through its radioactive properties.

Biochemical Applications.—The assimilation of lead by living plants has been investigated by activating the lead with thorium-B and following the material in its progress by radioactivity measurements.[3]

9. *Conclusion*

Before closing this chapter, some account must be given of the bearing of the isotopic theory upon the general question of the elements. It is not claiming too much to state that the isotopes furnish us with a means of defining the difference

[1] Paneth, *Z. Elektrochem.*, 1922, **28**, 113.
[2] Paneth, *Z. angew. Chem.*, 1922, **35**, 549.
* See Chapter XVII.
† Polonium is a synonym for radium-F.
[3] Hevesy, *Biochem. J.*, 1923, **17**, 439.

between one element and another to a degree which, twenty years ago, might have been thought impossible. Until the discovery of isotopy, it was assumed by the majority of chemists that chemical analysis did actually segregate matter into homogeneous classes if it were carried far enough; and those who held Crookes' ideas on the possibility of meta-elements were regarded as somewhat eccentric. It is true that in the field to which Crookes originally applied the meta-element view—the rare earths—the conception has not been substantiated; but the isotopes are exactly in agreement with the meta-element definition.

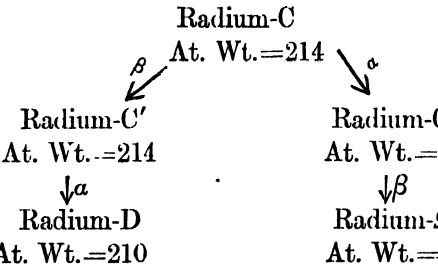
It is now known that chemical methods of separation are, at the best, superficial. To use a crude analogy, the local surveyor may say that three houses are absolutely identical in every way; but when the local registrar is called in he will be able to state that one house is inhabited by a bachelor, the next one by an old maid, whilst the third contains a family of seven. Chemical analysis is represented by the surveyor, whilst radioactivity measurements play the part of the registrar and reveal differences in the internal economy of the houses.

According to Soddy,[1] it may now be taken as proved that so long as the net charge on the atomic nucleus is the same, the element will showt he definite chemical and physico-chemical character associated with one or other of the ninety-two places of the Periodic Table, quite independently of the nature and constitution of the nucleus. Its light spectrum and its X-ray spectrum will be identical with that of any other element fulfilling the same conditions of net charge. But since the net charge on the nucleus depends not on the absolute but only on the relative numbers of positive and negative charges associated with it, it is clear that two atoms may possess identical chemical properties and yet differ in mass. For example, one atom may contain three negative and five positive charges; whilst another contains one negative and three positive charges. In both cases the net charge will be two positive; and the chemical characters of the two atoms will be identical; but their masses will be different, since mass appears to be a function of the total number of positive charges present.

Even this does not entirely state the case; for it is possible

[1] Soddy, *Annual Reports*, 1916, **13**, 245.

that two atoms may contain the same net nuclear charge and the same absolute number of opposite charges, and yet these two atoms may differ from one another in the structure of their nuclei. Among the radio-elements cases of this kind actually occur. For example, in the following scheme, it will be seen that radium-C may disintegrate in either of two ways :



In the one case, an α-particle is ejected first and then a β-ray is subsequently thrown off; in the second case, the order is inverted and the expulsion of the β-ray precedes that of the α-particle. The two end-products obviously have resulted from the same substance, radium-C, by the loss of exactly the same number of charges in each case; but they are not necessarily identical. In fact, it seems probable that radium-D and radium-Ω'' are not the same material, though definite proof is not yet available.

This example illustrates what might be called a finer degree of isotopy, since the two elements are alike in chemical character, spectrum, and atomic mass, and yet, as the difference in radioactivity shows, they are not identical.

Mass and chemical properties alone, then, cannot be taken as criteria of elemental homogeneity. If we mix together equimolecular quantities of two forms of lead, one having an atomic weight of 206·4 and the other with an atomic weight of 207·7, any chemist to whom we gave the mixture for analysis would find that the element lead was present and that its atomic weight was 207·05. Thus the mixture is a "chemical" element with an atomic weight which characterises it; and it cannot be separated by chemical means into anything simpler. Yet it is none the less an artificial product, capable of variation according to the recipe employed in its manufacture.

CHAPTER VIII

THE ISOBARES

1. *The Recognition of the Isobares*

ONE of the curiosities of science is the manner in which apparently obvious inferences are temporarily overlooked; and are drawn only after some time has elapsed since that became possible. By 1914, the publications of Soddy and others had focussed attention upon the case of the isotopes. The chemical world, with more than usual alertness, had assimilated the idea that two atoms might have unequal atomic weights and nevertheless exhibit identical chemical properties. Yet, strangely enough, four years elapsed before the complementary proposition was formulated.

In 1918, Stewart [1] drew attention to the result of a β-ray change taking place in a radio-element. Since the material loses one negative charge, the net result is the increase by one unit of the positive charge in the atom and hence the atomic number of the disintegration product is one unit higher than that of the parent material. Mesothorium-1, for example, has the atomic number 88. It undergoes a β-ray change and yields mesothorium-2, with the atomic number 89; and this in turn ejects an electron and gives rise to radiothorium, with the atomic number 90. Each of these materials has the chemical properties corresponding to its atomic number. Thus mesothorium-1 is chemically indistinguishable from radium and acts as a divalent element; mesothorium-2 is isotopic with actinium and exhibits trivalency; whilst radiothorium is a quadrivalent element which is inseparable from thorium itself by any known chemical process.

Now the ejection of the β-ray electron makes no difference

[1] A. W. Stewart, *Phil. Mag.*, 1918, **36**, 326.

in the atomic weight of the atom. The electron is shot out; and the resulting ion at once picks up a negative charge from the surroundings and thus becomes again a neutral atom of exactly the same mass as before the β-ray change occurred, but with a new atomic number.

From these considerations it is obvious that in addition to the isotopes there is another possibility to be taken into account. Two atoms may possess identical atomic weights and yet have different atomic numbers and different chemical properties.† To such atoms Stewart gave the name *isobares* * (from *isos*, equal, and *baros*, weight).

The relations between isotopes and isobares can be seen at a glance from the following table:

	Atomic Weights.	Atomic Numbers.
Isotopes	Different †	Identical
Isobares	Identical	Different †

The symmetry of the arrangement is at once apparent; and it is obvious that the conception of isobares furnishes a complement to that of the isotopes.

2. *β-Ray Electrons and Ionic Charges*

This conception of isobaric atoms brings to the front a novel problem. Taking the example put forward above, the divalent element mesothorium-1 suffers a β-ray change and yields the trivalent element mesothorium-2. Now the conversion of divalent ferrous iron into trivalent ferric iron furnishes an apparent parallel to this process. In both cases, the new atom has one positive valency more than the original material. In both cases, too, the chemical behaviour of the trivalent atom is entirely different from that of its divalent parent; for ferrous iron resembles magnesium, whilst ferric iron shows analogies with aluminium in its chemical behaviour. It is not unreasonable to inquire whether the mechanism of valency-change from mesothorium-1 to mesothorium-2 is the same as that which comes into operation when ferrous iron is oxidised to ferric iron.

At Soddy's suggestion,[1] this problem had already been

* The *e* is inserted merely to avoid confusion with the barometrical term isobar; but the word is pronounced i-so-bar.

† Except in the special case of isobaric isotopes; see p. 121.

[1] Soddy, *Nature*, 1913, **92**, 399.

investigated by Fleck[1] in 1914; and Fleck's demonstration furnishes conclusive proof that the two cases are not identical but merely parallel.

An examination of the chart at the end of this volume will show that the quadrivalent element uranium-X_1 loses two β-particles and is converted into the hexavalent element uranium-2. Parallel to this we have the conversion of quadrivalent uranous salt, such as UCl_4, into the hexavalent uranyl compound UO_2Cl_2. In both cases the parent substance gains two positive charges as a net result.

Now uranium-2 is isotopic with uranium-1 and is therefore chemically inseparable from the latter. If the β-ray change and the ordinary gain of two positive charges by an atom are identical processes, then the two original substances also should be isotopic and inseparable by chemical means. In other words, a uranous salt and a salt of uranium-X_1 ought to be chemically inseparable.

		Quadrivalent.		Isotopic and Hexavalent.	
			β-ray change →		
Isotopic	*Uranous uranium*-1	UX_1		U-II	
		U''''	→ Ionic change	U-I	*Uranyl uranium*-1
	Thorium	Th			

It is not necessary to select uranium-X_1 itself as the subject of the experiment; any of the five isotopes shown in the chart at the end of this volume will do equally well; and in practice thorium was chosen, since it is easily procurable.

Great precaution had to be taken to prevent the uranous salt being converted into the uranyl derivative during the process of separation; but by the use of a special air-free apparatus this was accomplished.

The results proved that when a mixture of uranous and thorium salts was fractionally precipitated either by means of oxalic acid or by boiling off the excess of ammonium carbonate which was used to hold the salts in solution, a separation of the thorium from the uranium was obtained.

This result shows that uranous uranium and thorium are not isotopic with one another; and hence the conversion of uranium-X_1 into uranium-2 by the loss of two β-particles is merely parallel to and not identical with the change which occurs when a uranous compound is converted into a uranyl

[1] Fleck, *J.*, 1914, **100**, 247.

derivative. Soddy inferred from these results that the electrons which are ejected during β-ray changes come from the nucleus of the atom, whilst mere alterations in valency affect only the outer group of electrons; and further, that there is no interchange of electrons between the nucleus and the shell of the atom in chemical or electrochemical changes.

3. *The β-Ray Change and its Ionic Parallel*

It is worth while to examine more closely this parallelism which exists between ferrous and ferric iron on the one hand and, say, mesothorium-1 and mesothorium-2 on the other; though it must be carefully borne in mind that the two cases are *not* identical. None the less the closeness of the parallelism suggests that, although the origins of the phenomena are different, there is marked kinship between the two transmutational processes which are at work.

Mesothorium-1 and ferrous iron both exhibit properties which are shown by elements in Group II of the Periodic Table. Both form salts of the type RCl_2, RSO_4, etc. Both are convertible into a form of matter which possesses an extra positive charge—mesothorium-2 in the one case and ferric iron in the other. On the other hand, mesothorium-2 and ferric iron are both trivalent; and each of them forms salts of the type RCl_3.

The obvious difference between the two pairs lies in the fact that ferrous iron can be converted into ferric iron or *vice versâ* at will; whilst the conversion of mesothorium-1 into mesothorium-2 proceeds spontaneously and irreversibly as far as our present means go. In both cases, negative electric charges are removed from the divalent atoms; but in the one case the charge is taken from a certain part of the atomic structure, whilst in the other case it comes from a different portion of the atom.

Even the spontaneity of the β-ray change finds its parallel among certain of the non-radioactive elements. Thus when the chloride of monovalent indium is dissolved in water it is *spontaneously* converted into metallic indium and the chloride of trivalent indium—

$$3InCl = InCl_3 + 2In$$

Reduced to its essentials, this corresponds to the loss of two

negative charges from each of the monovalent indium atoms; and no external forces are required in order to bring about the change. The case of indium is by no means an isolated one; for other elements exhibit a similar behaviour.*

Yet a further parallelism between the β-ray change and the conversion of an ion into one of a higher valency may be adduced here. In several cases, elements are found to exist in monovalent and trivalent forms, or in the divalent and quadrivalent condition only, instead of forming a complete series of mono-, di-, tri-, and quadrivalent varieties. Thus thallium forms the chlorides TlCl and $TlCl_3$, but does not yield the intermediate $TlCl_2$. Similarly, germanium forms $GeCl_2$ and $GeCl_4$ but not $GeCl_3$. It may be asked why these intermediate forms are not isolated as we remove electric charges from the substances of lower valency.

An examination of the state of affairs in the case of the radio-elements may throw some light upon this point. The conversion of $GeCl_2$ into $GeCl_4$ is paralleled by two successive β-ray changes in the radio-elements; and in the following table the results of such successive changes are given. The cases have been selected in which no disturbing factor in the shape of an alternative α-ray change occurs. The figures give the average life of the elements.

Group x	$\xrightarrow[\text{change}]{\beta\text{-ray}}$	*Group* $(x+1)$	$\xrightarrow[\text{change}]{\beta\text{-ray}}$	*Group* $(x+2)$
Uranium-X_1		Uranium-X_2		Uranium-II
35·5 days		1·65 minutes		3×10^6 years
Mesothorium-1		Mesothorium-2		Radiothorium
9·67 years		8·9 hours		2·01 years
Radium-D		Radium-E		Radium-F
24 years		7·20 days		196 days

It will be seen that the intermediate product in the double β-ray change has an average life very much shorter than those of the parent or the disintegration product. If the same reasoning holds good in the case of the salts of, say, thallium, we should

* I am indebted to Prof. Smiles for calling my attention to the fact that a reaction of this type is the most general one in chemistry. It finds its parallel in organic chemistry in such reactions as the conversion of benzaldehyde into benzoic acid and benzyl alcohol by treatment with alkali.

expect to find that when monovalent thallium loses an electric charge and passes into divalent thallium, the latter substance loses a second electric charge readily and passes almost immediately into trivalent thallium, just as mesothorium-2 soon breaks down to radiothorium. The parallel between the two cases is thus closer than appears at first sight.

The question of isobarism may be considered from another point of view. Hittorf observed from E.M.F. measurements that chromium [1] existed in no less than three forms; * and he stated that "*in the three conditions the metal exhibits differences of properties such as have been found only in different metals.*"

Again, just as two isotopes can be mixed in order to produce a new substance having an atomic weight dependent upon the proportions in which the two components are present, so two forms of chromium can co-exist and give rise to a material which has an E.M.F. intermediate between those of the two forms when alone.[2]

For the sake of clearness, it may be well to summarise the matter in a few words. It is now proved by experimental evidence that two elements having totally different chemical and radioactive properties may have the same atomic weight. This is termed isobarism. Parallel to this but *not* identical with it, is the case of an element exhibiting two or more degrees of valency. This might be termed pseudo-isobarism. Between isobarism and pseudo-isobarism there are certain resemblances which appear to point to a parallelism between the two phenomena in their ultimate origins. The origin of the resemblance will be clearer when the structure of the atom is considered.†

4. *The Complete Classification of Atoms*

It is not possible at this point to discuss the rather thorny question of defining the meaning of the word "element"; but

[1] Hittorf, *Z. physikal. Chem.*, 1898, **25**, 729; 1899, **30**, 481; 1900, **43**, 385. Compare also the cases of iron, Hittorf, *ibid.*, 1900, **43**, 385; Müller and Koenigsberger, *Physikal Z.*, 1904, **14**, 413, 797; Müller, *Z. physikal. Chem.*, 1904, **48**, 585; Finkelstein, *ibid.*, 1902, **39**, 91; cobalt and nickel, Hittorf, *ibid.*, 1900, **43**, 385.

* It is, of course, possible that these phenomena are due to a change in the state of aggregation of the metal and to oxide-film formation in the case of the passive form of chromium.

[2] Hittorf, *ibid.*, 1899, **30**, 505.

† See Chapters XII and XIII.

sufficient material is available to permit a classification of the possibilities which present themselves when two atoms are compared which differ from each other in any known respect.

By utilising his own view of isotopic atoms and Stewart's conception of the isobares, Soddy [1] has put forward what appears to be the final terminology in this branch of the subject. When two atoms have the same atomic number, they are termed isotopes; if they have different atomic numbers, they are named heterotopes. Two atoms of equal atomic weight are isobaric with one another; whilst if their atomic weights are different, they are said to be heterobaric. Using this nomenclature Soddy classifies pairs of atoms into the following four groups:

Type.	Atomic Weights.	Atomic Numbers.	Examples.
Heterobaric heterotopes	Different	Different	Lithium and chlorine
Heterobaric isotopes	Different	Same	Thorium and ionium
Isobaric heterotopes	Same	Different	Mesothorium-2 and radiothorium
Isobaric isotopes	Same	Same	Radium-D and radium-Ω''

Heterobaric heterotopes are separable from each other either by ordinary chemical analysis or by means of the mass spectrograph. In the case of heterobaric isotopes, no chemical separation is possible; but the materials can be separated in the mass spectrograph. Chemical analysis will separate isobaric heterotopes; but in this case the mass spectrograph fails. The final class—isobaric isotopes—is of special interest, since members of it cannot be separated from each other by any method known at present; and unless radioactivity is observed, there is no means even of demonstrating that the material under examination is inhomogeneous.

[1] Soddy, *J.*, 1919, **115**, 1.

CHAPTER IX

THE ANALYSIS OF POSITIVE RAYS

1. *The Original Apparatus*

In Chapter III it was pointed out that when the cathode of a Crookes tube is pierced with one or more apertures, a stream of "canal" or "positive" rays travels from the cathode in a direction opposite to that taken by the cathode rays. These positive rays are streams of the residual molecules of gas in the tube which have acquired a positive charge. Like the particles which make up the cathode stream, they can be deflected from their normal straight paths by the action of either magnetic or electric fields; and the deviation in each case is proportional to the ratio between the mass of the particle and the charge which it carries. Sir J. J. Thomson utilised this property in devising a method for the recognition of the nature of these residual molecules; and his work has led to one of the most far-reaching investigations of the present time.[1]

In order to employ the positive rays as a means of qualitative gas analysis, three things are required: (1) an apparatus for generating positive rays; (2) means of applying an electric and a magnetic field to the rays; and (3) a contrivance for registering the deviations thus produced. The essentials of the apparatus are shown in the diagram below (Fig. 6). A represents part of the glass flask which acts as the Crookes tube. It has a capacity of from 1 to 2 litres. The cathode C, of special construction, is placed in the neck, D, of the flask as shown; and protrudes into an ebonite box, UV. The joints are made gas-tight with sealing-wax; and this is protected from heating effects by the water-jacket J. L and M are pieces of

[1] For a full account of the early history of the subject, see Thomson, *Rays of Positive Electricity and their Application to Chemical Analysis* (1913). Aston's *Isotopes* (1924) describes the great advances made in more recent times.

soft iron which are used as poles for the electric field. They have plain faces which are about 3 cm. long, and they stand about 1·5 mm. apart from each other. They are connected with the terminals of a battery of storage cells and in this way any required difference in potential can be maintained between them. P and Q are the poles of an electro-magnet. F is a conical glass vessel about 40 cm. long which is fastened to a camera containing the photographic plate on which the results are recorded. WV are iron plates which are interposed in order to screen the positive ray generator from the influence of the electromagnet.

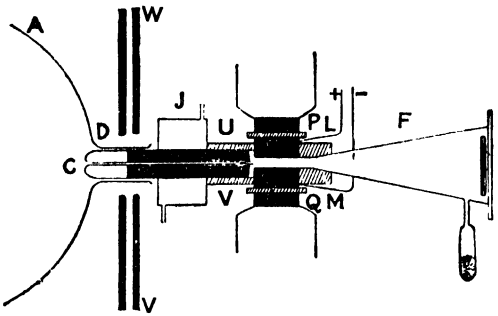


FIG. 6.

(*From Sir J. J. Thomson's "Rays of Positive Electricity."*)

The shape of the cathode, C, can be seen from the figure. The unshaded portion is made of aluminium; and the rest is composed of soft iron. Through the aperture down the centre passes a tube of copper with a bore of about 0·1 mm. and a length of about 7 cm.

One point of great importance must be mentioned. When a positively charged molecule enters the conical vessel F, it may ionise the residual gas contained therein. The result of this will be that its positively charged fellows which follow it may find awaiting them negatively charged gas molecules; and discharges may occur between the two sets. As a consequence, the incoming particles lose their charges and cease to be acted on by the electric and magnetic fields; and complications are introduced. To avoid this, the pressure in the vessel F is kept low by absorbing the gas by means of charcoal and liquid air; and since the leak from the generating flask is small—on account of the narrowness of the connecting tube in the cathode—it is possible to maintain a difference in pressure between the generator A and the receiver F.

2. *The Theory of the Parabola Method*

If a residual molecule of gas becomes charged in the vicinity of the anode of the Crookes tube which forms part of the positive ray apparatus, it will be driven towards the cathode by the electrical forces in the Crookes tube; and in this process it will acquire an energy which may be represented by $D \times e$, where D is the difference of potential between the electrodes and e is the charge on the particle. The velocity of the particle when it reaches the cathode will therefore be v in the equation—

$$v^2 = 2D \times \frac{e}{m}$$

when m is the mass of the particle in question.

This particular value of v represents a maximum velocity; for if the particle becomes charged at a point nearer the cathode, the driving force will have a shorter time to work upon it, and hence its velocity will be lower than if it started in close proximity to the anode.

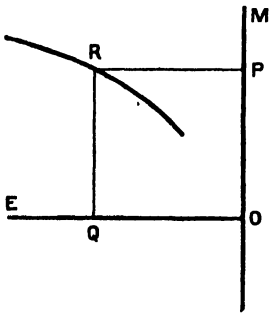


Fig. 7.

Now if neither the electro-magnet nor the static electrical field be in operation, the particle will pass through the cathode tube unaffected and will strike a point on the photographic plate directly opposite to the cathode aperture. Let this point be represented by O in Fig. 7.

The magnetic field may now be applied, which tends to deviate the next particle from its straight path in the direction of M in the figure. Instead of striking the plate at O, the new particle will fall at, say, the point P.

If now the magnetic field be switched off and the electric field is brought into operation instead, the deviation in this case will be at right angles to that produced by the magnetic field; and a particle under its influence will be deflected from O in the direction of E. Suppose that it strikes the plate at Q.

Obviously, if both fields are in operation at the same time, the particle will be deflected towards M and towards E simultaneously; and it will strike the plate at the point R. It is

now necessary to determine the position of R in terms of the forces in operation.

Without going into details [1] it may be said that if M be the magnetic field, the particle will be deflected through a distance $k_1 \cdot \frac{M \cdot e}{mv}$, where k_1 is a constant depending on the apparatus; and if E be the electric field, the deviation due to it will be measured by $k_2 \cdot \frac{E \cdot e}{mv^2}$. Or, in other words, calling the electric deflection x and the magnetic one y, we have

$$\text{Magnetic deflection} = OP = QR = k_1 \frac{M \cdot e}{mv} = y$$

$$\text{Electric deflection} = OQ = k_2 \cdot \frac{E \cdot e}{mv^2} = x$$

From this it follows that $$y/x = \left(\frac{k_1 M}{k_2 E}\right) v$$

and $$y^2/x = \left(\frac{k_1^2 M^2}{k_2 E}\right) \frac{e}{m}$$

Now if the magnetic and electric fields are not varied, it is clear that all the quantities within the brackets in the last two expressions are constant; and hence y/x forms a measure of the velocity of the deflected particles whilst y^2/x gives the ratio of the charge to the mass of a particle.

So far, consideration has been confined to a single particle; and the reasoning holds good for all identical particles, so that all such particles would strike the plate at the point R. In actual practice, however, the positive ray is made up of a series of particles which may be travelling at different velocities. The expression y/x will have a different value for each particle; but if the particles all have the same ratio of charge to mass, then the expression y^2/x will be constant for the whole series. In other words, these particles will strike the plate at a series of points which will lie on some curve which can be expressed by $y^2/x =$ constant. This curve is obviously a parabola.

A concrete example will make the point clear. Imagine that one particle is a helium atom and that another is an atom

[1] See Thomson, *Rays of Positive Electricity*, p. 7 (1913).

of argon, and that each carries a unit charge. Then the helium atom will have a ratio of mass to charge equal to 4 : 1, whilst the argon atom will have the ratio 40 : 1. Thus the helium atom will strike the plate somewhere on a curve represented by $y^2/x = k/4$; and the argon atom will strike the plate somewhere on a curve for which $y^2/x = k/40$. Thus the two atoms will be sifted away from each other on the plate. Further, if a stream of helium atoms be moving at different velocities in the ray, they will distribute themselves along the parabola $y^2/x = k/4$; and a similar stream of argon atoms will distribute themselves over the parabola $y^2/x = k/40$.

As will be seen in the next section, from the dimensions of the parabolas it is easy to calculate the ratio of the charge to the mass for those molecules which leave traces upon the photographic plate.

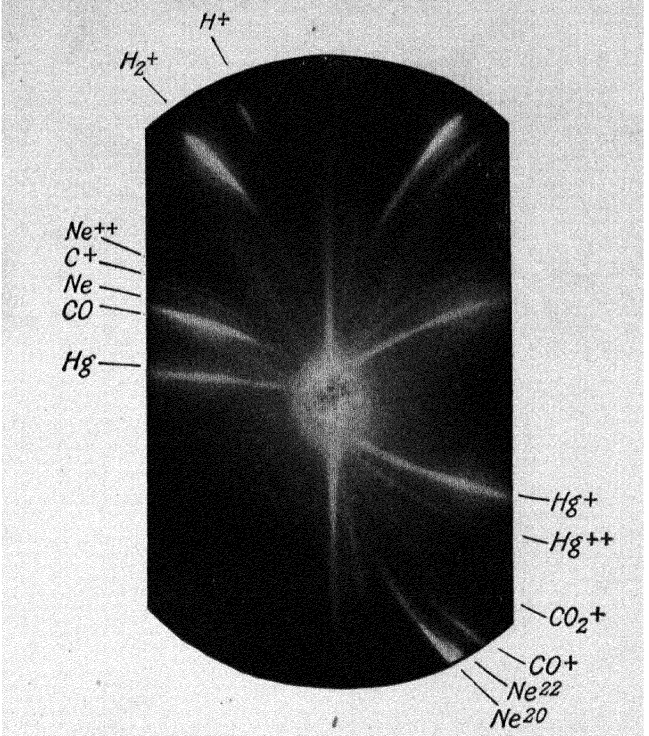
3. *The Interpretation of the Photographs*

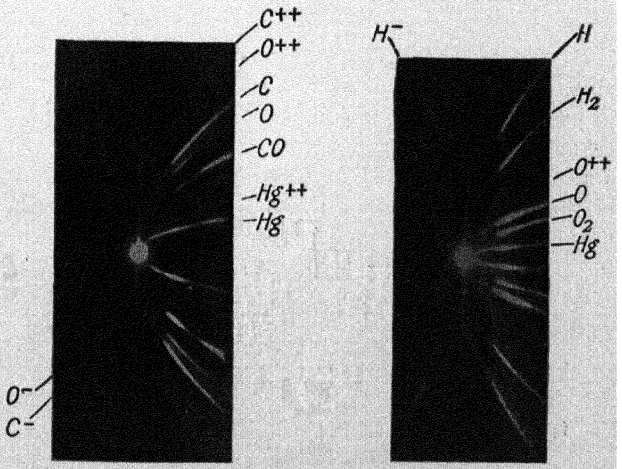
The illustrations (Plate III) give some idea of the results obtained by the use of Thomson's apparatus.

In the first place, all the photographs contain a bright spot at the apex of the parabola. This spot is the point of impact of the undeviated rays which pass when the electric and magnetic fields are not in operation. Secondly, it will be seen that in some of the photographs two branches of the parabolas are shown, one above and the other below the apex. These two branches are produced by taking two separate exposures in both of which the electric field is kept constant: in the one exposure the magnetic field operates in one direction; whilst in the second exposure it is reversed: so that the particles are diverted in opposite directions (up the plate in one case and down it in the second instance). The parabolic form of the curves is easily recognisable in the illustrations. It must be strongly emphasised that these tracks are *not* formed by the particles grazing along the plate; but that they represent a series of "bullet-marks" made by particles striking the plate from above, the separate "marks" being so close together that they merge into lines.

It will be noticed that some of the parabolas stop short and are not continued to the apex. The reason for this is obvious. In order that any particle should strike the plate in close proximity to the apex, the amount of deviation undergone

PLATE III.





POSITIVE RAY PARABOLAS

From Aston's 'Isotopes' (Edward Arnold & Co.)

by it would need to be small; and hence its velocity would need to be very great. But there is a limit to the velocity of the particles owing to the limited difference in potential between the electrodes of the Crookes tube: and thus it comes about that no traces are found of particles travelling with a velocity higher than a certain maximum. This maximum velocity is sufficient to bring them within a certain distance of the apex, but it is not sufficient to over-step this point; so that no particles strike the plate in the neighbourhood of the apex.

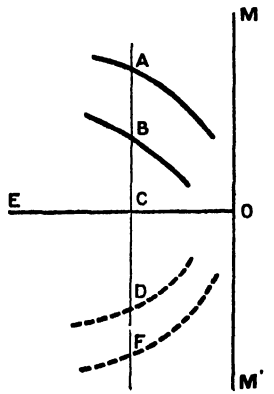


FIG. 8.

The method of measuring the plates can be seen from Fig. 8. Draw any line AF parallel to OM, cutting the two parabolas at A, B, D, and F and meeting the line OE at C. The value of y_1 (for the outermost parabola) is equal to CA; the value y^2 (for the innermost parabola) is equal to CB. In both cases the value of x is the same, being equal to OC. Now from the equations in the last section the value of the fraction $\frac{\text{charge}}{\text{mass}}$ for any particle is given by y^2/kx. Therefore, if m_1 and e_1 be the mass and charge for particles on the outermost parabola and m_2 and e_2 be the corresponding factors for particles on the second parabola, we have—

$$AC^2 \div BC^2 = y_1^2 \div y_2^2 = \frac{y_1^2}{kx} \div \frac{y_2^2}{kx} = \frac{e_1}{m_1} \div \frac{e_2}{m_2} = \frac{m_2 e_1}{m_1 e_2}$$

and if $e_1 = e_2$ then $\dfrac{AC^2}{BC^2} = \dfrac{m_2}{m_1}$

Thus if all the particles carry the same charge, the ratio of the masses of the two sets of particles is given by the ratio $AC^2 : BC^2$, or from the more easily measurable ratio $AF^2 : BD^2$, since $AF = 2AC$ and $BD = 2BC$. In actual practice it is found that this condition is fulfilled in most cases; and when any deviation occurs owing to a particle carrying more than one charge the matter is not serious, for the number of charges carried by any particle is always small.

The following table [1] gives an idea of the manner in which the results obtained from the photographs are interpreted. The first column gives the square of the distance y, of the different parabolas from the axis OE, measured along a common ordinate. The second column gives the ratio of mass to charge, assuming that all the particles carry the same charge. The third column gives an interpretation of this when modified by the assumption of varying charges.

y^2.	m/e.	Probable Cause of Line.	
53·3	200	Hg+	Mercury atom with single charge
106·1	100	Hg++	Mercury atom with two charges
153·8	67	Hg+++	Mercury atom with three charges
237·2	44	CO_2+	Molecule of carbon dioxide with single charge
272·3	39	A+	Argon atom with single charge
376·4	28	N_2+	Nitrogen molecule with single charge
*533·6	20	Ne+	Neon atom with single charge
655·4	15·9	O+	Oxygen atom with single charge
761·8	14	N+	Nitrogen atom with single charge
900·0	12	C+	Carbon atom with single charge
1498·0	7	N++	Nitrogen atom with two charges

The gas under examination in this case is air contaminated with mercury vapour from the pump; and hence the heaviest atom will be the mercury atom with a mass of 200. It is therefore reasonable to assume that the parabola of smallest diameter has been produced by mercury atoms each carrying unit charge, since this case corresponds to the minimum deviation of the particles by the magneto-electric fields. As a basis, then, it is postulated that when $y^2=53{\cdot}3$, the ratio $m/e=200$, as shown in the second column of the table; and the interpretation is given in the third column.

Take the next parabola, for which $y^2=106{\cdot}1$. It was shown above that

$$\frac{y_1^2}{y_2^2} = \frac{m_2 e_1}{m_1 e_2}$$

Putting $y_1^2=53{\cdot}3$, and $m_1/e_1=200$, and $y_2^2=106{\cdot}1$, it is found that the value of $m_2/e_2=100$ approximately. Hence we have to identify a particle with a ratio of mass to charge equal to 100. This would represent an element of atomic weight of 100 with

[1] Crowther, *Molecular Physics*, p. 52 (1914).

a single charge on the atom or an element of atomic weight of 200 with two charges on the atom. It is therefore necessary to choose between the probability that the line is produced by a mercury atom carrying two charges or by an atom of, say, ruthenium, with one charge. Obviously the mercury hypothesis is the more probable one. Then again, in the case of the third line, the atomic weight of the element must be approximately 67 or 134 or 201. Neither zinc nor caesium is likely to be present under the experimental conditions, so it is assumed that the " 67 " line is due to an atom of mercury carrying three charges.

The only point about which there might be a doubt in the above interpretation is in the case marked with an asterisk; for the value 20 might be obtained either from a neon atom with one charge or from an argon atom with two charges. The chance of its being due to a mercury atom with ten charges is ruled out by the fact that it is rare that mercury carries even as many as eight charges, to judge from the general run of results.

From the above it will be clear that in the stream of positive rays there may be: (1) positively electrified atoms with one charge; (2) positively electrified molecules with one charge; and (3) positively electrified atoms with multiple charges. In addition to these, tracks * may be found due to negatively electrified atoms and molecules which have become neutralised on passing through the cathode and have picked up a cathode particle *en route*.[1] From the chemical point of view it is interesting to note that among the carbon compounds the negatively charged molecule is not detected in the case of methane, carbon dioxide, phosgene, etc., wherein carbon is linked only to other elements; but negatively charged molecules are found when the compound examined contains two directly linked carbon atoms, as in the cases of acetylene, ethylene, or ethane. In the examination of benzene vapour, negatively electrified triplets of carbon atoms were observed, and there seems to be a possibility that quartets may have been present.

* See Plate III, where a hydrogen parabola of this type is illustrated.

[1] Thomson, *Proc. Roy. Soc.*, 1914, A, **89**, 1.

4. *The Mass Spectrograph*

Though the work done by the original parabola-producing apparatus was of the first importance, the machine was found in practice to be incapable of yielding refined measurements; and it has now been entirely superseded by the new mass spectrograph, designed by Aston on a fresh principle. Only the main features of this instrument need be dealt with here.[1]

In the mass spectrograph, as in the older apparatus, the positive ray is allowed to pass through a pierced cathode. It then traverses two minute slits, S_1 and S_2, as shown in Fig. 9.

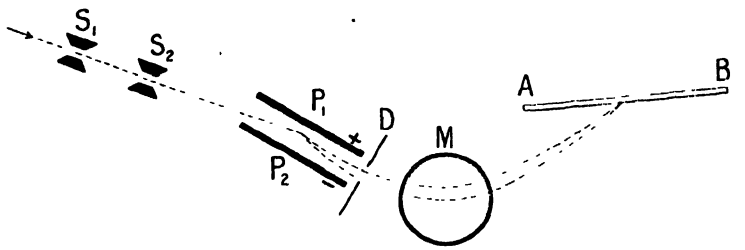
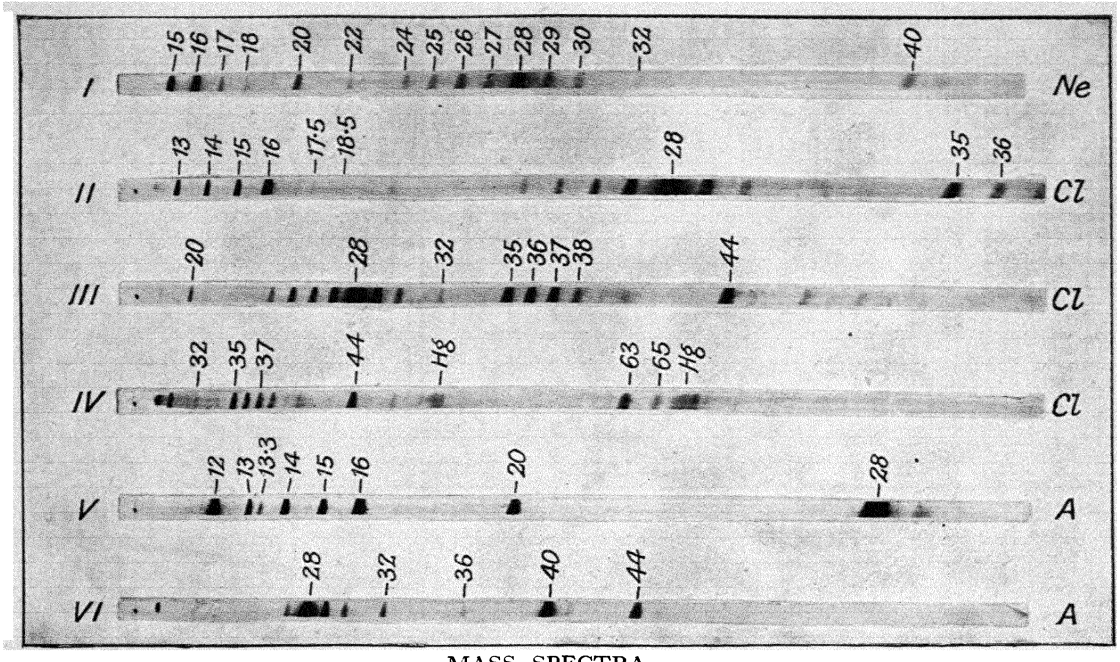


FIG 9.

It emerges from the slits in a thin, ribbon-like form, and then passes between metal plates, P_1 and P_2, which are oppositely charged with electricity. Since the gas particles in the stream are positively charged, they are diverted towards the negatively charged plate, P_1, and away from the positively charged plate, P_2, as shown in the diagram. If the electrical field be constant, the deflection of any particle from its original straight path will be proportional to e/mv^2, when e is the charge on the particle, and m and v are its mass and velocity respectively. Put in another form, this means that the deflection suffered by any given particle increases with the charge on the particle and diminishes in proportion to the product of the mass and velocity of the particle.

It was already mentioned in connection with the parabola instrument that particles emerge from the pierced cathode at different velocities; and they will therefore suffer different deflections by the plates P_1 and P_2. Thus by the action of the

[1] For a full account of the instrument, see Aston, *Isotopes*, Chapter V (1924). For the theory underlying the action of the machine, see Aston and Fowler, *Phil. Mag.*, 1922, **43**, 514.



MASS SPECTRA

From Aston's 'Isotopes' (Edward Arnold & Co.)

plates, the ribbon is spread out into a " spectrum " the dispersion of which is governed by the values of e/mv^2 for the various particles in the stream.

The problem which Aston set himelf to solve was how to bring to a focus all the particles of the same mass which exist in the stream even though their velocities are different. By this means accuracy of measurement would be increased, and, further, gas-traces which were spread over a parabola in the older instrument would in the new one be brought to a single small area on the photographic plate, and would therefore produce a more concentrated effect upon the film.

After leaving the plates P_1 and P_2, the stream of particles passes through a slit in a movable diaphragm, D, which permits a selection to be made of any particular region of the stream's " spectrum." Thereafter, the stream passes between the poles of a large electromagnet which is indicated by the circle M on the diagram. The direction of the magnetic field is chosen so that the deflection produced by it on the particles is opposite to that already induced by the electrical field at P_1P_2; and thus the stream of particles is now bent back again as shown in the diagram. As has already been seen in the case of the parabola instrument, the magnetic deflection varies directly with the fraction e/mv; so that by balancing the action of the electrical field with that of a certain magnetic field it is possible to focus on one strip of the photographic plate, AB, all particles selected by the slits and having the same value for e/m. Further, the position of the plate can be so adjusted that the foci of streams of particles with different values of e/m will all lie on the surface of the film and give sharp impressions.

The experience gained in the earlier experiments led Aston [1] to devise an improved type of mass-spectrograph which has an accuracy almost five times as great as that of the original design. The photographed spectrum is nearly 16 cm. in length; and for a change of 1 per cent. in the mass of the particles the dispersion is from 3 mm. to 1·5 mm. The instrument yields results accurate to 1 part in 10,000, a refinement which brings the mass of the electron into the problem.

Some photographs taken with the older form of mass-spectrograph are shown in Plate IV.

[1] Aston, *Proc. Roy. Soc.*, 1927 (A), **115**, 487; see also Costa, *Ann. Physique*, 1925, **4**, 425.

5. *The Hot-Anode Apparatus*

The normal form of mass spectrograph was devised for the examination of easily-vaporised materials; but it naturally would fail in those cases in which positive particles are not produced owing to the low volatility of the substance under investigation. This difficulty is overcome in an apparatus devised by Dempster[1] on a principle which may be briefly described.

If a series of positively-charged particles of different masses be allowed to fall through a definite potential difference, they form a stream which can be dispersed according to their masses by means of a magnet alone and without the application of any electrical field. If the stream is bent into a semicircular path by means of a magnetic field, then the following relation holds good:

$$\frac{e}{m} = \frac{2P}{H^2r^2}$$

in which e/m is the ratio of charge to mass on a particle, H is the strength of the magnetic field, r is the radius of curvature of the path, and P is the potential difference.

In Dempster's instrument, charged particles are generated at a source and allowed to fall through a definite potential difference. By means of a slit, a portion of the stream of particles is segregated from the rest and forced by the action of a magnetic field to pursue a semicircular path. In the course of this trajectory, they encounter a second slit; and those which pass through it are allowed to fall on a plate connected with an electrometer. In practice, the magnetic field, H, is kept constant; and the results are obtained by plotting the potential, P, against the ionic current indicated by the electrometer, since under the experimental conditions this current gives a measure of e/m.

This instrument is not so refined as Aston's mass spectrograph; for its accuracy seems to be about 1 part in 100. But since a hot anode is used to produce the positive particles, it has distinct advantages in certain fields, for by this means positively charged ions can be obtained even from fairly refractory metals.

The following figure (Fig. 10) shows the manner of plotting

[1] Dempster, *Phys. Rev.*, 1918, **11**, 316.

the results obtained in the case of zinc. Since the four peaks of the curve occur at the abscissæ 64, 66, 68, and 70, it is to be inferred that zinc has four isotopes corresponding to these atomic weights. The proportions of the isotopes in the metal can be estimated from the ordinates of the peaks. It may be pointed out that if the weight of the isotope corresponding to one peak is known,* the remainder can be identified, since the product of atomic weight and voltage is a constant; and the voltage for each peak has been determined experimentally. Thus if we know that a voltage of 966 corresponds to the isotope of atomic weight 64, then the voltage peak at 936·5 must correspond to an atomic weight of $(966 \times 64) \div 936{\cdot}5$, that is 66; and hence the graduation of the lower scale in atomic weights is simple enough.

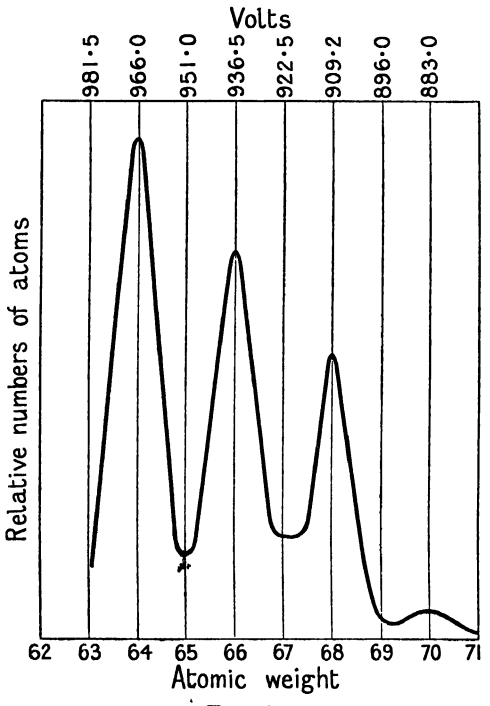


FIG. 10.

The heated anode is applicable to the mass spectrograph also and has been employed by Aston with success.[1]

* In case of doubt, a known peak may be used as a standard by introducing some of an element of ascertained atomic weight into the material placed on the hot anode. For instance, in the case of zinc, some calcium was used; and from the position of known peak of Ca^{40}, the zinc ordinates were reduced to standard.

[1] See Aston, *Isotopes*, Chapter VII (1924).

CHAPTER X

THE RESULTS OBTAINED WITH THE MASS SPECTROGRAPH

1. *Isotopy and Isobarism among the Non-radioactive Elements*

As has been mentioned on an earlier page, the positive ray method of analysis was responsible for the earliest detection of isotopes; since the discovery of the two forms of neon by the parabola method pre-dates the recognition of isotopy in the radioactive elements. That observation, however, remained isolated for years, while the complete theory of isotopic atoms was being built up from chemical evidence; and it was only when the chemistry of the isotopes had been fully worked out that the physical side again came into prominence and extended our ideas of isotopy and isobarism into the field of the non-radioactive elements where the electroscope could give no assistance. Once Aston's mass spectrograph came into play, our knowledge of the composition of the ordinary elements extended by leaps and bounds; and the advance of the subject since 1919 has been marked by a rapidity almost without parallel in the history of chemistry. It is now known that isotopy is not confined to a restricted group of elements with peculiar properties of their own; but is, in fact, a general property of matter which includes in its scope the majority of the elemental forms.

By 1924, a complete series of forty elements had been examined, starting with hydrogen and extending up to zirconium; and in addition to this, sixteen other elements of higher atomic numbers had been investigated. Taking the Periodic Table, with the exception of gold and its successors of higher atomic weight, Aston's work supplemented by that of Dempster furnished a complete knowledge of the state of affairs in the Zero Group, Group I, Group II, Group III, Group IV, Group V$_B$, Group VI$_B$, and Group VII—a marvellous achievement for so short a period.

A general idea of the results can be obtained from the 1929

Table of Atomic Weights.[1] Out of fifty-six elements examined, no fewer than twenty-four are apparently homogeneous, since only a single type of atom has been detected in each of them. Sixteen elements contain mixtures of two isotopes. Six elements are conglomerations of three isotopic forms. Zirconium and neodymium have four isotopes each. Zinc, selenium, krypton, and cadmium are built up from six isotopic varieties. Mercury has seven isotopes; germanium has eight; and xenon has nine. Tin is the most complex of all, since its elemental mixture has been found to contain no fewer than eleven different kinds of atom.

Turning now to the isobares, the results are given in the following table in which the figures represent the weights of the atoms:

40	Argon	Calcium
65	Copper	Zinc
69	Zinc	Gallium
70	Zinc	Germanium
71	Gallium	Germanium
74	Germanium	Selenium
75	Germanium	Arsenic
76	Germanium	Selenium
77	Germanium	Selenium
78	Selenium	Krypton
80	Selenium	Krypton
82	Selenium	Krypton
86	Krypton	Strontium
112	Cadmium	Tin
114	Cadmium	Tin
115	Indium	Tin
116	Cadmium	Tin
121	Tin	Antimony
124	Tin	Xenon
126	Tellurium	Xenon
128	Tellurium	Xenon
130	Tellurium	Xenon
142	Cerium	Praseodymium

From this table it appears that among the fifty-six elements examined, no fewer than twenty-three cases of isobarism have been detected: a proportion which indicates clearly how common the isobares may be among the non-radioactive elements. The elements germanium, selenium, and tin each yield six cases of isobarism; xenon and krypton are members of four pairs; zinc, cadmium, and tellurium are triple isobares; whilst gallium is isobaric with zinc and germanium.

It should be remembered that this does not necessarily

[1] *Ann. Reports*, 1928, **25**, 360.

include all the cases of isobarism which are possible ; for among the non-radioactive elements there may be cases like that of radium-D and radium-Ω'' which have the same atomic weight and are therefore inseparable by the mass-spectrograph.

The argon-calcium isobares are of interest for two reasons. In the first place, this pair was the first example of isobarism detected by the mass spectrograph ; and in the second place, the pair is unique in that it consists of the two preponderant isotopes of its constituent elements. These two isotopic forms, as Aston points out, are actually the most abundant inert gas and the most abundant form of alkaline earth metal which exist terrestrially.

2. *Mass Numbers and the Packing Effect*

The results summarised in the foregoing section are in themselves of fundamental importance ; but the mass spectrograph has brought to light something which exceeds even these in its theoretical interest. The point will best be understood if we follow the historical development of the subject.

Let us first consider the results obtained by Aston with his first mass spectrograph. Taking as a standard the oxygen atom with a mass of 16, and omitting hydrogen from the survey, Aston [1] found that the weights of all the atoms measured by him could be represented by round numbers, the deviation from integral figures being in most cases only one part in a thousand. This surprising discovery removed the only serious objection to a unitary theory of matter.

To make the point clear, the element chlorine may be chosen as a convenient example. The " atomic weight " of chlorine, determined by purely chemical analysis, is found to be 35·46. When the mass spectrograph is applied, this chemically homogeneous material is split up into two fractions, one of which contains atoms each weighing 35 (when the oxygen atom is taken as weighing 16), whilst the other fraction contains chlorine atoms each of which weighs 37 on the same standard. The " chemical atomic weight," therefore, is merely the average weight of two sets of particles some of which weigh 35 whilst others weigh 37 ; and the value 35·46 is not a physical constant, but is only

[1] Aston, *Isotopes*, p. 108 (1924).

a figure obtained from a fortuitous mixture of the two chlorine isotopes in proportions roughly of 3 : 1.

At this point it evidently becomes necessary to find some means of distinguishing between the isotopic forms on paper, and Aston adopted the convenient system of Mass Numbers. The chemical symbol of the element has attached to it an index corresponding to the mass of the isotope in question. For example, the chlorine isotope composed of atoms weighing 35 is represented by Cl^{35}; the isotopes of lithium are symbolised by Li^6 and Li^7 respectively; the three known forms of magnesium can be defined by Mg^{24}, Mg^{25}, and Mg^{26}. Since the index number is placed in an upper line, it runs no risk of being confused with the customary suffix which indicates the number of atoms in a molecule. Lithium oxide derived entirely from lithium atoms weighing 6 units would be expressed by $Li^6{}_2O$.

In order to appreciate the full importance of Aston's discovery of the Whole Number Rule, it is necessary to consider for a moment the state of affairs which existed before the mass spectrograph was constructed. The transfer of the atomic weight standard from hydrogen to oxygen led to a simplification of some atomic weight figures by the elimination of fractional values. On the basis of H=1, not a single element in the first Short Series had an atomic weight which could be expressed accurately in integers, whereas on the basis of O=16, no less than four elements show values which do not differ from the round numbers in the first two decimal places (C=12·00; N=14·00; O=16·00; F=19·00). A similar simplification occurred at other points in the Table.

This, so far as it went, was an improvement; but it left the majority of elements still with fractional values for their atomic weights; and so long as this state of things persisted, it was useless to look for any simple relationship among the masses of the elements. Prout's hypothesis of elements built up by the combination of hydrogen atoms was wrecked in its day by this incommensurability of the atomic weights; and so long as the "chemical atomic weight" dominated the scientific mind, it was impossible to produce any satisfying hypothesis which would represent the elementary atoms as systems built up from a common material.

In less than five years, the whole of this had passed away.

The results of the mass spectrograph seemed to have established that the masses of the atoms could be expressed by a series of integers; and thus the human mind, with its instinctive desire for simplification, found itself once more free to picture the elements as conglomerations of some protyle material which lies at the base of them all. After almost exactly a hundred years of scepticism, the ideas of Prout came again into the forefront of chemistry, and a unitary conception of matter replaced the unsatisfactory and disjointed conceptions of last century.

In view of Aston's Whole Number Rule, the difficulty of accepting Prout's Hypothesis appears at first sight to be cleared away; and it would not seem rash to assume that Prout was justified in his belief that the elements are built up by the polymerisation of hydrogen into atoms of different masses. But here again the mass spectrograph furnished a surprise. When it was applied to hydrogen, it yielded results which indicated beyond any possible doubt that the mass of the hydrogen atom was not unity but had, instead, the value 1·008. Thus Prout's Hypothesis appeared to be once more discredited: for the key-element of the whole elemental series seemed to stand completely outside the system; and the apparent simplicity, which appeared to be coming in sight, was again lost.

It was natural that a matter of such importance should be submitted to an exhaustive examination; and a new method of "bracketing" was devised for the purpose.[1] From the design of the mass spectrograph[2] it can be shown that when the magnetic field is kept constant, the position of a particle's point of impact on the photographic plate depends upon the potential applied to the plates P_1P_2 in Fig. 8, and in order to produce coincidence in the points of impact in the case of two particles of masses m_1 and m_2 the two potentials of the plates must fulfil the relation:

$$\frac{m_1}{m_2} = \frac{X_2}{X_1}$$

where X_1 and X_2 represent the respective potentials. From this it is clear that if the one mass be double that of the other, then the two particles can be brought to a common point of impact

[1] Aston, *Isotopes*, p. 70 (1924).
[2] Aston and Fowler, *Phil. Mag.*, 1922, **43**, 514.

by using a potential X for the one experiment and a potential 2X for the second particle.

In Aston's method of bracketing, a mixture of hydrogen and helium was used. If one exposure was made with X=250 volts and a second with X=500 volts, then the hydrogen molecule under the influence of 500 volts will impinge on the same spot on the plate as the helium atom under the influence of 250 volts, *provided that the mass of the helium atom is exactly twice that of the hydrogen molecule.*

As a coincidence in point of impact does not lead to a sharp photograph, three exposures were made: one with 250 volts potential, one with 500+12 volts, and a third with 500−12 volts. In this way, two hydrogen lines are obtained; and if the hydrogen molecule were exactly double the mass of the helium atom, these two lines would be equally spaced on either side of the central helium line. It has been found that this is not the case in practice. The helium line in the photographs lies much nearer to one hydrogen line than to the other, which proves that if helium has a mass 4, then the hydrogen molecule has a mass different from 2.

These results demonstrate conclusively that the mass of the helium atom (4) is less than the mass of two hydrogen molecules (4·032). On this basis, it appears as though the hydrogen atom could not be the foundation of the atomic system; and that further search might reveal some as yet undiscovered material with unitary atomic weight.

A possible escape from this apparent difficulty is to be found by assuming that when two electrical charges of opposite sign are brought sufficiently close to each other, the mass of the system is reduced. In the case of the hydrogen atom, the system consists of one proton carrying one positive charge, and one electron carrying a unit negative charge. In this system, the two charges are supposed to be comparatively far apart; and the system has a mass of 1·008. Now the helium atom's nucleus is believed to contain four protons and two electrons which are jammed together in a space so small that it is almost completely filled by the two electrons alone. Around this nucleus are placed the remaining two electrons required to make up the total of four hydrogen atomic systems. On the view just described, the electromagnetic fields of the nuclear four protons and two

electrons interfere with each other owing to the close approximation of the charged bodies; and hence the total mass of the system is diminished until instead of being 4·032 it sinks to 4·00, and thus gives the correct value for the helium atom's mass.[1]

Putting the matter generally, the suggested explanation assumes that in the nuclei of normal atoms the packing of electrons and protons is so close that the additive law of mass will not hold; and the mass of the nucleus will be less than the sum of the masses of its constituent charges.

Aston [2] pointed out that if this suggestion were adopted, the Whole Number Rule could be simply translated into a statement that the mean packing effect in all atoms is approximately constant. In his view, the Whole Number Rule, though it held good for the current experimental measurements, could not be absolutely exact, since an identical packing effect in all atoms seems improbable.

This caution on Aston's part has been fully justified by the results obtained[3] by means of the later form of mass spectrograph which yields much more accurate measurements of the atomic masses. It now appears that Aston's Whole Number Rule is merely a very accurate approximation. The true values for the masses of the atoms (on the basis O=16) are not all integers but differ from the round number in many cases by fractional amounts. For instance, the true mass of Li^6 is 6·012; the true mass of the carbon atom is 12·0036; and the true mass of Ne^{20} is 20·0004. Thus Aston's prevision has been fulfilled; and we must accept the idea that the packing effect makes its influence felt in the architecture of the atoms.

Let us now examine the numerical side of this packing question. As a standard, we choose the packing of the oxygen nucleus; and to represent deviations from this standard, we calculate what is called the *packing fraction*. The numerator of this fraction is simply the difference between the actual mass of the atom and the mass which it would have if the Whole Number Rule held good. For example, Aston found that the atom Li^7 had a mass of 7·012, instead of 7·000. The numerator

[1] See Silberstein, *Phil. Mag.*, 1915 (vi), **30**, 370; Nicholson, *ibid.*, 659; *Proc. Physical Soc.*, 1915, **27**, 217; Harkins and Wilson, *J. Amer. Chem. Soc.*, 1915, **37**, 1367, 1383, 1396; 1916, **38**, 169.

[2] Aston, *Isotopes*, p. 120 (1924).

[3] Aston, *Proc. Roy. Soc.*, 1927 (A), **115**, 487; *Nature*, 1927, **120**, 956.

of the packing fraction in this case would be 0·012. The denominator of the packing fraction is the number of protons in the nucleus, which in the case of Li^7 is obviously 7.

$$\text{Packing fraction for } Li^7 = \frac{7{\cdot}012 - 7{\cdot}000}{7{\cdot}000} = 0{\cdot}0017$$

This figure obviously represents the gain of mass per proton when the nuclear packing is altered from the standard packing of oxygen to the type of packing existing in the Li^7 atom. In view of the smallness of these packing fractions, it is convenient to multiply them by 10^4.

The following table shows the value of the packing fraction in the case of a number of elements which Aston has examined :

PACKING FRACTIONS OF CERTAIN ELEMENTS

Atom.	Packing fraction $\times 10^4$	Atomic Mass (O = 16)
H	+77·8±1·5	1·00778
He	+ 5·4±1	4·00216
*Li^6	+20·0±3	6·012
*Li^7	+17·0±3	7·012
B^{10}	+13·5±1·5	10·0135
B^{11}	+10·0±1·5	11·0110
C	+3·0±1	12·0036
N	+5·7±2	14·008
O	0 0	16·0000
F	0 0±1	19·0000
Ne^{20}	+0·2±1	20·0004
Ne^{22}	(circa) 2·2	22 0048
P	−5·6±1·5	30·9825
Cl^{35}	−4·8±1·5	34·983
A^{36}	−6·6±1·5	35·976
Cl^{37}	−5 0±1 5	36·980
A^{40}	−7·2±1	39·971
As	−8·8±1·5	74·934
Kr^{78}	−9·4±2	77·926
Br^{79}	−9·0±1·5	78·929
Kr^{80}	−9·1±2	79·926
Br^{81}	−8·6±1·5	80·926
Kr^{82}	−8·8±1·5	81·927
Kr^{83}	−8·7±1·5	82·927
Kr^{84}	−8·5±1·5	83·928
Kr^{86}	−8·2±1·5	85·929
Sn^{120}	−7·3±2	119·912
I	−5·3±2	126·932
Xe^{134}	−5·3±2	133·929
Hg^{200}	+0·8±2	200·016
Pb^{206}	+0·1±2	206·016

* Calculated from Costa's results (*Ann. Physique*, 1925, (x), **4**, 425).

It may be desirable to indicate some of the inferences which can be drawn from the data in the above table. If the packing fraction is positive, it represents the gain of mass due to the change of packing from the standard oxygen system to the system existing in the atom under examination. Such a gain implies that the protons and electrons of the nucleus are less closely grouped than in oxygen, so that their electrical fields are not subject to so much mutual interference as is found in the oxygen arrangement. A high positive packing fraction should

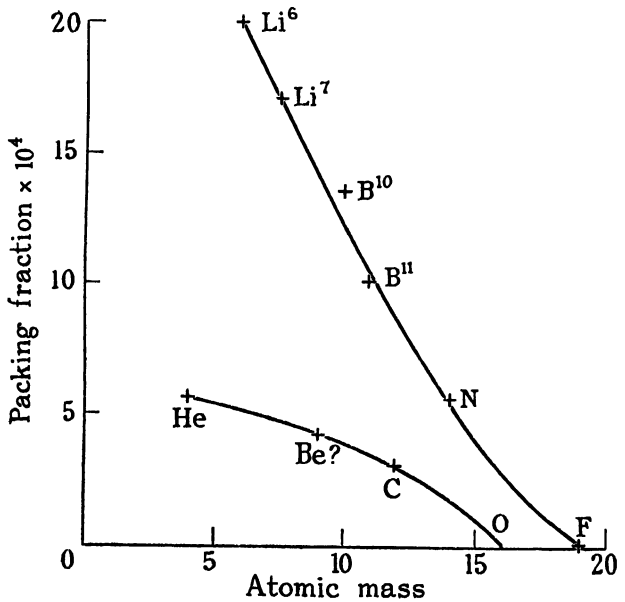


Fig. 11.

therefore indicate a loose grouping in the atomic nucleus, whilst a negative value for the packing fraction suggests a loss of mass in a tightly packed assemblage of protons and electrons.

If the packing fractions of the atoms be plotted against their mass numbers, a graph is obtained which descends from hydrogen (77·8) to bromine (—9·0) and subsequently rises and recrosses the zero line in the neighbourhood of mercury. Further inspection of this graph elicits that its earlier section is separable into two distinct lines which are shown in Fig. 11 for the elemental series between helium and neon.

From this graph it is evident that the elements with even atomic numbers belong to a different class from those with odd atomic numbers, since the two lines descend at entirely different slopes. These two lines join at a point corresponding roughly to the mass number 40 ; so that the difference between them persists over the first two (short) series of the Periodic Table. As will be seen in Chapter XII, a difference between the odd-numbered and even-numbered elements is traceable in their behaviour under the impact of α-particles.

The curve for the packing effect is obviously a non-periodic one, and bears no resemblance to the Lothar Meyer curve of atomic volumes.

3. *Some General Relationships*

In a survey of his mass spectrographic observations, Aston [1] has indicated a number of interesting relationships, some of which may be dealt with in this place.

If the first ninety natural numbers be written down and then all those are erased which represent the mass numbers of atoms detected by means of the mass spectrograph, it is found that the following figures remain: 2, 3, 5, 8, 13, 15, 17, 18, 38, 42, 43, 46, 47, 49, 50, 53, 57, 61, 62. These figures, then, correspond to blanks in the elemental mass series, since there are no known atoms having weights represented by them. So far as can be seen at present, no regularity underlies this distribution.

A rule to which no exception has been discovered is formulated by Aston as follows. In the nucleus of an atom there is never less than one electron to every two protons. This can be restated in another form, viz. if an element has an atomic number N, its lightest isotope cannot have an atomic weight of less than 2N. For example, lithium has the atomic number 3, so that the weight of its lightest isotope cannot be less than 6, and the existence of such a material as Li^5 is not to be expected.

Since the atomic number of an element depends only on the number of protons in excess of electrons in the atomic nucleus, it is evident that theoretically the possible number of isotopes of any element is infinite. The atomic number 1, for instance,

[1] Aston, *Isotopes*, p. 131 ff. (1924).

would be possessed by any material which had x electrons and $(x+1)$ protons in its nucleus; and since x may have any value, there might be an infinite number of hydrogen isotopes. Since the highest number of isotopes discovered for a single element is eleven (in the case of tin), Aston considers that there must be a higher limit to the number of possible isotopic forms.

In connection with the elements of odd atomic numbers, Aston points out that, without exception, none of these have more than two isotopes. This is correct in so far as the mass spectrograph's results go; but it is obviously not accurate in the case of the radioactive isotopes. For element No. 81 three radioactive isotopes are known in addition to thallium, which may itself be complex; whilst element No. 83 consists of four radioactive isotopes in addition to bismuth.*

An interesting point comes to light, however, when the average life of each of these elements is noted. The three radioactive isotopes of No. 81 have average lives of 6·8 minutes, 4·5 minutes, and 1·9 minutes. In the case of the four radioactive isotopes of No. 83, the figures are: 7·2 days, 3·1 minutes, 87 minutes, and 28·1 minutes. Obviously these are all extremely short-lived materials; and if they were withdrawn from their ancestors they would die out in course of time and leave only thallium and bismuth as representatives of their respective types. Some process of this sort might account for the rule which Aston has detected among the non-radioactive isotopes. It should also be remembered that inactive analogues of the radioactive isobaric isotopes may possibly exist among the atoms of the ordinary elements; and in this case the mass spectrograph could not separate these isotopic forms from each other.

A less general rule than the foregoing is of interest in connection with G. N. Lewis's views on the pairing of electrons.† Aston points out that in the great majority of cases an even atomic number is associated with an even mass number, whilst an odd atomic number is associated with an odd mass number. This indicates that the number of electrons in the nucleus tends to be even. Glucinum and nitrogen are apparently the only elements consisting entirely of atoms whose nuclei contain odd numbers of electrons.

* See the Chart at the end of this volume.

† See Chapter XIII.

4. *Conclusion*

In view of the fundamental importance of Aston's results, it seems advisable to summarise here his contribution to our knowledge of atomic architecture.

From the fact that the unit mass of hydrogen (the proton) carries a positive charge, it may be inferred that the nucleus of any atom contains a number of positive charges equal to the number of atomic weight units contained in its mass. But since the atomic number of the element corresponds to the number of *surplus* positive charges in the nucleus, it is evident that this nucleus must also contain electrons equal in number to the difference between the figure representing atomic number and the figure representing atomic weight for that particular atom. Until the publication of Aston's work, the fractional figures of the chemical " atomic weights " prevented the recognition of this simple relationship between mass and electrical charge.

If it be assumed that at close range two electrical charges react upon each other so as to produce a diminution in mass of the system as a whole, then hydrogen can be regarded as the primal material from which the elements are constructed; and the incommensurability of the hydrogen atomic weight in the general system is explained by what is termed " packing effect." On this basis, Prout's Hypothesis regains its probability.

CHAPTER XI

THE SEGREGATION OF ISOTOPES

So far as our present knowledge goes, the only method whereby the isotopic forms of an element can be completely segregated from each other is by the electro-magnetic analysis of positive rays. By means of parabolic slits leading into separate containers, it would be quite possible to separate from each other the isotopes in a complex gaseous element. The quantities thus obtained would be small, but certainly not negligible. Aston [1] has calculated that by applying this method in the case of neon —assuming that the trapping of the two forms was complete— it would be possible to obtain about 0·1 cub. mm. of the Ne^{20} variety and 0·01 cub. mm. of the Ne^{22} form for every hundred seconds during which the apparatus was run. Owing to experimental difficulties, however, the yields in practice would probably be minute.

It is not without interest to survey some of the other suggestions [2] which have been put forward with a view to solving the problem. Some of these have been tried experimentally and have led to a partial separation of isotopic forms from each other. Less success in practice has been noted with other methods. Finally, some modes of separation have never reached the stage of practice at all; but they are still of interest to the extent that they suggest possibilities.

Diffusion.—Since the velocity of diffusion of a gas is inversely proportional to the square root of the gaseous density, it is self-evident that two isotopic gases must diffuse at different rates; and therefore a separation of one from the other is theoretically to be expected, if the ordinary method of separating a light gas from a heavy one be employed. Owing to the very

[1] Aston, *Isotopes*, p. 170 (1924).

[2] See Mulliken and Harkins, *J. Amer. Chem. Soc.*, 1922, **44**, 37, for a general synopsis of possible modes of separation.

slight difference in density between those gaseous isotopes which can be obtained in quantity, however, the separation in practice is bound to be a most laborious process.

The first success in this field fell to Aston,[1] who, by a prolonged series of diffusion experiments, succeeded in preparing two specimens of neon having respectively the densities 20·15 and 20·28 (oxygen=32), and this despite the unfortunate accidental loss of the whole of his lightest fraction at one point in the process.

A partial separation of hydrogen chloride was announced by Harkins.[2] The increase in atomic weight of the chlorine is given as 1 part in 645. The diffusion of the hydrogen chloride was carried out at ordinary pressure; and some 19,000 litres of gas were employed in the experiments.

Thermal Diffusion.—It has been shown experimentally by Chapman and Dootson[3] that if a mixture of gases of different densities (carbon dioxide and hydrogen) be allowed to diffuse freely in a vessel which has its two ends at different temperatures, a partial separation of the mixture will take place. Chapman[4] has suggested the application of this method to the separation of isotopes; but up to the present no practical results have been published.

Pressure Diffusion.—Theoretically, if a heterogeneous fluid is exposed to the action of a gravitational field and if no mixing process intervenes, the fluid should become separated into two portions; for the heavier particles will sink to the bottom whilst the lighter particles tend to accumulate at the top. It was suggested by Lindemann and Aston[5] that the lighter isotope of neon will be more plentiful in the air at great heights than near the ground. According to calculation, at a height of 100,000 feet, the atmospheric neon should have an average atomic weight of 20·163; and at double this altitude the average atomic weight would be reduced to 20·12, instead of the 20·2 found at

[1] Aston, *Isotopes*, p. 41 (1924).

[2] Harkins, *Phys. Rev.*, 1920, **15**, 74; Harkins and Hayes, *J. Amer. Chem. Soc.*, 1921, **43**, 1803; Mulliken and Harkins, *ibid.*, 1922, **44**, 37; Harkins and Jenkins, *J. Amer. Chem. Soc.*, 1926, **48**, 58.

[3] Chapman and Dootson, *Phil. Mag.*, 1917, **34**, 248; see also Ibbs, *Proc. Roy. Soc.*, 1921, A, **99**, 385.

[4] Chapman, *Phil. Mag.*, 1919, **38**, 182.

[5] Lindemann and Aston, *Phil. Mag.*, 1919, **37**, 530.

ground-level. This suggestion, however, is of only theoretical interest.

In practice, the employment of a high-speed centrifuge will produce an artificial gravitational field much more powerful than our natural one; and therefore it seems possible to devise a method of separating isotopes in this way.[1] The results in practice, however, have been disappointing. Joly and Poole[2] attempted to segregate the isotopes of lead in this manner, but the results were negative.

Fractional Distillation.—This was attempted by Aston[3] in the case of neon at an early date; but the results were negative, though theoretically the process appears to be possible.[4]

Evaporation under Low Pressure (Ideal Distillation).—If a liquid consisting of a mixture of two isotopes of different mass be evaporated so slowly that diffusion keeps the liquid phase a perfect mixture, then the molecules of the two isotopes will distil at rates inversely proportional to the square roots of their masses. Now when the pressure in such a system is reduced so far that no molecule, after escaping, ever returns to the liquid, it is obvious that a partial separation of the two isotopes will occur. The lighter isotope will accumulate in the earlier fractions, whilst the heavier isotope will be concentrated in the remaining liquid.[5]

Brönsted and Hevesy[6] evaporated mercury at temperatures between 40° and 60° under the highest attainable vacuum; and by placing a condensing surface, cooled with liquid air, within a couple of centimetres of the liquid surface, they were able to capture in solid form the mercury which escaped by vaporisation. In the course of the research, 2,700 c.c. of mercury were systematically fractionated to about 1/100,000 of the original volume in each direction. Taking the density of ordinary mercury as unity, the densities of the two final fractions were as follows:

Lightest fraction	0·99974
Heaviest fraction	1·00023

[1] For the theory of the matter, see Mulliken, *J. Amer. Chem. Soc.*, 1922, **44**, 1033; Poole, *Phil. Mag.*, 1921, **41**, 818.

[2] Joly and Poole, *Phil. Mag.*, 1920, **39**, 372.

[3] Aston, *Isotopes*, p. 39 (1924).

[4] Lindemann, *Phil. Mag.*, 1919, **37**, 523; 1919, **38**, 173.

[5] A discussion of the theory of the matter will be found in Mulliken's papers: *J. Amer. Chem. Soc.*, 1922, **44**, 2387; 1923, **45**, 1592.

[6] Brönsted and Hevesy, *Phil. Mag.*, 1922, **43**, 31.

Hönigschmid and Birckenbach [1] have determined by chemical methods the atomic weights of fractions of mercury obtained by the Brönsted and Hevesy method, with the following results :

	Densities.	Atomic Weights.
Lightest fraction . .	0·999824	200·564±0·006
Ordinary mercury . .	1·000000	200·61 ±0·006
Heaviest fraction . .	1·000164	200·632±0·007

It is evident that quite a marked separation can be effected in this manner. Later work by Harkins and Mortimer [2] produced a sample with an atomic weight differing by 0·189 unit from that of normal mercury.

By the same method, Brönsted and Hevesy [3] obtained a partial separation of chlorine isotopes. Hydrochloric acid was allowed to evaporate at a temperature of —50° C. and was condensed as described above. Sodium chloride was then prepared from the distillate and from the residue ; and the densities of the two salt specimens were determined. A difference was observed which corresponded to a change in atomic weight of 0·024 unit ; and a chemical check gave a result of 0·021 unit. This evidence is sufficient to prove that partial separation has been achieved.

Egerton and Lee [4] used the free evaporation method to separate zinc isotopes. The density increase in the residual material was about 1 part in 3700 ; whilst the density decrease in the distillate was about 1 part in 3600.

The attempt to separate ordinary lead into fractions was made by Brönsted and Hevesy, who distilled lead chloride in vacuo. Atomic weight determinations made on the fractions [5] obtained, however, were not conclusively in favour of the success of the experiments.

We now come to one of the most interesting cases in this field.[6] The chemical atomic weight of potassium is 39·1 ; and as Aston has proved that the element contains K^{39} and K^{41}, these two forms must be present in the ratio of 19 : 1. If it can be

[1] Hönigschmid and Birckenbach, *Ber.*, 1923, **56**, B, 1219.

[2] Harkins and Mortimer, *Phil. Mag.*, 1928, **6**, 601 ; see also Harkins and Madorsky, *J. Amer. Chem. Soc.*, 1923, **45**, 591.

[3] Brönsted and Hevesey, *Nature*, 1921, **107**, 619.

[4] Egerton and Lee, *Proc. Roy. Soc.*, 1923, **103**, A, 499.

[5] Hönigschmid and Steinheil, *Ber.*, 1923, **56** (B), 1831.

[6] Hevesy, *Nature*, 1927, **120**, 838 ; Biltz and Zeigert, *Physikal. Z.*, 1928, **29**, 197 ; Hevesy and Lögstrup, *Z. anorgan. Chem.*, 1928, **171**, 1.

established that K^{39} is inactive and that all the observed radioactivity of potassium is to be ascribed to the small quantity of K^{41} which is present in the mixture, then the feeble radioactive power of potassium would be explained.

One litre of metallic potassium was subjected to "ideal distillation" by keeping the liquid metal at 160° C. and condensing the vapour on a potassium surface 1 cm. distant, which was cooled with solid carbon dioxide. The residual fraction was examined by Hönigschmid, who reported that its atomic weight was 39·109 instead of 39·104. This fraction, therefore, contains 4·8±1 per cent. more K^{41} than natural potassium does.

A determination of the β-ray radioactivity of this heavy sample showed that it had 4·2±0·7 per cent. greater activity than normal potassium.

This seems to establish that the radioactive powers of potassium reside entirely in the K^{41} isotope; and thus the remarkable feebleness of the potassium activity is explained.

Further confirmation of these results seems possible from a different line of investigation. If a potassium atom loses a β-electron, it will be converted into an isobare having the atomic weight 41 and the atomic number 20—that is, into an isotope of calcium. Calculation shows that the maximum proportion of this Ca^{41} which could accumulate in potassium minerals during the whole of geological time would be 0·1 per cent.; so that the isolation of such a substance is not outside the scope of chemical analysis.

This work on potassium may serve to account for further matters. Rubidium contains 155 parts of Rb^{85} to 45 parts of Rb^{87}; so that in its case the heavier isotope is present in much greater proportion than is the case with potassium. If Rb^{87} be the bearer of the radioactivity of rubidium, then the fact that rubidium is more active than potassium is simply explained. Again, caesium is inactive. According to Aston, it is a pure element having only Cs^{133} in its composition. This may represent the lighter, stable form of the element corresponding to the inactive types Rb^{85} and K^{39}.

Adsorption.—An attempt to produce a separation of isotopes by adsorption in charcoal led to a negative result.[1]

[1] Sameshima, Aihara, and Shirai, *J. Chem. Soc. Japan*, 1922, **43**, 761.

Ionic Migration.—Lindemann [1] suggested that the rates of migration of isotopic ions might be different and that the lighter isotope might accumulate at the head of the ionic column in the case of electrolysis in gelatine. The results in practice have been negative.[2]

Photochemical Methods.—The suggestion has been put forward [3] that the ordinary combination of hydrogen and chlorine under the action of light might serve as a means of separating the chlorine isotopes Cl^{35} and Cl^{37}. The following assumptions are necessary: (1) that the light acts by activating the chlorine and not merely by activating the hydrogen; (2) that a specific wavelength (which for convenience we may call λ_{35}) will activate Cl^{35} but will not activate Cl^{37}; (3) *vice versâ*, the wavelength, λ_{37}, which activates Cl^{37}, will not activate Cl^{35}; (4) that Cl^{35} will absorb λ_{35} but not λ_{37}. Some of these postulates seem to depend upon a theory of photochemical action which is now very largely discredited. Granting them, however, it is clear that if a screen of Cl^{35} be interposed between a light source and a vessel containing Cl^{35}, Cl^{37} and hydrogen, the screen of Cl^{35} will absorb all light of wavelength λ_{35}, leaving light of wavelength λ_{37} to pass on, activate the Cl^{37}, and permit its combination with the hydrogen, whilst the Cl^{35}, having no λ_{35} light to activate it, will remain inert. Since ordinary chlorine contains thrice as much Cl^{35} as Cl^{37}, it should be possible, on the foregoing premises, to use it as a screen to reduce the λ_{35} light to zero whilst still allowing some light of λ_{37} to pass. By these means it was supposed that differential combination between hydrogen and the isotopes might be produced. The results in practice were negative.

Other methods of separation which have been suggested depend on the action of light upon metallic chlorides,[4] fractional crystallisation,[5] irreversible evaporation,[6] and differential electrolysis [7] on the assumption that the isotopic ions have slightly

[1] Lindemann, *Phil. Mag.*, 1922, **43**, 430; compare however, Jette, *ibid.*, 1927, **3**, 258.

[2] Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 1923, **9**, 75; Murmann, *Oester. Chem. Ztg.*, 1923, **26**, 14; Pittey, *Phil. Mag.*, 1925, **49**, 889.

[3] Merton and Hartley, *Phil. Mag.*, 1922, **43**, 430.

[4] Renz, *Z. anorg. Chem.*, 1921, **116**, 62.

[5] Atkinson, *Nature*, 1923, **112**, 283; Robinson and Briscoe, *J.*, 1925, **127**, 138.

[6] Richards, King, and Hall, *J. Amer. Chem. Soc.*, 1926, **48**, 1530.

[7] Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 1923, **9**, 75.

different E.M.F.'s. No success seems to have attended any of them.

In 1907, Hoffmann and Wolf [1] claimed that they had achieved a separation of lead from radium-D by the use of phenyl magnesium bromide. An analogous method has been tried by Dillon, Clarke, and Hinchy [2]; but later workers have failed to obtain positive results in this way.[3]

[1] Hoffmann and Wolf, *Ber.*, 1907, **40**, 2425.

[2] Dillon, Clarke, and Hinchy, *Sci., Proc. Royal Dublin Soc.*, 1922, **17**, 53.

[3] Brennen, *Compt. rend.*, 1925, **180**, 282; *Ann. chim.*, 1925 (X), **4**, 127; Richards, King, and Hall, *J. Amer. Chem. Soc.*, 1926, **48**, 1530; King, *ibid.*, 1927, **49**, 1500.

CHAPTER XII

THE ATOMIC NUCLEUS AND ITS ARTIFICIAL DISRUPTION

1. *Introductory*

In the course of the foregoing chapters, various lines of evidence have been indicated, all of which point to a particular structure for the atoms in general. In order to agree with the facts, it is necessary to postulate an atomic arrangement which contains two essentials: a nucleus and an outer region. The nucleus must contain both protons and electrons; the outer region is inhabited by electrons only: and the total positive charge of the atom is exactly neutralised by the number of electrons contained in the atomic structure.

These two regions of the atom possess different attributes. In the nucleus, or its immediate vicinity, is concentrated the mechanism which gives rise to the most permanent characteristics of the ordinary elements: the X-ray spectra which are associated with atomic numbers. The "planetary" electronic zone, on the other hand, appears to control some characteristics which can be varied in the laboratory: optical emission spectra, absorption spectra, refractivity, valency, chemical reactivity and others.*

In considering the architecture of the atoms, it will be convenient to take advantage of this natural division between the nucleus and the electronic zone and to consider each region separately, while not losing sight of the fact that each portion of the atom contributes its own share to the elemental charac-

* Optical emission spectra change with the mode of excitation—flame, arc, or spark; the absorption spectra of ferrous and ferric salts are obviously different and the change of iron from the ferrous to the ferric condition is easily carried out in the laboratory; refractivity is altered by temperature change; a change of valency can be produced in many elements by oxidation or reduction; while chemical reactivity is readily varied by a rise or fall in the surrounding temperature.

teristics. Since the atomic nucleus has been the subject of a large amount of refined experimental work, it will be best to deal first with it; and a subsequent chapter will be devoted to the electronic zone of the atom, which has been mainly, in recent years, the playground of theory.

2. *The Scattering of α-Rays*

The conception of a Saturnian * atom, with a positively-charged nucleus surrounded by a zone containing electrons, appears to date from 1904, when Nagaoka [1] published a mathematical investigation of the stability of such a system. His reasoning showed that atoms constructed on this principle would be stable, provided that the attraction of the nucleus was great and that electrons were in rapid motion. This pure speculation, however, led to no practical advances; and the experimental work of Rutherford and his collaborators has furnished the greater part of our knowledge of the atomic nucleus. On this account, the nuclear model atom is generally referred to as "Rutherford's atom."

When α-particles are projected against a sheet of matter, many of them traverse the material screen without suffering deflection from their original course. In 1906, however, Rutherford [2] detected in some cases a "scattering" of the particles in their passage through matter, a phenomenon which indicated that the material screen had produced a swerving of these particular particles at some point in their course. Further investigation by Geiger [3] established that the angle of scattering depended greatly upon the atomic weight of the metal employed as a screen; and eventually it was inferred that the average angle of scattering per atom of matter traversed is approximately proportional to the atomic weight. Geiger and Marsden [4] detected an even more surprising phenomenon when they observed that some α-particles are thrown out again on the same side of the screen as they entered. The fraction of α-particles

* The adjective is suggested by the similarity of this type of model atom to the system of the planet Saturn and its satellites.

[1] Nagaoka, *Phil. Mag.*, 1904, **7**, 445.

[2] Rutherford, *Phil. Mag.*, 1906, **11**, 166; *Radioactive Substances and their Radiations*, p. 181 (1913).

[3] Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 174; 1910, **83**, A, 492.

[4] Geiger and Marsden, *Proc. Roy. Soc.*, 1909, **82**, A, 495.

thus rejected is much smaller with an aluminium screen than with a gold one.

There appears to be no doubt that this scattering effect in its extreme phase is the result of a close encounter with a single atom of the screen; and on this basis Rutherford [1] was forced to the conclusion that the atoms of ordinary matter must have at their centres concentrated positive charges which act on the positive charges of α-particles and drive the particles out of their normal courses when they approach within close range of the nuclear charge, as shown in Fig. 12. Since this nuclear positive charge must be counterbalanced in order to make the atom neutral as a whole, Rutherford assumed that sufficient electrons surrounded the nucleus to produce this effect. This line of reasoning gives us the Rutherford model atom, or nuclear atom, as it is sometimes termed.

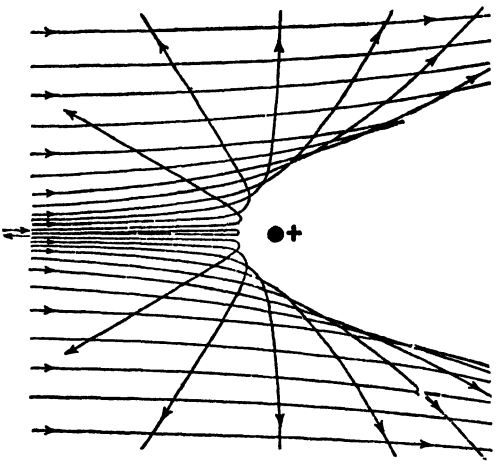


FIG. 12.—Paths of a Stream of α-particles in the Vicinity of the Positive Nucleus.

(*From Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry."*)

Rutherford inferred from the scattering data that the central charge of an atom corresponded roughly to the charge on one electron multiplied by half the atomic weight of the atom. The gold atom, for instance, was regarded by him as having a nuclear positive charge equivalent to about 100e and surrounded by 100 electrons which he assumed to be distributed through a spherical volume or to be ranged in concentric coplanar rings. The radius of the nucleus was estimated by Rutherford to be of the order of 10^{-12} cms.

[1] Rutherford, *Phil. Mag.*, 1911, **21**, 669.

3. *The Composition of the Nucleus*

These early estimations of the atomic nuclear charges were too rough to suggest the simplicity of the underlying truth; and it was not until 1913 that light was thrown upon the subject from another direction. Van den Broek[1] put forward the suggestion that there was a direct relationship between the numerical value of the nuclear charge and the position which the element occupied in the Periodic System. Experimental evidence tending to confirm this view was supplied by Moseley's investigations of the X-ray spectra of the elements, which showed a clear connection between the atomic number of an element and the frequency of the X-ray spectrum emitted by its atoms. In 1913, too, Soddy published his diagram of the radioactive changes, which contained a scale showing the electrical grading of the elements in terms of electrons; so that in that year four lines of evidence were converging upon the nuclear problem, and the solution had become almost obvious. Fleck's investigations upon the relationship between β-ray and valency changes gave a sound experimental basis for the idea that there were two sets of electrons within the atomic structure. And, finally, the Whole Number Rule of Aston removed the last difficulties in the way of a complete theory of the nuclear composition.

The present-day view of the atom postulates a nucleus wherein the whole mass of the atom is concentrated. The general results of experiment suggest that the diameter of the nucleus in heavy atoms is of the order 4×10^{-12} cms., or about 1/5000 of the diameter of the whole structure of the atom.[2] This nucleus contains protons (hydrogen nuclei) equal in number to the mass number of the atom; and as each of these protons carries one positive charge, the *total* number of positive charges in the nucleus is equal to the mass number of the atom under consideration. Closely associated with these protons is a group of electrons; and the number of these electrons is found by subtracting the atomic number of the element from the mass number of the atom in question. This arrangement yields a nucleus having a *surplus* positive charge numerically equal to the atomic number of the element.

[1] Van den Broek, *Physikal Z.*, 1913, **14**, 33; *Nature*, 1913, **93**, 373, 476; Soddy, *ibid.*, 399, 452; Rutherford, *ibid.*, 423; Bohr, *Phil. Mag.*, 1913, **26**, 1.

[2] Rutherford, *J.*, 1922, **121**, 400.

As a concrete example, the element lithium may be chosen. Its atomic number is 3; and Aston has detected two isotopes Li^6 and Li^7. Taking the Li^6 atom first, its nucleus contains six protons. Associated with these are (6—3)=3 electrons, which reduce the surplus positive charge on the nucleus from 6 to 3, which is the atomic number of the element. In the case of the Li^7 atom, the nucleus contains seven protons. Four electrons are also present, so that the surplus positive charge is again 3 and equal to the atomic number.

This conception of the nucleus furnishes a clear picture of the mechanism of the Law of Group Displacement. When the nucleus loses a single electron in the β-ray change, the surplus positive charge obviously is raised by one unit; and hence the product has an atomic number one unit higher than that of the parent material. The α-ray change is capable of an equally simple illustration. The α-particle is a system of four protons and two electrons. When this system is removed from the nucleus of any atom, it is obvious that the net result is a loss of four mass-units and (4—2)=2 positive charges. Thus the mass of the product will be less than that of the parent atom by four units; and the electrical positive charge of the product's nucleus will be two units lower than that of the parent—which corresponds to a loss of two units in atomic number.

The existence of the isobares is also readily accounted for on this view. The ejection of an electron from the nucleus during a β-ray change produces no alteration in the mass of the atom as a whole (since an electron is immediately picked up by the outer region of the atom in order to re-establish electrical neutrality). But the loss of this nuclear electron raises the surplus positive charge of the nucleus by one unit and so increases the atomic number by one unit also. Thus the parent atom and its disintegration product have equal masses; but the disintegration product has an atomic number different from that of its parent.

4. *A Magnetic Model Atom*

In 1878, Mayer[1] drew attention to the curious regularities which can be observed when the south pole of a large magnet is placed over a dish of water in which a number of equally powerful

[1] Mayer, *Phil. Mag.*, 1878 (v), **5**, 397.

small magnets are floated vertically with their north poles upwards. The floating magnets arrange themselves in rings which vary in structure with the number of floating magnets employed.

Thomson [1] attempted to draw a parallel between the electronic structure of atoms and the arrangements into which these floating magnets group themselves; but this parallelism suffered from the fundamental flaw that there was no numerical relationship between the strength of his central pole and the united strengths of the floating magnets. In order to have a true parallel between electronic arrangements and magnet groupings, it is essential that the strength of the central pole should increase *pari passu* with the number of magnets afloat at one time; for only in this way can a "magnetic neutrality" be obtained which will represent the electrical neutrality of the electrons and protons in the atom.

This parallelism has been attained in an experiment by Marsh and Stewart [2] which brings to light a surprisingly close analogy between the two systems. A series of fine bar magnets was prepared, each of which had the same strength as the others. A single magnet was fixed vertically at the bottom of a leaden tank filled with water, above the surface of which a second vertical magnet was suspended by placing it in a glass tube held in a clamp. On the water surface, a third vertical magnet was floated by means of a cork disc. All the magnets were placed with their north poles upward. The two fixed magnets taken together represent *one* magnetic unit, since the poles furthest removed from the water surface hardly affect the system owing to the lengths of the magnets employed in the experiment. When two floats were in the water, two magnets were placed at the bottom of the tank and two in the glass tube, and so on. In this way the combined strength of the floating magnets was equal to the oppositely magnetised central field produced by the fixed magnets; and an exact parallel is obtained to the negatively charged electrons and positively charged protons in the structure of the atom.

When this arrangement was tested with numbers of floating magnets corresponding to the mass numbers of the elements up to neon, the floating magnets in each case arranged themselves

[1] Thomson, *The Corpuscular Theory of Matter*, pp. 103 ff. (1907).
[2] Marsh and Stewart, *Nature*, 1922, **109**, 340.

in two sharply defined and clearly separated groups, the central one of which may for convenience be termed the "nucleus," whilst the second, outer, group may be named the "ring." The following table shows the results observed. It will be seen that the "ring" electrons are in each case equal in number to the atomic number of the corresponding element, so that they represent exactly the non-nuclear electrons of the atoms, which also are equal in number to the atom's atomic number.

Fixed Magnetic Units.	Floating Magnetic Units.		Corresponds to
"Nuclear protons" ("Atomic Mass").	In "Nucleus."	In "Ring" ("Atomic Number").	
1	1	0	Hydrogen
4	2	2	Helium
6	3	3	Lithium-6
7	4	3	Lithium-7
9	5	4	Beryllium
10	5	5	Boron-10
11	6	5	Boron-11
12	6	6	Carbon
14	7	7	Nitrogen
16	8	8	Oxygen
19	10	9	Fluorine
20	10	10	Neon-20

Inspection will show that these groupings of the floating magnets correspond exactly to the accepted distribution of electrons between the atomic nucleus and the outer electronic region; and, further, they provide an exact parallel to the known cases of isotopy so far as the model has been tested. For example, in the model of the B^{10} atom, the central pole contains ten magnetic units: five of these are "neutralised" by the five nuclear floating magnets, leaving a net "charge" of five—which is the atomic number of boron. In the case of the model of the B^{11} atom, there are eleven magnetic units in the central pole: six floating magnets "neutralise" six of these, leaving free five floats —the atomic number again. The apparent anomaly in the case of hydrogen is due to the fact that the single float has been reckoned as nuclear, whereas it is just as reasonable to regard it as a ring magnet, which would give the proper value for the atomic number.

One point of interest may be mentioned. In the models of

the B^{11} atom and the carbon atom, the nuclei each contain six floats arranged in two concentric triangles. In view of the close general resemblance in physical characteristics between boron and carbon, and especially in view of the fact that boron is quadrivalent in its hydrides * like carbon, instead of forming the hydride BH_3 as it might be expected to do, this peculiarity in the model seems suggestive.

Attempts to extend the model to atoms of higher mass number were not successful, probably on account of the influence of the second poles of the fixed magnets coming into play as the diameter of the groupings increased; but among the lower members it is evident that the method furnishes a perfect picture of the main aspect of atomic structure. It seems possible that some modification of the model might yield a most interesting insight into the statical side of atomic relations.

5. *The Disruption of the Nucleus*

Although laboratory methods are sufficient to change the constitution of the outer zone of electrons in the atom, the nucleus is much more resistant to alteration; and only the employment of enormously concentrated energy can break up its structure, whatever that may be. Ramsay was the first to see that the energy of the α-particle offered our best chance in this field; and Rutherford's recent researches have proved the accuracy of Ramsay's insight.†

The α-particle is a sub-microscopic projectile with a diameter estimated at 8×10^{-13} cms. and a speed of about 10,000 miles per second in its free path. Mass for mass, its energy is four hundred millions as great as that of a rifle bullet. It is evident that when such a body is suddenly brought to a standstill by

* See Chapter XVI.

† In addition to the α-particle, other agents have been utilised in the hope of transmuting elements, but none of the results can as yet be regarded as fully authenticated. See *Nature*, 1926, **117**, 758; Riding and Baly, *Proc. Roy. Soc.*, 1925 (A), **109**, 106; Smits, *Nature*, 1926, **117**, 13; Paneth and Peters, *Ber.*, 1926, **59** (B), 2039; Bernhardt, *Physikal Z.*, 1926, **27**, 515; Smits and Karssen, *Z. Elektrochem.*, 1926, **32**, 577; Sheldon and Estey, *Physical Rev.*, 1926, **27**, 515; Thomassen, *Nature*, 1927, **119**, 813; Smits, *Nature*, 1927, **120**, 475; Smits and Frederikse, *Z. Elektrochem.*, 1928, **34**, 350; Walter, *Z. Physik*, 1926, **39**, 337; Herzfinkel and Wertenstein, *Nature*, 1928, **122**, 504; Günther, *Ber.*, 1927, **60** (B), 808; Paneth, *Nature*, 1927, **119**, 706.

collision with matter, the energy-change will far exceed anything which can be produced artificially on the same scale.

By using a method devised by C. T. R. Wilson, it is possible to photograph the actual tracks of α-particles through gases; and in many of the photographs a sharp kink appears at the extreme end of the trail, just before the particle has come to rest. This kink indicates that the α-particle has been violently diverted from its original path by some obstacle; and this obstacle has now been shown to be an atom. This phenomenon is obviously akin to the process of "scattering" which occurs when a stream of α-particles is shot into a screen of solid matter.

An investigation of phenomena on a scale so extraordinarily minute as this, might well seem beyond the limits of experimental

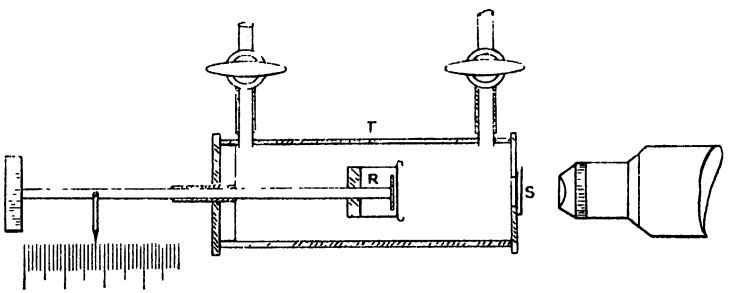


FIG. 13.

refinement; but Rutherford [1] has solved the problem by devising an apparatus which is almost as wonderful in its simplicity as in the results which it yields.

In Fig. 13, T is a brass tube of 3 cms. diameter with side-tubes and stopcock for the circulation of dry gases. At the right-hand end of the tube is a hole covered with a thin silver plate. A zinc sulphide screen, S, is fixed 1·3 mm. distant from the opening, leaving a slot into which mica screens can be slid. The radioactive material yielding the α-rays is fixed at R to the end of a rod, so that its distance from the screen S can be varied.

[1] Rutherford, *Phil. Mag.*, 1919, **37**, 537, 562, 571, 581; 1921, **42**, 809; Rutherford and Chadwick, *ibid.*, 1922, **44**, 417; *Nature*, 1924, **113**, 457. A general account is to be found in Sir Ernest Rutherford's lecture to the Chemical Society (*J.*, 1922, **121**, 400). See also Darwin, *Phil. Mag.*, 1914 (vi), **27**, 499; Rutherford, *ibid.*, 488; Marsden, *ibid.*, 824; Marsden and Lantsberry, *ibid.*, 1915 (vi), **30**, 240; Chadwick, *ibid.*, 1920 (vi), **40**, 734; Chadwick and Bieler, *ibid*, 1921 (vi), **42**, 923.

Since β-rays are also given off from the source and would illuminate the zinc sulphide screen if they were allowed to reach it, a strong magnetic field is applied to the whole apparatus; and this diverts the β-ray electrons away from the screen while allowing the α-particles to reach it. A short-focus microscope is placed as shown, for the purpose of examining the scintillations produced on the screen S by the impact of the α-particles from the source.

When radium-C is used as a source, the α-rays have an extreme range of 7 cms. in air. If now mica screens be introduced into the slot which make the total stopping power of the materials between source and screen equal to the stopping power of 20 cms. of air, it is obvious that no α-particles can reach the screen from the source. It is found, however, that when the tube T is filled with hydrogen, scintillations do appear on the screen at S. These are believed to be caused by particles of hydrogen—termed H-particles for convenience—which have been directly struck by α-particles and which have acquired a high velocity and long trajectory from the violence of the collision.

If the hydrogen in the tube T be now replaced by pure oxygen, no scintillations are observed under the same conditions. This is due to the fact that the momentum of the α-particle is not sufficient to drive the heavy oxygen atom through a range of 20 cms. in air as the light hydrogen atom can be driven.

When the oxygen is in turn replaced by nitrogen, scintillations at once appear on the screen, just as in the case of hydrogen. By applying a measured magnetic field, it is found that the particles producing these scintillations are actually H-particles. These H-particles are found to have a range of 40 cms. in air, whereas the ordinary H-particles derived from pure hydrogen have an extreme range of 30 cms. in air.

Putting the matter concisely, this amounts to saying that by bombarding nitrogen with α-rays, we can liberate H-particles which are travelling at higher velocities than any H-particle produced by the bombardment of hydrogen itself with α-rays. The only possible inference from this, in view of the precautions taken by Rutherford, is that under the impact of the α-particles some of the nitrogen atoms are shattered, and among the disruption products is hydrogen. The H-particles so produced have velocities higher than normal H-particles, because in

addition to the ordinary energy of collision, the new H-particles have extra energy conferred upon them by the forces at work during the destruction of the nitrogen nucleus, the mechanism of which will be discussed presently.

This method has been applied to a study of all the elements up to an atomic weight of 40 (with the exception of helium, neon, and argon); but no element of atomic weight greater than phosphorus was found to yield these new swift H-particles. The following table shows the results observed in each case up to sulphur. The column headed *Particles* shows the number of scintillations observed per minute per milligramme activity of the source (Radium-C) for an absorption of 32 cms. of air. The last column shows the maximum range of the particles expressed in cms. of air.

Element.	Material used.	Particles.	Maximum Range.
Lithium	Li_2O	—	—
Glucinum	BeO	—	—
Boron	B	0·15	ca. 45
Carbon	CO_2	—	—
Nitrogen	Air	0·7	40
Oxygen	O_2	—	—
Fluorine	CaF_2	0·4	over 40
Sodium	Na_2O	0·2	ca. 42
Magnesium	MgO	—	—
Aluminium	Al, Al_2O_3	1·1	90
Silicon	Si	—	—
Phosphorus	P (red)	0·7	ca. 65
Sulphur	S, SO_2	—	—

By a new method,[1] it was found that the following elements eject particles with a range above 7 cms. in air: neon, magnesium, silicon, sulphur, chlorine, argon, and potassium. Hydrogen, helium, lithium, carbon, and oxygen give no detectable effect beyond 7 cms. Other elements have been examined; but the results were indefinite. In the case of atoms with high atomic numbers it seems quite probable that the strong positive charge on the nucleus deflects the α-particle completely and prevents it from disrupting the nuclear system.

It should be noticed that all the elements yielding long-range H-particles have odd atomic numbers, but that the converse proposition does not hold, if lithium yields no H-particles at all.

[1] Rutherford and Chadwick, *Nature*, 1924, **113**, 457.

Investigations along similar lines were made by Pettersson and Kirsch.[1] In addition to the elements mentioned above, the Vienna workers found evidence for disintegration in the cases of titanium, chromium, iron, copper, selenium, bromine, zirconium, tin, tellurium, and iodine. In the cases of lithium, glucinum, carbon, oxygen, magnesium, and silicon, they claimed to have established disintegration which had not been observed by Rutherford and Chadwick. Chadwick[2] reinvestigated the matter, using more refined optical aids than in earlier experiments, but he was unable to detect the emission of protons of a range greater than 4 cm. in air in the cases of glucinum, carbon, or oxygen. A positive result in the case of lithium, being very small, was ascribed by him to traces of impurity in the lithium salt.

Actual photographs of the disintegration of nitrogen atoms have been obtained by Blackett,[3] using the Wilson fog-track method. Some 40,000 photographs were taken; and from these were selected all the examples showing collisions. The majority of these, on measurement, proved to be ordinary collisions; but eight cases were found wherein the ordinary collision laws were disobeyed; and these eight evidently represent true disintegrations. The photographs show only two branches from the collision point, which proves that the α-particle does not rebound from the disintegrating nucleus after impact but is carried along with it for a time at least. The second branch is evidently the track of the new-born H-particle. If the α-particle is permanently captured by the shattered nitrogen nucleus, the resulting product should be an isotope of oxygen with a mass of 17; since the broken nitrogen nucleus has lost one unit of mass and one positive charge in the H-particle, and has gained two positive charges and four units of mass from the α-particle.

At an earlier date, Harkins and Ryan[4] published results obtained by a similar method in which a track was shown with *three* branches after the point of impact. According to Aston,[5]

[1] Pettersson and Kirsch, *Physikal Z.*, 1924, **25**, 588; Kirsch, *ibid.*, 1925, **26**, 379, 457 See also Pettersson: *Kunstliche Verwandlung der Elemente* (1929), which gives an interesting account of the whole subject.

[2] Chadwick, *Phil. Mag.*, 1926 (7), **2**, 1056.

[3] Blackett, *Proc. Roy. Soc.*, 1925 (A), **107**, 349.

[4] Harkins and Ryan, *Nature*, 1923, **112**, 54; *J. Amer. Chem. Soc.*, 1923, **45**, 2095.

[5] Aston, *Ann. Report*, 1924, **21**, 247.

this is not an example of disintegration at all; for it occurs at a point so near the end of the normal track of the α-particle that the particle would not then have sufficient energy to disrupt an atom; and, further, the track bears no resemblance to those obtained by Blackett. Aston suggests that Harkins and Ryan's results may be due to the effect of radioactive contamination superposed accidentally upon the ordinary forked collision-track.

An interesting method of detecting H-particles has been devised,[1] which depends on the utilisation of amplifying valves. The apparatus permits detection to be registered on headphones or through a loud speaker; and the Vienna wireless station has actually broadcast to listeners the sounds produced by the entry of α-particles and β-ray electrons into the receiving chamber.

6. *The Mechanism of Disruption*

Investigations by Rutherford and Chadwick appear to establish definitely the nature of the swift particles from nitrogen, fluorine, phosphorus, and aluminium. These particles behave in all respects like high-speed H-particles carrying a positive charge; whence it must be inferred that they are hydrogen protons derived from the breakdown of the N, F, P, and Al nuclei under the α-ray bombardment.*

It has been calculated and confirmed by experiment that when an α-particle strikes a free hydrogen atom "head-on" the hydrogen atom will recoil with a range in air of 28 cms. But in the case of the H-particles observed in the bombardment of aluminium, this range is much exceeded; for the particles have a trajectory extending to 90 cms. in air. Obviously such particles as these have more kinetic energy than the free hydrogen particle. Further calculation shows that they actually have 1·4 times the energy of the incident α-particle itself. This gain in energy cannot be accounted for by anything in the α-particle or the H-particle, since both of these are common factors in the two sets of experiments. It must therefore be looked for in the atomic nucleus of the shattered aluminium atom.

[1] Photographs of the apparatus are given in Pettersson's *Kunstliche Verwandlung der Elemente*, pp. 104, 105 (1929).

* The alternative suggestion, that they are derived from a disruption of the α-particle itself, seems to be based on false premises, and to be incapable of accounting for the non-production of H-particles from heavy atoms.

A further observation throws light upon this point. It might have been expected that the liberated particles would be projected in the same direction as the bombarding α-particles. In the case of aluminium, however, it was found that nearly as many H-particles were shot backward as in the forward direction; and it seems probable that the ejection of H-particles from aluminium takes place in all directions. How is this backward projection to be explained?

The phenomenon can be accounted for with ease if it be assumed that in the aluminium nucleus independent H-particles are travelling in closed paths as shown in Fig. 14. In the col-

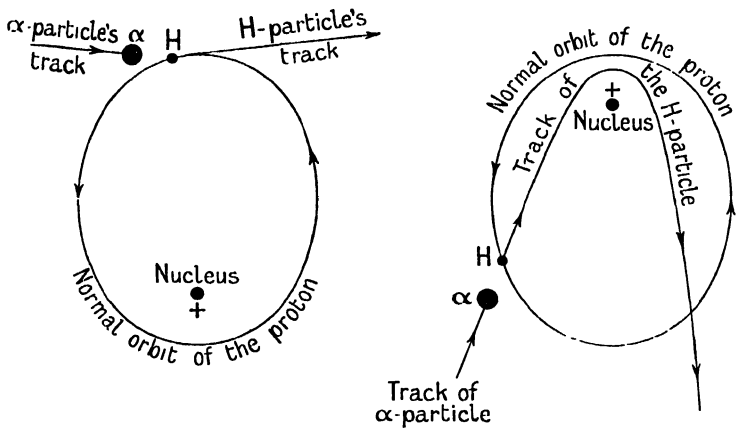


FIG. 14.

lision represented in the left-hand diagram, the H-particle will be shot out of its orbit in a forward direction; whilst if the collision takes place as shown in the right-hand diagram, the H-particle will describe an orbit round the main nucleus of the atom and will escape in a backward direction as indicated by the arrow.

7. *The Structure of the Nucleus*

The possible constitution of atomic nuclei furnishes such a wide field for speculative thinkers that it is quite impossible to deal with all the hypotheses which have been put forward from time to time.[1] It will be sufficient here to consider some of

[1] See, *inter alia*, Harkins, *J. Amer. Chem. Soc.*, 1920, **42**, 1956; Kossel, *Physikal. Z.*, 1919, **20**, 265; Haas, *ibid.*, 1917, **18**, 400; Schmidt, *ibid.*, 1919, **20**, 448;

the most interesting points which are suggested by recent experimental work in this field.

In the first place, it seems desirable to recall the relevant facts which have been experimentally established with regard to the behaviour of the atomic nucleus.

(1) Three types of particle have been identified as appearing during changes in the nucleus. The heaviest of these is the α-particle, ejected during α-ray changes in the radio-elements and consisting of four protons and two electrons. The simple proton is driven out of the nucleus of some (but not all) light atoms under the influence of α-ray bombardment. Finally, the electron is detected, being shot out from the nucleus in the course of the β-ray changes of radio-elements. Protons and electrons are thus the ultimate bricks with which the nucleus is built.

(2) The number of protons in the nucleus is equal to the mass number of the atom; the number of nuclear electrons is equal to the difference between the mass number and the atomic number of the atom.

(3) Some nuclear systems are stable, others are unstable. The stability has no relation to either atomic number or mass number.

(4) All atoms having the same atomic number emit identical characteristic X-rays.

There is at present no dispute as to the composition of the nucleus: the numbers of protons and electrons in each of the 92 known nuclei are quite accepted.[1] It is when the internal groupings of these constituents are considered that modern opinions differ.

At the present time, the main difference of opinion seems to be concentrated on the question: "Are helium nuclei present *as such* in the atoms of the heavier elements?" No definite

van den Broek, *ibid.*, 1916, **17**, 260; 1920, **21**, 337; Meitner, *Z. Physik*, 1921, **4**, 146; Neuburger, *Physikal. Z.*, 1922, **23**, 133; Silberstein, *Phil. Mag.*, 1920, **39**, 46; Kohlweiler, *Z. Physikal. Chem.*, 1920, **94**, 513; Chwolson, *Z. Physik*, 1921, **7**, 268; Gehrcke, *Physikal. Z.*, 1921, **22**, 151; Brösslera, *Rev. chim.*, 1921, **1**, 42, 74; Puig, *Estudios del Instituto Quimico de Sarria*, No. 16 (1924); Saz, *Iberica*, 1922, **1**, 168, 296; Cabrera, *La Estructura del átomo y las Propriedades magnéticas* (1921); Rosseland, *Nature*, 1923, **111**, 357; van der Berg, *Chem. Weekblad*, 1923, **20**, 54; Neuberger, *Ann. Physik*, 1923, **68**, 574; **70**, 139; 1923, **17**, 54; **19**, 307; and the discussion reported in *Proc. Roy. Soc.*, 1929, [A], **123**, 373.

[1] Aston, *Isotopes*, p. 106 (1922).

answer can as yet be given to this inquiry, and all that is necessary in this place is to give some examples of the arguments which have been brought forward in the discussion.

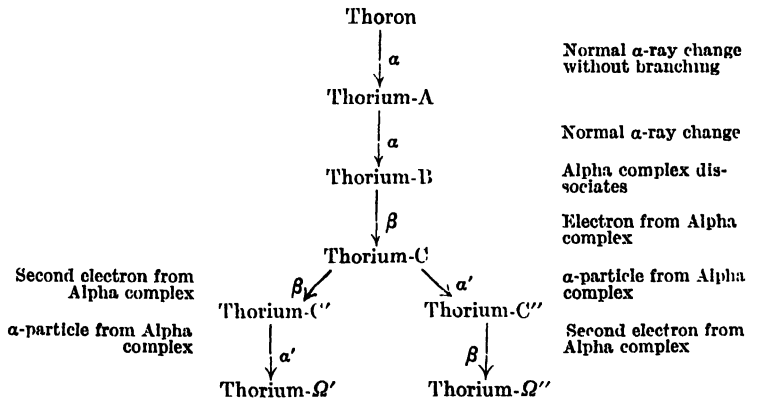
The most obvious argument in favour of the existence of actual helium nuclei within some atoms is to be found in the ejection of these nuclei during the α-ray change of the radio-elements. Here, undoubtedly, this group of protons and electrons is found intact under the most trying conditions conceivable. Aston,[1] however, rather caustically points out that by the same reasoning a pistol must contain smoke, since smoke is ejected when the pistol is fired. It is quite possible that the α-particle, like the smoke of the pistol, is only formed at the moment of its ejection. Since there is no experimental evidence on either side, this argument in favour of the intra-nuclear existence of helium nuclei will probably carry a weight exactly corresponding to the prejudice in the mind which receives it.

A second argument is adduced by Rutherford, based on his atomic disruption experiments. Helium, carbon, and oxygen were not broken down by the α-particle bombardment; and their mass numbers indicate that they might be built up from one, two, and three helium nuclei respectively. On the other hand, the elements which yield long-range H-particles have mass numbers which, when divided by 4, leave remainders of 2 and 3. On this basis, it may be imagined that the latter atoms are composed of a central nucleus (possibly complex) of helium nuclei, which is surrounded by satellite hydrogen nuclei capable of being torn away by the α-particle bombardment. Within limits, this argument seems to have some weight; but it fails to account for the stability of Li^6 and Li^7, which must contain between them both the critical groupings (He+2H) and (He+3H). It seems to break down in the case of sulphur, which can be supposed to be built up from eight helium nuclei and yet yields short-range particles on bombardment. Nor does it leave an altogether satisfactory feeling in the mind when it is remembered that no H-particles seem to have been detected in the very case where nuclear turmoil is at its utmost violence—at the moment of the ejection of an α-particle from a spontaneously disintegrating radio-atom such as one of the radium-A atoms, which from its atomic number must obviously possess at least two satellite

[1] Aston, *Isotopes*, p. 122 (1924).

hydrogen protons in its nucleus. Any ejection of long-ranged H-particles from atoms of the radium series could hardly have escaped discovery if it really occurred.[1]

An even more complex type of nucleus is postulated by Meitner [2] in order to account for the sequence of disintegrations in the radioactive series. It is assumed that the radioactive nuclei contain: (1) a series of protons neutralised by an equal number of electrons; (2) a series of ordinary α-particles; and (3) a series of α-particles loosely conjoined with electrons though not so firmly attached to these as to constitute true helium atoms. These last groups may be designated Alpha particles to distinguish them from the normal α-particles which they contain. The hypothesis is put forward to account for the fact that except at the tail-end of the series, β-ray changes always occur in pairs; and this is done by assuming that, before the first β-ray change takes place, the complex Alpha particle is resolved into a true α-particle and a pair of electrons. One of these electrons is shot out in the first β-ray change. This leaves a true α-particle and an electron. At this point the disintegration chain branches; part of the atoms shoot out α-particles whilst the remainder shoot out electrons, both of which are provided from the wreck of the original Alpha particle. Thus branching of the disintegration chain—involving a double β-ray change—takes place whenever an Alpha particle breaks up; whereas if a normal α-particle is shot out, no branching occurs. The following diagram will make the matter clearer:



[1] See Rutherford and Robinson, *Phil. Mag.*, 1914, (iv), **28**, 552.

[2] Meitner, *Z. Physik*, 1921, **4**, 146.

Meitner's hypothesis is interesting; but there is hardly enough evidence to make it convincing. A crucial test of it will perhaps be applied when the actinium chain of descent is fully established; and until then judgment may be left suspended.

This section may fittingly be closed with an account of Rutherford's picture of the atomic structure.[1]

According to Rutherford, the atomic structure, in the case of heavy elements, can be best conceived as triune, built up from the following:

(*a*) A central nucleus, which is assumed to be a closely-ordered, semi-crystalline arrangement of electrons and helium nuclei, with a radius of 1×10^{-12} cm.

(*b*) A region, extending to a radius of about $1{\cdot}5 \times 10^{-12}$ cm., occupied by electrons and possibly also by charged nuclei of small mass which are held in equilibrium by attractive forces arising from the distortion or polarisation of the central nucleus. The electrons in this region are supposed to revolve at velocities approaching that of light.

(*c*) An external region, with an outer radius of about 6×10^{-12} cm., may be occupied by neutral satellites held in equilibrium by the polarising action of the electric field arising in the nucleus. In the case of the radioactive elements, this region is assumed to be the sphere of origin of the α-particles. In addition to satellites of mass 4, Rutherford believes that this sphere may contain satellites with masses of 3, 2, or 1.

Let us now take up one or two points suggested by this model of the atom.

Rutherford assumes that the satellites which eventually produce α-particles during radioactive change are electrically neutral during their habitation of the intra-atomic system; and he pictures them as helium nuclei, each of which has gained two electrons.* These two electrons do not occupy the same position as they do in the state of free helium gas; for if they did the helium satellite could not exist within the heavy atom. Rutherford postulates that these extra two electrons are associated

[1] Rutherford, *Phil. Mag.*, 1927, (7), **4**, 580.

* *I.e.* Each satellite is a group of two electrons and four protons (helium nucleus) with which two extra electrons are associated.

with the helium nucleus much more closely than in helium gas.

Now it is known from experiment that the α-particles ejected by a given radio-element travel with equal velocities; and Rutherford suggests that this can best be accounted for by assuming that these neutral satellites revolve within the atom in orbits governed by quantum conditions. Rutherford has shown that this supposition is in agreement with the experimental facts with regard to the ejection of α-particles from the atom.

Since it is experimentally established that the α-particle consists of four protons and two electrons, it is evident that Rutherford's neutral satellites must leave behind them in the atom two electrons when they make their escape from the radioactive system; and he assumes that these two freed electrons drop into the atomic nucleus and so change the atomic number by two units.

We may now turn to the problem of the origin of the γ-rays emitted in radioactive changes. Kuhn [1] showed theoretically that if the γ-rays originated from high-speed electrons, they would not give sharp lines, as experimentally observed, but broad bands. On the other hand, quantum transitions of heavy particles would yield agreement between theory and practice. Further, experiment has shown that γ-rays are emitted during radioactive changes concerned only with α-particles—a state of affairs which negatives any idea that the γ-ray is excited by electronic impact on matter. Rutherford therefore assumes that the γ-rays have their origin in leaps of the neutral satellites from one quantum level to another within the atomic structure.

We are now in a position to deal with Rutherford's view of radioactive change. For some reason, one of the neutral α-satellites, circulating in a quantised orbit around the central nucleus, becomes unstable and escapes from the atomic structure —losing its two electrons when the electric field of the atomic nucleus falls below a certain critical value. It escapes as a doubly-charged helium nucleus (four protons and two electrons) at a velocity depending on its quantum orbit and the charge on the central nucleus. The two discarded electrons fall inwards towards the central atomic nucleus, probably circulating with nearly the speed of light close to the central nucleus and inside the

[1] Kuhn, *Z. Physik*, 1927, **43**, 56; **44**, 32.

region occupied by the neutral satellites. Occasionally, one of these electrons is hurled from the system, forming a β-ray electron. The disturbance of the neutral satellite system by the liberation of the α-particle or of the swift electron may lead to internal rearrangement, involving the transition of one or more satellites from one quantum orbit to another with the emission of γ-rays of a frequency determined by the quantum conditions.

8. *Cosmic Rays and the Evolution of Matter*

Experiment proves that the air of the lower atmosphere is ionised to a certain extent; and it is not difficult to suggest possible causes for this phenomenon. Many rocks and waters contain radio-elements; and the air, by diffusion into porous mineral matter or by solution in water, may pick up some of this solid or gaseous active material and transport it into the atmosphere. In this process, the layer of air nearest the ground will be most heavily charged with the active substances; for at higher levels the radioactive materials will be spread abroad by currents, while at the same time the short-lived emanations of thorium and actinium will decay and leave less active products to take their place. A second cause of atmospheric ionisation can be traced in the penetrating rays thrown out by radioactive materials in the soil or dissolved in natural waters.

On these assumptions, it might be expected that the highest degree of ionisation would be found near ground-level and that as the height of the measuring instrument was raised, there would be a fairly steady fall-off in the ionisation observed, provided that there is no great disturbance due to air-currents in the atmosphere.

By proper screening of the measuring instruments, it is possible to evaluate the ionisations due to α- and β-rays. The influence of the γ-rays from the earth is measured by difference. Observations are made on the ground surface, and a comparison is made with another set of results obtained on a lake or on the top of a glacier. The water or ice acts as a screen; and the difference between the two sets of measurements gives the γ-ray activity of the ground surface, since the air-factor is the same in both observations.

On conducting a series of investigations at different elevations,

Hess and Schmidt [1] and Kolhörster [2] arrived at wholly unexpected results. As the observer increases his elevation, the ionisation falls off at first, which is obviously what might be expected if the layers of air act as a screen to cut off the weaker portions of the earth-radiation. Just above 500 metres, the ionisation reaches a minimum; and as the instruments are taken higher, the ionisation begins to increase instead of diminishing as one might expect. At 1,700 metres, the ionisation again touches the original value found in the ground-level air. A further rise to 5,000 metres is accompanied by a slow increase in ionisation; and beyond the 5,000 metre level the increase grows rapidly as the instruments are carried further and further upward. In the following table the column headed "Ions" represents the difference between the ground-level ionisation and the value obtained at the given height:

Elevation in metres.	Ions.
500	− 1·7
1,000	− 1·5
1,500	− 0·4
2,000	+ 1·0
2,500	+ 2·6
3,000	+ 4·2
4,000	+ 9·1
5,000	+16·2
*6,770	+39·0

These facts make it evident that some hitherto undiscussed source of ionisation makes its appearance as the measuring instrument is taken to a height at which the earth-radiation has ceased to be of importance.

Further investigation has proved that this ionisation of the upper air is produced by extraordinarily penetrating rays having wave-lengths of 0·00063 Å.U. and 0·00038 Å.U. Some idea of the character of these rays will be obtained when it is pointed out that the latter type have a frequency fifty times as great as that of the γ-rays.[3] The hardness of the cosmic rays is so great that they are capable of penetrating no less then six feet of lead. They pass through space in all directions with equal intensity

[1] Hess and Schmidt, *Physikal Z.*, 1918, **19**, 109; Hess, *Elektrische Leitfähigkeit d. Atmosphäre* (1926).

[2] Kolhörster, *Ber.*, 1923, **34**, 366; *Probleme d. kosm. Phys.*, vol. v (1924).

* Measured in an aeroplane flight by Büttner (*Z. Geophys.*, 1926, **2**, 254).

[3] Millikan, *Science*, 1925, **62**, 446; Millikan and Cameron, *Physical Rev.*, 1926, **28**, 851; see also Myssovski and Tuwim, *Z. Physik*, 1925, **35**, 299.

by day and by night; and when they strike matter, softer rays are given off which have frequencies which agree with the values calculated from the theory of the Compton effect.

Later investigations extended our knowledge still further.[2] Experiments with pilot balloons failed to detect in the atmosphere any rays intermediate in wave-length between the cosmic rays and the γ-rays. The cosmic ray spectrum contains four bands.

The place of origin of these cosmic rays is quite clearly extra-terrestrial; for no radiation of such intensity could escape detection at the surface of the earth and we know of no radioactive process which develops radiation of so penetrating a character. Taking the extra-terrestrial origin for granted, it is evident that a wide field is opened to speculation.

The fact that the cosmic rays take the form of a band spectrum (unlike X-rays) is adduced by Millikan and Cameron as a proof that the cosmic rays owe their origin to a process quite different from that which gives rise to X-rays. The discoverers believe that the cosmic rays are probably produced by definite and continually recurring atomic transformations involving energy changes far greater than any yet observed in radioactivity.

Two possible processes have been suggested as producers of the cosmic rays: (1) the capture of an electron by a proton; and (2) the building up of hydrogen into more massive elements. Calculation shows that either of these processes would yield radiation of the kind which had been observed; but the second alternative seems to account better for all the facts.

Einstein's equation ($E=Mc^2$) gives a means of predicting the absorption coefficient per metre of water for radiation produced by (1) the union of four protons and two electrons to form a helium nucleus; (2) the synthesis of an oxygen nucleus from the protons and electrons of hydrogen atoms; and (3) the production of silicon by a similar method. When these three calculated values are placed alongside the observed values for the cosmic rays, the agreement is something more than striking:

Calculated values	0·30	0·075	0·043
Observed in cosmic rays . .	0·35	0·08	0·04

The synthesis of iron from hydrogen or helium would also give

[1] Millikan and Cameron, *Science*, 1928, **67**, 401; *Physical Rev.*, 1928, **31**, 921; **32**, 533; *Proc. Nat. Acad. Sci.*, 1928, **14**, 445.

radiation corresponding to that detected in the cosmic bands. It seems worth noting that these particular elements are common constituents of meteorites and that they also exist in the stars.

As to the regions in which such transmutations can occur, Millikan and Cameron make a bold assumption. Rejecting the star-furnaces as transformers, they suggest that these synthetic processes take place at points of low pressure where the temperature is not much above zero on the Absolute scale. Such points would be found in inter-stellar or, even more remote, inter-galactic space. There, it is suggested, the radiation of the stars is converted into protons and electrons, and then, by a further synthesis, the common elements are built up.

It is natural that this bold theory of a self-compensating Universe has not passed without criticism [1]; and it is of interest to compare it with another view of the cosmic processes.[2]

According to Jeans, the stars contain in their interiors elements unknown (and unknowable) to us. To these hypothetical elements he ascribes atomic weights as high as 300. To account for the stellar energy, he assumes that in the atoms of these elements a planetary electron may fall into the nucleus, neutralise a proton, and annihilate it in the process. In order to evade the sequel to this—explosive instability of the star—he postulates that with a rise of temperature in the star the atoms have their planetary electrons stripped from their nuclei, and hence any further fall of electrons into the atomic nucleus becomes impossible. With the loss of the planetary electron shells, the nuclei suffer closer aggregation and the star becomes one of the "white dwarf" class. This hypothesis depicts the galaxies as a series of clocks which cannot be rewound but which will eventually part with all radiatable energy. It suffers the disadvantage that the type of energy-change involved in it does not seem quite suited for the production of cosmic rays.

Quite possibly, both Millikan's and Jeans's theories may be true, as they are not mutually exclusive. At the present time, however, the safest standpoint in the matter is one of philosophic doubt.

[1] Rutherford, *Proc. Roy. Soc.*, 1929, (A), **122**, 1.

[2] Jeans, *Astronomy and Cosmogony* (1928); *Nature*, 1926, **118** (Supp.), 29.

CHAPTER XIII

THE OUTER SPHERE OF THE ATOM

1. *General*

In considering the problem of atomic structure, two things must be kept distinct from each other: the atomic order and the periodic arrangement of the elements. The atomic numbers, determined from X-ray spectra, suffice to place the elements in their natural sequence, beginning with hydrogen and ending with uranium; but these numbers in themselves offer nothing which suggests a repetition of analogous chemical properties at given points in the elemental series.

In earlier chapters it was seen that modern theory associates the atomic number with the nucleus of the atom, making it equal to the number of surplus positive charges in that region. This surplus nuclear charge is not, however, the only factor which has to be taken into account when chemical properties come under consideration; for if this were so, then ferrous iron and ferric iron, having different chemical qualities, would have different atomic numbers. There is evidently a second factor which plays its part in governing the chemistry of the elements.

At this point, attention may be drawn to the type of resemblances which are found in the Periodic Table. Why are boron and aluminium, for example, placed in the same group? One is a typical non-metal, while the other is characteristically metallic. Boron forms an acidic oxide, whereas the oxide of aluminium yields salts with acids. Again, in Group IV, carbon and silicon are associated, though the chlorine derivative of carbon is quite stable in presence of water, whereas silicon tetrachloride is readily decomposed by water, and in Group VI, chromium and sulphur are brought together, though the differences between them in physical and chemical properties are quite as striking as their resemblances.

Very little thought will bring to light the real nature of the periodicities in the Mendeléef Table of the elements. The recurrences on which such stress is laid are not necessarily *chemical* analogies; they are *valency* resemblances. Boron and aluminium yield the chlorides BCl_3 and $AlCl_3$; and this trivalency of the two elements is sufficient to persuade us that they are in some way alike, although the properties of the chlorides are entirely different.* Similarly, though silica and carbon dioxide differ greatly in properties, we are quite ready to trace an analogy between them, on the ground that their respective formulæ are CO_2 and SiO_2, which have an obvious resemblance. Again, the formula-resemblance of K_2CrO_4 and K_2SO_4 suggests an analogy, which is only partial if the whole chemical properties of the two salts be taken into account.

The true periodicity in the Mendeléef Table, then, is one which depends on valency rather than on the complete analogy of chemical properties; and if the secret of the table is to be found, it must be sought for in that region of the atom which controls the valency of the atomic system. In modern theories, this region is the outer sphere of the atomic system, the group of electrons which lies outside the nucleus and which serves to neutralise the surplus positive charge at the centre of the atom.

On this reasoning, the chemical character of a given element is controlled by two factors: (1) the surplus positive nuclear charge, which is termed the atomic number; and (2) the electronic grouping in the outer zone of the atom, which is connected with valency. The second factor determines the Group of the Periodic Table into which an element will fall; whilst the first factor settles the position which the given element will occupy among its congeners in that particular Group.

At the present day, the problem of the outer sphere of the atom is being attacked from two different points of view. The chemical requirements—with which we are mainly concerned here—seem to demand a static grouping; whereas the majority of physicists, with emission spectra in their minds, tend to follow Bohr and regard the electronic zone of the atom as a system in movement. In the following pages, the static atom will be described, as the dynamic model, which has not as yet proved

* On the other hand, ferric iron and aluminium are in different groups although they have quite marked similarities in some respects.

of much assistance to the chemist, has already been dealt with in Chapter II.

2. *Polar and Non-Polar Compounds*

Before dealing with the details of the model atom's outer sphere, it is necessary to draw attention to some fundamental peculiarities of the atomic systems; for from these it is possible to determine the essentials which must be embodied in a model atomic structure if it is to fit the known facts.

In the first place, a comparison of a hydrocarbon such as methane with a normal salt like sodium chloride will bring to light immediately the fact that compounds seem to be divisible into two main groups: for sodium chloride yields charged ions when it is fused or dissolved in alcohol, whereas methane shows but little sign of breaking up ionically under the same conditions. Further consideration will show, however, that there is no rigid separation of matter on these lines. Acetic acid combines the qualities of methane with those of an ordinary acid, so that logically it belongs to both groups: the hydrogen atoms of the methyl radicle are non-ionisable, whereas the hydrogen of the carboxyl group is easily separated in ionic form from the rest of the molecule. Nevertheless, when extreme cases are taken as examples, it is possible to see very marked distinctions between the properties of polar compounds such as sodium chloride on the one hand, and non-polar materials like methane on the other.

G. N. Lewis [1] has grouped together the main characteristics of the two extreme types in the following table:

Polar Type	Non-Polar Type
Mobile	Immobile
Reactive	Inert
Condensed structure	Frame structure
Tautomerism	Isomerism
Electrophiles	Non-electrophiles
Ionised	Not ionised
Ionising solvents	Not ionising solvents
High dielectric constant	Low dielectric constant
Molecular complexes	No molecular complexes
Association	No association
Abnormal liquids	Normal liquids

In G. N. Lewis's view, all these differences can be accounted for on a single hypothesis, viz., that in the case of the non-polar

[1] G. N. Lewis, *J. Amer. Chem. Soc.*, 1913, **35**, 1448; compare Bray and Branch, *ibid.*, 1440; Thomson, *Phil. Mag.*, 1914, **27**, 757.

molecules the electrons of the structure are firmly held in place by certain (unknown) forces; whereas in the polar class, one or more electrons are only weakly held and are thus able to leave their original places in the atomic grouping; and in the extreme case of ionising molecules, these electrons may actually become entirely detached from their primal positions and pass completely into the structure of another atom. On this basis, the gradual shading of the non-polar into the polar type of molecule corresponds simply to a loosening of the rigidity of the atomic structure ending, in the extreme polar type, in an actual passing of an electron from its original atom into the system of a second atom.

3. *Normal Valencies and Contra-valencies*

A second general idea must now be described, which is due to Abegg and Bodländer.[1] According to them, every element possesses a maximum positive and a maximum negative valency. The numerical value of the positive valencies is the same as the number of the group in the Periodic Table which contains the element; and the sum of the positive and negative valencies is invariably 8. When the valencies (whether positive or negative) amount to less than 4, they are named *normal valencies;* when their number exceeds 4, they are termed *contra-valencies.* The following table shows the relations of valencies and contra-valencies through a Short Series of the Periodic Table:

Group.	I.	II.	III.	IV.	V.	VI.	VII.
Element	Na	Mg	Al	Si	P	S	Cl
Normal valencies	+1	+2	+3	+4	−3	−2	−1
Contra-valencies	−7	−6	−5	−4	+5	+6	+7

Thus chlorine possesses one negative normal valency corresponding to its action in forming HCl, and seven positive contra-valencies which come into action during the forming of Cl_2O_7. On Abegg's view, when a normal valency is in action, a corresponding contra-valency is extinguished. Further, an atom does not necessarily exercise its full valency, either positive or negative; and the higher the atomic weight becomes, the more do the normal valencies diminish in activity, whilst concurrently the contra-valencies grow active. Thus in the case of fluorine, the negative normal valency is strong; whereas in the heavier

[1] Abegg and Bodländer, *Z. anorg. Chem.*, 1899, **20**, 453; Abegg, *ibid.*, 1904 **39**, 330.

atom of iodine it is weaker, as can be seen by comparing HF with HI. On the other hand, the seven contra-valencies of fluorine show no sign of their existence, since fluorine forms no compound with oxygen; whilst the whole seven contra-valencies of iodine play their parts in the formation of I_2O_7.

At the time of its original publication, the Abegg-Bodländer hypothesis seemed to be a mere guess; for even in the first Short Series of the Periodic Table it demanded the existence of a number of valencies for which no experimental evidence could be adduced.* When the modern theory of the atom is considered, later in this chapter, however, it will be found that the views of Abegg and Bodländer dovetail neatly into their proper place in the scheme.

4. *The Inert Gas Group*

It has already been pointed out more than once that the atomic number of an element is believed to be the same as the number of electrons in the outer sphere of the atom; and the problem before us at present is to discover, if possible, the manner in which these electrons are arranged around the nucleus.

Now there is one set of elements which suggests itself at once as a good starting-point in any discussion of this question: the inert gases of the Zero Group. There are two main reasons why this group is of importance for the present purpose. In the first place, the inert gases show no changes in valency; and thus the matter is freed from the minor complexities which are offered by elements such as nitrogen or sulphur: and, in the second place, the inert gases evidently contain the most stable types of atomic systems, since no inert gas has ever been known to take part in a chemical reaction.

The atomic numbers of the inert gases are as follows:

Helium	= 2
Neon	=10
Argon	=18
Krypton	=36
Xenon	=54
Radon	=86

At the first glance, these numbers suggest nothing; but Ryd-

* *E.g.* seven negative valencies for lithium and seven positive valencies for fluorine.

berg [1] pointed out that they can be reconstructed so as to indicate a certain regularity in their progression:

Helium $= 2 = 2(1^2)$
Neon $= 10 = 2(1^2+2^2)$
Argon $= 18 = 2(1^2+2^2+2^2)$
Krypton $= 36 = 2(1^2+2^2+2^2+3^2)$
Xenon $= 54 = 2(1^2+2^2+2^2+3^2+3^2)$
Radon $= 86 = 2(1^2+2^2+2^2+3^2+3^2+4^2)$

The atomic numbers of the inert gases are thus seen to fall into a peculiar series * built up from the squares of the integers 1, 2, 3, etc. The regularity of the series is such that it can hardly be dismissed as a mere matter of chance; and some account of it must be taken in the course of any attempt to deal with the grouping of electrons in the outer atomic region.

Rydberg drew the inference that a natural grouping of the elements should correspond to the gradual development of the mathematical series which he had discovered; and he therefore suggested that, if each of the inert gases be taken as the end of an elemental series, then the elements will fall into the following grouping: (1) a series of eight members ending with neon; (2) a series of eight elements ending with argon; (3) a series of eighteen elements ending with krypton; (4) a series of eighteen elements ending with xenon; (5) a series of thirty-two elements ending with radon. As is now known from the experimental determination of X-ray frequencies, the number of the elements intervening between the various inert gases corresponds exactly to Rydberg's requirements. We are thus led to group the elements from lithium onwards in the following way: two series of 8; two series of 18; a series of 32. Thereafter comes an incomplete set of elements ending with uranium, a series which, as Soddy [2] pointed out, does not run parallel with the one immediately preceding it, but instead shows a marked analogy with the set of elements beginning with rubidium.

The origin of the Rydberg series is still undiscovered. All that can be inferred from it is that particular numbers of electrons

[1] Rydberg, *Phil. Mag.*, 1914, **28**, 144.

* The series proposed by Rydberg was actually more regular, as he introduced two unknown elements with atomic numbers 2 and 3, between hydrogen and helium, thus making helium No. 4, neon No. 12, argon No. 20, etc. On this basis, the series took the form:

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

[2] Soddy, *Ann. Reports*, 1916, **13**, 254.

represent stable groupings in the atom; and that these stable groupings bear a certain simple relationship to one another. Why these particular groupings of electrons are stable, whilst others are unstable, is a problem which at present lies beyond our analysis. We have simply to take the facts and try to use them in the construction of model atoms, without seeking to discover the ultimate cause of stability in these specially inert electronic arrangements.

5. *Kossel's Views*

Almost simultaneously, Kossel [1] and G. N. Lewis [2] published suggestions which, though differing in some respects, contain certain common ground. As Kossel's ideas do not go so far as those of G. N. Lewis, it will be best to consider them first and take up Lewis's views in more detail in a later section.

Kossel put forward the idea that the electrons of the outer atomic zone were disposed in a series of "shells." In passing along the elemental sequence, each fresh atom contains one electron more than its predecessor; and Kossel suggested that the opening of each fresh period in the Table corresponded to the birth of a new "shell" in the atomic structure. On his view, hydrogen has a single shell containing one electron; helium has the same shell with a pair of electrons in it. The opening of the next period demands the formation of a fresh shell, external to the first; and in the case of lithium this second shell will contain a single electron. The glucinum atom will be built up on similar lines: it will contain an inner shell of two electrons, whilst the outer shell will also contain a pair of electrons. The boron atom will have the helium two-electron shell like the others; and its outer shell will contain three electrons. At the end of this period comes neon, wherein the second shell contains eight electrons and is supposed by Kossel to be then complete. The next alkali, sodiu,m is built up analogously to lithium by beginning a fresh shell with one electron in it; so that the sodium atom contains: (1) the helium shell with two electrons; (2) a second shell with eight electrons; and (3) an outer shell with one electron.

Kossel's hypothesis, reduced to its simplest terms, contains

[1] Kossel, *Ann. Physik*, 1916, **49**, 229; see also Kossel, *Valenzkräfte und Röntgenspektren* (1921).

[2] G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; see also G. N. Lewis, *Valence and Structure of Atoms and Molecules* (1923).

two germs of thought on atomic structure. In the first place, it pictures the outer sphere of the atom as containing a series of zones or shells, each of which can contain a definite maximum number of electrons, and of which only the outermost shell can contain less than the possible maximum. Secondly, it yields for the elements up to manganese a model with an outermost shell containing a number of electrons equal to the maximum valency of the atom. It is also worth noticing that Kossel's arrangement groups the electrons into a series of sets; and the numbers in these sets correspond, on Kossel's postulates, to the numbers in the Rydberg atomic number series which has just been discussed.

Kossel's views on chemical combination must now be examined, at least so far as they are concerned with simple compounds. They are based upon the idea that the electronic

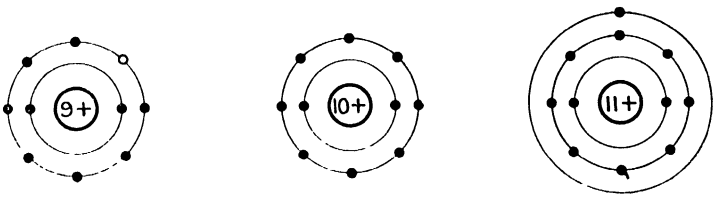


FIG. 15.

groupings of the inert gases represent the most stable arrangements of the atomic system; and that all other arrangements of electrons will strive to bring themselves into line with the inert gas type if it is possible for them to do so. For example, the diagram (Fig. 15) represents the Kossel models of fluorine, neon, and sodium.

The electrons are shown as black dots (the vacant place in fluorine being marked by a small circle), and the various regions by the circles on which the dots lie. Inspection of the diagram will make it obvious that if the sodium atom were to lose the electron from its outermost ring, it would then revert to a form with eight electrons in its new outermost ring; and that this, superficially, would resemble the arrangement in the neon system.* On the other hand, fluorine has only seven electrons

* The two systems are of course not identical, since neon has a nucleus with only ten surplus positive charges on it, whereas the sodium nucleus has eleven surplus positive charges. The resemblance is merely in the electronic region.

in its outer sphere; and if it could acquire an electron from outside, it would then possess the "magic number" of eight electrons in its outer zone; and would thus become identical in electronic arrangement with neon.

Thus by losing an electron, sodium becomes an electronic analogue of neon; and the same will happen to fluorine if it can gain an electron. But these changes are exactly what occurs when the atoms are converted into ions. Sodium ion is sodium atom minus an electron; fluorine ion is fluorine atom plus an electron. Thus the process of ionisation, on Kossel's view, is

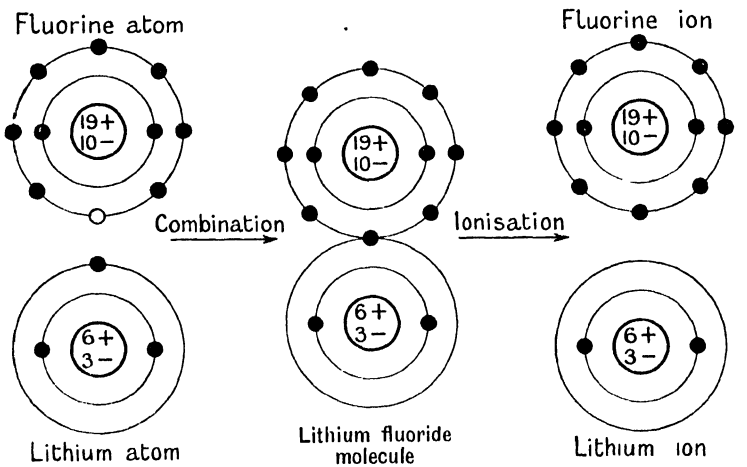


FIG. 16.

simply a reversion of the atom to an electronic analogue of the nearest inert gas. In the case of glucinum, for example, since there are two electrons in the outermost ring, the atom must lose both of these if it is to revert to the inert gas form of helium; whereas in the case of oxygen, two electrons must be picked up from somewhere if the system is to become the electronic analogue of neon. Thus the elements which yield positive ions tend to yield up electrons and revert to the type of the next lower inert gas; whilst elements producing negative ions tend to acquire electrons sufficient to make their electronic system resemble that of the next higher member of the Zero Group.

From the foregoing, it is an easy matter to symbolise Kossel's ideas of chemical combination and ionisation (see Fig. 16). The

two atoms, one with an extra electron in its outer zone, the other with a deficit of one electron as compared with the analogous inert gas atom, meet together. By the passing of one electron from atom to atom, chemical combination takes place; and thereafter, by a separation of the two systems, ionisation occurs, resulting in the production of two electronic analogues of helium and neon.*

It is worthy of special attention that Kossel implicitly suggests that only one electron is concerned in the union of two monovalent atoms. It is at this point especially that his ideas differ fundamentally from those of G. N. Lewis, which will be described in the following section.

6. *The Theory of G. N. Lewis*

By one of those coincidences which occur so frequently in the history of science, the appearance of Kossel's paper on the structure of atoms synchronised almost exactly with the publication of a much more far-reaching treatise on the same subject by G. N. Lewis.[1] Kossel's paper contained a germ of truth; but in Lewis's memoir a similar root-idea was developed on a much wider scale, and the views of Lewis have to a large extent moulded current chemical conceptions of atomic structure and the mechanism of chemical combination between atoms. Lewis's system of atomic architecture is based upon the following assumptions:

(1) Every atom contains a nucleus which remains unaltered in all ordinary chemical changes and which possesses an excess of positive charges corresponding in number to the atomic number of the atom.

(2) The atom is composed of a nucleus and a shell which, in the case of a neutral atom, contains negative electrons equal in number to the excess of positive charges in the nucleus; but the number of electrons in the shell may vary during chemical change between 0 and 8.

(3) The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons, which are normally arranged at the eight corners of a cube.

* This is obviously a mere restatement of Sir J. J. Thomson's early views on the same question. See his *Corpuscular Theory of Matter* (1907).

[1] G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.

(4) Two atomic shells are mutually interpenetrable.

(5) Electrons may ordinarily pass readily from one position to another on the outer shell, though they are held in position by rigid constraints determined by the nature of the atom and of other atoms with which it may be combined.

(6) Electrical forces between closely adjacent particles do not obey the law of inverse squares.

One or two comments on these assumptions may throw a little more light on the subject.

The first assumption is, of course, common ground to all modern hypotheses of atomic structure. The second assumption in its first clause also deals with common ground; but the second clause presents something new. It will be remembered that Kossel's ideas yielded a series of zones in the atom wherein the numbers of electrons corresponded to successive terms of the Rydberg quadratic series. This conception, though it sufficed to divide the elements into sets terminating with inert gases, failed to throw any light upon the fact that the Mendeléef Table shows certain analogies between corresponding elements of the A and B sub-groups. G. N. Lewis's hypothesis involves a periodicity based on a series of 8; and thus promises to go much further than Kossel's view could do. On this ground, Lewis's views have often been termed the Octet Theory; but Lewis himself [1] objects to this terminology on the ground that it over-emphasises what is, after all, only one feature of this new view of valency. The title Octet Theory, however, is a convenient one for descriptive purposes, and will serve well enough if it is not used in a misleading way to suggest that the theory depends on the matter of octets; for, as will be seen later, there are exceptions to the rule of eight.

Much more important than the rule of eight is the third assumption which lays stress upon the peculiar stability of groupings of *even* numbers of electrons in the atomic shell. On Lewis's view, chemical bonds between atoms are formed by *pairs* of electrons; and hence the even-number rule is related to the fundamental processes of chemistry.

The second proviso in the third assumption again differentiates Lewis's views from those of Kossel; since it implies a three-dimensional grouping of the electrons within the atom, whereas

[1] G. N. Lewis, *Valence*, p. 97 (1923).

Kossel's " zones " might have contained all the electrons in a plane.

The fourth assumption of Lewis is necessary in order to allow the formation of triple bonds in carbon compounds; and the fifth assumption is needed to account for the tetrahedral grouping which is believed to exist in optically active molecules derived from quadrivalent elements such as carbon, sulphur, tin, etc.

The sixth assumption hardly concerns us here. It is obvious that the state of affairs in the atomic nucleus, for example, can hardly be reconciled with ordinary laws of attraction and repulsion; so there is no reason why Lewis's postulate should not be granted.

On the basis of these assumptions, Lewis suggested a very simple atomic structure of the following type. The electrons

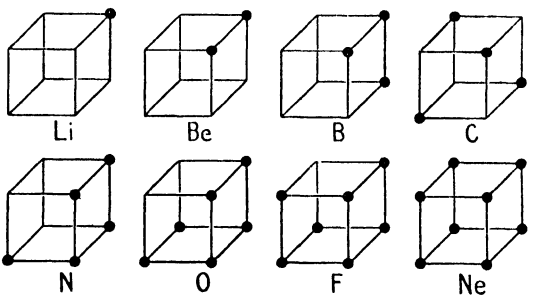


FIG. 17.

of the atom are arranged about the nucleus in concentric shells; and those electrons which occupy the outermost shell are termed valency electrons. The *valency shell* of a free (uncombined) atom never contains more then eight electrons. The remainder of the atom—which includes the nucleus and the inner shells—is called the *kernel*. In the inert gas atoms there is no valency shell; and the whole atom is regarded as a kernel. Thus, if the helium atom be taken as a starting-point, the elements of the first short period can be constructed by placing 1, 2, 3 . . . 8 electrons in an outer valency shell, each electron being situated at one corner of an imaginary cube; and when the eighth electron is in place, the shell is completed and we have a model of the neon atom which—like the helium atom—is a complete kernel without any detachable valency electrons. Omitting the inner helium kernel for the sake of simplicity, the diagrams (Fig. 17)

show the structures of the valency shells of the elements from lithium to neon.

A comparison between the table on p. 179 and the atomic structures in Fig. 17 will bring to light an interesting point. In the valency shell of the Lewis atom there are eight points which can be occupied by electrons. This corresponds to the number 8, which is the sum of Abegg's normal valencies plus contra-valencies. The numbers of electrons in the valency shell of the Lewis atom correspond to the positive figures in Abegg's table, whilst the number of unoccupied corners in the Lewis cube corresponds to the number of negative valencies assumed by Abegg for the atom under examination. For example, on Abegg's scheme, nitrogen has five contra-valencies; whilst in the Lewis atom there are five electrons in the valency shell; and Abegg

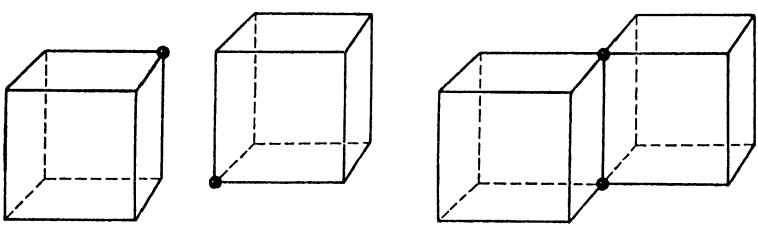


FIG. 18.

allows three negative valencies for nitrogen, which corresponds to the three vacant points at the corners of the Lewis cube. Again, in the case of glucinum, Abegg assumes two normal and six contra-valencies; and this corresponds to the two electrons and six vacant corners in the cubical arrangement.

The Lewis atom thus includes in its structure a possible origin of the phenomena indicated by Abegg; and, further, it give us a definite mechanical model instead of the rather vague conception which was all that Abegg's view could provide.

Having now a clear conception of the Lewis atom before us, we must turn next to the question of chemical combination between two or more atoms and see how this union is symbolised by Lewis. Since the hydrogen molecule is the simplest compound of all, it will be convenient to begin with it.

In Fig. 18 two things can be seen on inspection. In the first place, the union of the two atoms has resulted in the formation of a system in which *the two electrons* are held in common

by both atoms, for they may be considered as forming part of either atomic system. And in the second place, this combination has resulted in the formation of a shell containing two electrons, *i.e.* a shell corresponding to the shell of the inert gas helium which also contains two electrons.

The first of these conceptions is the most important part of Lewis's contribution to our ideas of valency. It suggests that in order to form a single bond between two atoms, *a pair of electrons* is required; and, further, that these two electrons are " shared " between the two atomic systems * (or are common to both systems, if that wording be preferred).

Consideration must now be given to a more complex case: the combination of sodium and chlorine to form sodium chloride, and the subsequent disruption of the molecule into ions of opposite charge. The outer shells of the atoms are all that need be considered, in order to keep the diagram simple (see Fig. 19).

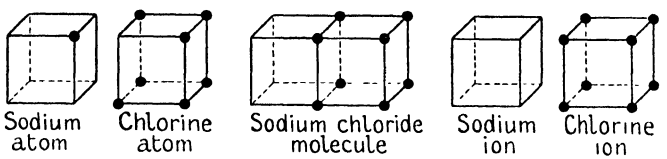


FIG. 19

On the left of the diagram, the sodium atom is shown with its single electron in the outer shell and the chlorine atom with its seven electrons and one vacant corner on the cube. The central part of the diagram shows how these two systems can fit together so as to form a cubical grouping of eight electrons. If this arrangement be examined, it will be found that the chlorine half contains a complete octet. The sodium half has the pseudo-neon shell of ten electrons, though this inner shell is not shown in the diagram; and the single bond of Na-Cl is represented by two electrons which are common to the two shells. On the right of the diagram is shown the result of ionisation. The two shells have fallen apart and the electron previously associated with the sodium shell has drifted into the chlorine shell. Thus

* This idea of shared electrons was adumbrated by Ramsay (Presidential Address to the Chemical Society, *J.*, 1908, **93**, 774) and developed by Stark (*Prinzipien d. Atomdynamik*, III (1910)) into a somewhat grotesque form; but Lewis was the first to make it generally accepted.

the original outer shell of the sodium system now contains no electron, and its inner grouping is an electronic analogue of neon; whilst the chlorine shell has acquired its full possible total of eight electrons, and thus it also has a grouping analogous to that of an inert gas atom. There is, however, no identity between these ions and the atoms of inert gases: for by the loss of its electron the sodium system has acquired a single positive charge; and the chlorine system, by gaining an electron, has received an extra negative charge. Thus Lewis's model agrees with the experimental facts that sodium ion is entirely different from metallic sodium, and that the metallic and acidic ions carry opposite charges.

Since the single bond between two atoms is represented by a pair of electrons held in common by the two systems, it is obvious that a double bond will be represented by four electrons shared between two systems. Thus the ethylenic bond between two carbon atoms can be represented as shown in Fig. 20.

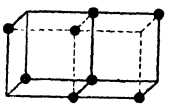


FIG. 20.

The triple bond between two atoms should, by analogy, be represented on Lewis's theory by three pairs of electrons held in common by the two united systems; but Lewis [1] is inclined to leave the question open for the present, since it is possible to symbolise the treble linkage in other ways.

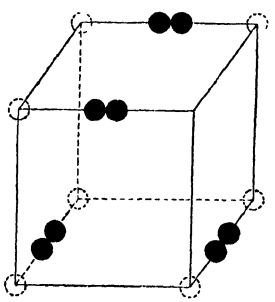


FIG. 21.

It may be recalled that Lewis, in his fifth postulate, left a loophole open for a possible movement of the electrons out of the cubic arrangement. In order to account for the tetrahedral grouping in optically active compounds of carbon, he assumes that the eight electrons in the system of a saturated carbon atom may move along the sides of the cube so as to take up fresh positions as shown by the black circles in Fig. 21, in which the original positions are indicated by dotted circles.

The diagrammatic representation of the cubic atom would occupy too much space for general printing purposes; and Lewis

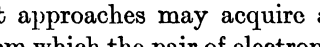
[1] Lewis, *Valence*, p. 93 (1923).

has proposed a symbolic method of expressing his ideas more compactly. In this system, the electrons of an octet are represented by dots arranged in pairs around the symbol of the atom. For example, the formulæ of methane and carbon tetrachloride are written as follows :

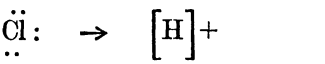


This form of expression brings out clearly another refinement of the Lewis theory which is apt to be obscured when the cubical representation is employed. In Lewis's view, the pair of electrons which constitutes the single valency bond may lie between two atomic centres in such a way that there is no electric polarisation ; or it may be shifted towards one atom or the other, in which case the atom which it approaches may acquire a negative charge, whilst the atom from which the pair of electrons recedes may gain a positive charge if the process reaches its limit, and ionisation occurs. The simplicity of Lewis's mode of representation can be seen from one or two concrete examples.

He imagines that in the normal hydrogen molecule, the electron pair is symmetrically placed between the two atoms ; whereas in sodium hydride, the bonding pair of electrons lies nearer to the hydrogen than to the sodium, making the hydrogen negative :



In the case of hydrochloric acid the electronic pair lies near the chlorine, leaving the hydrogen with a positive charge ; and in an ionising solvent, the displacement is complete and the two oppositely-charged portions separate from each other :



The ammonium ion, on Lewis's assumptions, furnishes an interesting parallel to the methane molecule :



Thus the optical activity of ammonium compounds in which

four different alkyl radicles are attached to the nitrogen is brought by Lewis into harmony with the case of the asymmetric carbon atom, which is also attached to four different groups.

7. *The Langmuir Model Atom*

Before Lewis had carried his suggestions further, Langmuir [1] published a paper on the atom which contained an extension of Lewis's theory. Langmuir's views have not passed without criticism; but, whether they be right or wrong, it is undeniable that they attracted general attention, and the discussion of them has stimulated interest in the whole problem.

Langmuir's starting-point is the Rydberg [2] analysis of the atomic numbers of the inert gases into the series:

$$N=2(1^2+2^2+2^2+3^2+3^2+4^2 \ldots)$$

and in the factor 2 he found the suggestion of a twofold symmetry existing in the structure of the inert gas atoms. He was thus led to the idea that in the atoms of the inert gases the electrons of the outer region occupy positions symmetrical with respect to a plane, termed by him the equatorial plane, which passes through the atomic nucleus. Perpendicular to the equatorial plane, he imagines a polar axis; and he further postulates four secondary planes of symmetry each containing the polar axis, and forming angles of 45° with each other. As can be seen, this model has the symmetry of a tetragonal crystal. Since the electrons are assumed to occur in pairs symmetrically placed with respect to the equatorial plane, it is evident that this plane contains none of the electrons.

A slight complexity now enters into the model. It is necessary to imagine a series of spherical * shells describing around the atomic nucleus as a centre and having their radii proportional respectively to the terms of the arithmetical series: 1, 2, 3, 4 . . . The surfaces of the shells will thus be respectively proportional to 1^2, 2^2, 3^2, 4^2 . . .

All the shells in a given atom are assumed to be of the same thickness; and each spherical shell is supposed to be divided

[1] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 868.

[2] Rydberg, *Phil. Mag.*, 1914, **28**, 144.

* Spheres are chosen for simplicity in presentation; but the argument will apply equally well if the shells be ellipsoidal.

into a number of cells proportional to the surface area of the shell. It follows that all the cells in a given atom have equal volumes.

The innermost shell of any atom, therefore, contains two cells which are obtained by dividing the sphere into hemispheres by means of the equatorial plane. The next shell, with radius 2, has four times the surface of the innermost shell; and it therefore contains eight cells. Fig. 22 shows the outer cells of the neon

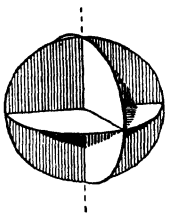


FIG. 22. — Outer Shell of Neon with Eight Cells.

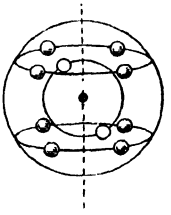


FIG. 23.—Neon Atom.

(*From Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry."*)

atom and Fig. 23 the arrangement of electrons in neon. The third shell, with nine times the surface of the innermost shell, has eighteen cells; whilst the fourth shell contains thirty-two cells. If either half of the model be examined (using the equatorial plane as the division between the two halves) 1, 4, 9, and 16 electrons, *i.e.* 1^2, 2^2, 3^2, and 4^2, will be found in successive shells; and it becomes clear that the Langmuir model is coming into touch with Rydberg's series of factors.

Now comes a postulate of Langmuir which has been subjected to criticism. Each of the innermost cells can contain only one electron, but any other cell in the atom can hold two electrons. *There can be no electrons in the outside shell until all the inner shells contain their maximum number of electrons.* In an outside shell, two electrons can occupy a single cell only when all the other cells contain at least one electron each.

Another postulate, which has met with even more severe criticism, states that two electrons in the same cell do not attract or repel each other * strongly; but electrons in the outer shell

* Langmuir postulates a magnetic attraction between electrons at close quarters which practically counterbalances the electrostatic repulsion between them.

repel each other and thus tend to arrange themselves among the vacant cells of this shell so as to be as far apart as possible. At the same time, they are assumed to have a tendency to line themselves up radially with the electrons in the underlying shell. The position taken up by an electron in the outermost shell (when that shell does not contain its full cargo of electrons) is thus governed by the interplay of three forces: (1) a magnetic attraction of the inner electrons which tends to line up the outer electrons radially with the inner set; (2) an electrostatic repulsion between electrons in the outer shell and those belonging to the inner layers, which tends to move the two sets apart; and (3) an electrostatic repulsion between electrons of the outer layer which tends to move them into positions as far from each other as possible in the same shell. Finally, (4) two electrons in the same cell have next to no effect upon one another.

It is clear that (4) is in contradiction with all our knowledge of electronic behaviour; (1) is an assumption of doubtful value, since there are no means of establishing its plausibility; (2) and (3) are in agreement without normal ideas of the electron. It is perhaps unfair to go so far as one critic has done, and to state that "the electrons of the Langmuir atom have in fact so few of the known properties of electrons that it is not immediately clear why they are called electrons at all"; but it may be reasonably said that the mechanism devised seems to be rather complicated.

In the remainder of his hypothesis, Langmuir employs the ideas of Lewis with regard to the sharing of pairs of electrons and the stability of the electronic octet. Since we have already indicated the application of these to the two short Periods in the Periodic Table, it will be sufficient here to consider Langmuir's views on the first long Period, beginning with potassium.

The argon atom is assumed to contain at its core the helium nucleus of two electrons, surrounded by the octet of electrons which makes up the outer zone of the neon atom, and by the outermost shell of eight electrons which completes the stable octet and brings the total up to 18, which is the atomic number of argon. In order to add the extra electron which potassium contains, it is necessary to begin a fresh outer shell which, on Langmuir's hypothesis, will eventually contain nine electrons in each hemisphere.

The first few electrons are assumed to arrange themselves

much in the same way as in the first two Periods, so that potassium, calcium, and scandium atoms have groupings in their outer shells similar to those of sodium, magnesium, and aluminium. But at this point the two Periods differ from each other. In the short Periods, the atoms of elements up to Group IV can revert to a pseudo-form of the inert gas type by losing 1, 2, or 3 electrons from the outer shell; and the elements after Group IV can also attain to the inert gas type by assimilating 3, 2, and 1 electrons into their systems. In the first long Period, however, the eighth element of the Period, iron, has no completed outer shell like an inert gas atom; for it contains only eight electrons distributed among eighteen cells. Its stability is therefore not comparable to that of an inert gas atom; and hence the assimilation of electrons by the atoms of titanium, vanadium, etc., would not yield a stable system on the completion of the octet in pseudo-iron. There is, therefore, according to Langmuir, no reason why these atoms should strive to take up electrons for the completion of the octet; and thus the atoms remain predominantly positive in electrochemical character.

Potassium, calcium, and scandium give up their electrons readily in order to revert to the pseudo-argon type. The case of vanadium, chromium, and manganese, however, is not so simple. In order to revert to pseudo-argon types, these atoms would have to give up respectively 5, 6, and 7 electrons; and Langmuir believes that the electrostatic forces at work are sufficient to prevent the formation of ions carrying such large charges. In practice it is found that these elements form divalent or trivalent cations; but yield no monovalent or quadrivalent ions; and from this Langmuir draws the inference that the stability of the electronic arrangements in these atoms is very nearly the same. This he explains by assuming that the tendency of the electrons to line up radially with those in the interior shell is conflicting with the mutual electrostatic repulsion; so that, according to him, the various atoms should not differ greatly in their tendency to give up electrons.

The state of affairs in the iron atom may now be considered. Langmuir pictures its system as follows. Close to the nucleus are two electrons. The remaining 24 electrons of the system are arranged in three layers at the corners of three concentric cubes, the diagonals of which coincide with each other. This

system possesses a degree of symmetry comparable to that of the argon system; but it differs from the latter in that all the cells of the outer shell are not occupied, only four cells out of nine in each hemisphere being filled. The eight electrons of the outer shell, however, according to Langmuir, are exerting strong repulsive forces on each other, tending to drive each other out of the system and thus the system is unstable; and in this state of affairs he sees the reason why chromium and manganese do not exhibit the electronegative qualities of sulphur and chlorine.

On passing to cobalt and nickel, a new factor enters into the problem. The eight electrons of iron's outer shell could arrange themselves radially over the eight electrons of the next inner shell of the atom; but cobalt has nine electrons in its outer shell and nickel has ten; so that there are too many electrons for the radial grouping's formation. In the nickel atom, each outer hemisphere contains five electrons instead of the four in the shell below; and Langmuir suggests that the extra electron takes up its position at the extremity of the polar axis, whilst the remaining four station themselves radially above the four electrons of the inner hemisphere. In cobalt one end of the polar axis is occupied by an electron whilst the other pole is unoccupied.

At this point, Langmuir brings in a subsidiary hypothesis. He assumes that the other shell of the nickel atom can revolve about the polar axis through an angle of 45°, whilst the inner shells remain unmoved. This new grouping he terms the β-form of the nickel atom, whilst the original one is called the α-form. This β-form arrangement has a high degree of symmetry; and Langmuir assumes that the elements of the Period immediately above nickel will tend to give up electrons and revert to the pseudo-nickel arrangement. He thus accounts for the valencies of the remaining elements from copper to bromine. Cuprous copper, for example, can lose one electron and revert to the pseudo-nickel grouping; zinc can do the same by a loss of two electrons, etc. At the extreme end of the Period, we are approaching the completion of the shell by filling up the cells; and hence the tendency in elements like selenium and bromine is to equip themselves with extra electrons and form the pseudo-system corresponding to the next inert gas krypton, just as sulphur and chlorine tended to complete their octets by taking up electrons from the outside.

The foregoing summary gives only an outline of the ideas put forward by Langmuir; and, of necessity, some of his reasoning has been omitted. It is sufficient, however, to show that he has made a bold—and apparently partially successful—attempt to account for some of the most difficult points which present themselves when the Periodic Table is examined. At the same time, it must be admitted that even Langmuir himself has had to abandon the case of the last long Period as inexplicable on his hypothesis. The succession of elements beginning with radon is exactly analogous to that which begins with krypton and does not follow the same lines as the series starting with xenon and including the rare earth group; but on Langmuir's hypothesis, radon set ought to run parallel to xenon and its successors and to include from Group III onwards a number of radioactive congeners of praseodymium, etc., for which no place can be found in Moseley's series of atomic numbers.

8. *The Bury Model Atom*

Bury [1] has suggested a modification of Langmuir's hypothesis which rescues it from some of its obvious difficulties. The basis of this new idea is as follows. The maximum number of electrons in each atomic layer is proportional to the surface of the layer; so that successive layers can contain, respectively, 2, 8, 18, and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when the layer is capable of containing a large number of electrons. The maximum number of electrons in the outer layer is 8; more than 8 electrons can exist in a layer only when there is an accumulation of electrons in the outer layer. During the change in an inner layer from a stable group of 8 to one of 18 electrons, or from 18 to 32, there comes into existence a transition series of elements whose atoms may have more than one structure.

From the foregoing, it is evident that Bury's view differs from that of Langmuir in several crucial matters. In the first place, the idea of cells disappears; and with it goes the difficulty of two electrons lying passively together in the same cell. Secondly, while Langmuir insists that all the inner shells of an atom must be fully occupied by electrons before an outer shell can be begun, Bury demands that as soon as eight electrons have

[1] Bury, *J. Amer. Chem. Soc.*, 1921, **43**, 1602.

been placed in a shell a fresh outer shell must be formed and must contain some electrons before the number in the inner shell can be raised above eight, even when this inner shell is capable of holding, say, eighteen electrons. In other words, for an element of a given atomic number, Langmuir postulates a fixed atomic structure with all layers completed except the last, whereas Bury suggests a possibility of fluctuation in the arrangement in the two exterior layers, which may both be incompletely provided with electrons. Thirdly, Bury ascribes a peculiar stability to octets of electrons, apart altogether from the capacity of the layer in which they lie; whereas Langmuir admits stability only when the layer has attained its full electronic load. Finally, by his insistence on a maximum of eight electrons in the outermost layer of any atom, Bury retains the simplicity of the Lewis cubical atom, which was submerged in the complexities of the electronic arrangements demanded by Langmuir's models.

Some examples will indicate the results to which Bury's reasoning leads. For the elements up to neon, his model is identical with Langmuir's, so far as distribution of electrons is concerned, since each of them contains a pair of electrons at the core and a layer of eight electrons as an outer sheath. With the next element, sodium, however, a divergence in plan occurs. Langmuir's sodium model is obtained by placing the extra necessary electron in one of the cells of his outer shell which is already occupied by an electron; Bury, on the other hand, begins *a fresh layer* of electrons which will eventually contain eighteen.

Bury's model of the sodium atom thus contains 2 electrons in its innermost layer, 8 in the next layer, and 1 in the new outermost layer. This grouping may be symbolised by the expression (2, 8, 1). Magnesium contains an extra electron in the outermost layer, so that the corresponding expression is (2, 8, 2). Continuing in this manner, we reach argon, with a system expressed by (2, 8, 8). At this point the most striking difference between Langmuir and Bury is reached. Since Bury's electronic layer is capable of containing ten more electrons it could not, on Langmuir's view, represent the completely stable grouping characteristic of the inert gases. On Bury's assumptions, however, the octet of electrons in the outer layer is a stable system, quite apart from the question of whether or not the layer is completely filled up.

With the next elements, a further divergence between Bury and Langmuir becomes evident. On Langmuir's view, since there are still vacant places in the outermost layer, these ought to be filled up before a further exterior layer is begun. Bury, however, assumes that as soon as any layer—no matter what its full capacity may be—contains eight electrons, a new exterior layer must come into existence. On this basis, Bury places the next electron in a fresh layer ; and the system of potassium thus becomes representable by (2, 8, 8, 1). Calcium and scandium are respectively (2, 8, 8, 2) and (2, 8, 8, 3).

We now reach a series of " interpolated " elements beginning with titanium, elements which do not form exact analogies with the elements previously placed in like Groups of the Table. Carbon and silicon are invariably quadrivalent in their simple compounds ; whereas titanium forms three chlorides with the formulæ : $TiCl_2$, $TiCl_3$, and $TiCl_4$. The titanium atom must therefore be capable of parting with 2, 3, or 4 valency electrons. In order to account for these facts, Bury postulates a series of alternative groupings of the titanium system :

(2, 8, 8, 4) (2, 8, 9, 3) (2, 8, 10, 2)

Thus in the outermost layer there are, in the three cases, respectively, 4, 3, and 2 electrons capable of forming parts of chemical bonds. This is certainly one of the most ingenious points in the Bury hypothesis. It suggests that in the elemental systems there exists something akin to isomerism among the carbon compounds ; and it seems to give a hint as to the origin of the phenomena of allotropy.

Vanadium and chromium are assumed by Bury to have variable arrangements of this type in their atomic structure. In the case of manganese, five different arrangements can be written down which correspond to the various valency-capacities which the element exhibits in practice :

(2, 8, 8, 7) (2, 8, 9, 6) (2, 8, 11, 4) (2, 8, 12, 3) (2, 8, 13, 2)

Iron presents no difficulties on Bury's hypothesis, since the following arrangements cover all the essential demands arising from our experimental knowledge :

(2, 8, 10, 6) (2, 8, 12, 4) (2, 8, 13, 3) (2, 8, 14, 2)

Let us now come to copper. Here it is necessary to account

for the formation of a monovalent and a divalent ion, each of which has peculiar properties of its own. Bury readily meets this case with the two arrangements : (2, 8, 17, 2) and (2, 8, 18, 1), wherein the removal of one electron from the last and two electrons from the first grouping will leave two obviously different residues as ions.

9. *Isosterism*

In 1918, Allen [1] suggested, from the analogy of molecular weights, that there should be molecular numbers, which would be obtained by adding together the atomic numbers of the atoms in any molecule, just as the molecular weight is got by taking the sum of the atomic weights. He drew attention to the fact that the ions of sodium and ammonium, which show a certain kinship in chemical behaviour, both have the molecular number 11.

A year later, Langmuir,[2] by utilising the cubical atom of G. N. Lewis, threw a new light on the subject. If the cubical models of nitrous oxide and carbon dioxide are built up, it is found that both of them have the arrangement shown in Fig. 24. They are, in fact, identical in electronic grouping; and the only difference between them lies in the nuclear charges of the various atoms. The same may be said for the molecules of nitrogen and carbon monoxide, each of which contains a system of ten electrons in the cubic grouping.

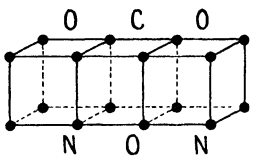


FIG. 24.

When the physical properties of these substances are examined it is found that a surprising resemblance exists between the two members of each pair. Nitrous oxide and carbon dioxide, for example, are identical in viscosity at 20° C., in heat conductivity at 100° C., and in magnetic susceptibility under the same conditions. Their critical pressures, critical temperatures, densities at 10° C., refractivities, and solubilities, are very near to each other.

When two compounds contain the same number of atoms and the same total number of electrons, Langmuir designates

[1] Allen, *J.*, 1918, **113**, 389.

[2] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 1543.

them as *isosteric*; and he suggests that isosteres should show remarkable similarities in those properties which do not involve a separation of the atoms in the molecule.

In the case of isomorphism, he has been able to bring forward a number of curious examples to show that isosteric molecules tend to crystallise in the same form; and this throws light upon peculiar resemblances in crystallographic character—such as the isomorphism of sodium fluoride and beryllium oxide—which have hitherto been without explanation.

10. *The Bohr Model Atom*

In earlier chapters, the value of the Bohr theory in the field of spectra was emphasised; but at the same time it was pointed out that the conditions under which a gas emits a spectrum are totally different from those existing during our normal chemical reactions in flasks. Further, it will be recalled that the purely mathematical basis of the Bohr theory extends only to hydrogen and ionised helium; so that beyond this very narrow region of two elements, Bohr's views have exactly the same value as those of other speculators.

According to Bohr,[1] the inert gases have the following orbital arrangements of the electrons in their outer atomic spheres:

Element.	Numbers of Electrons in various Orbits.																
	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2
Helium .	2																
Neon .	2	4	4														
Argon .	2	4	4	4	4	–											
Krypton .	2	4	4	6	6	6	4	4	–	–							
Xenon .	2	4	4	6	6	6	6	6	6	–	4	4	–	–	–		
Radon .	2	4	4	6	6	6	8	8	8	8	6	6	6	–	–	4	4

Inspection will show that if we lump together the electrons in orbits having the same quantum number, Bohr's arrangement is simply that suggested earlier by Bury *:

[1] Bohr, *Fysisk Tidsskrift*, 1921, **19**, 153; *The Theory of Spectra and Atomic Constitution* (1924).

* It should be borne in mind, of course, that the radii of Bury's spheres are in the ratio $1 : 2 : 3 : 4 \ldots$ whilst the radii of the Bohr orbits bear the relationship $1^2 : 2^2 : 3^2 : 4^2 \ldots$

Element.	1	2	3	4	5	6	Principal Quantum Number.
Helium .	2						Electrons in orbits.
Neon .	2	8					
Argon .	2	8	8				
Krypton .	2	8	18	8			
Xenon .	2	8	18	18	8		
Radon .	2	8	18	32	18	8	

So far as chemistry is concerned, then, Bohr's views support Bury's conception of the atom rather than Langmuir's; but they did not carry the matter any further than Bury had already done.

The limitations of Bohr's assistance to chemistry are shown even in the first short series of elements. The electrons of helium are supposed to move in 1_1 orbits. The extra electron in lithium moves in a 2_1 orbit. At this early stage Bohr seems to reach his limit, as he frankly admits [1]; and he had to make a guess at the orbital relations in the carbon atom, which unfortunately turned out to be incorrect.[2]

11. *Conclusion*

The ideas which have been described in this and in the preceding chapter may now be reduced to a symbolic form in order to show how well they agree with the facts known with regard to atoms; and since the crucial cases are those of isotopy and isobarism, an example of each type will be given.

In the diagrams of Fig. 25, the central circles represent the atomic nuclei; and the numbers of protons and intra-nuclear electrons are indicated by the numerals. The outer circles represent sections of the electronic spheres, and the small black discs show the electrons in each sphere.

As examples of a pair of isotopes, the two forms of lithium discovered by Aston, Li^6 and Li^7, have been selected. Since the one system has six protons in its nucleus whilst the other has seven, this arrangement yields the proper atomic weights. As the nuclei contain respectively three and four electrons, the surplus positive charge in each case is 3, which is the atomic number of lithium. Finally, each system has a single electron

[1] Bohr, *The Theory of Spectra and Atomic Constitution*, p. 91 (1924).
[2] *Ibid.*, Appendix, p. 133 (1924).

in its outer orbit, which expresses the fact that lithium is a monovalent element.

The case of the isobares is here illustrated by the argon-calcium pair, also discovered by Aston. Here both atoms have a mass of 40, which is represented by the forty protons in the nucleus of each system. Since the atomic number of argon is 18, this implies that there must be 22 electrons in its nucleus;

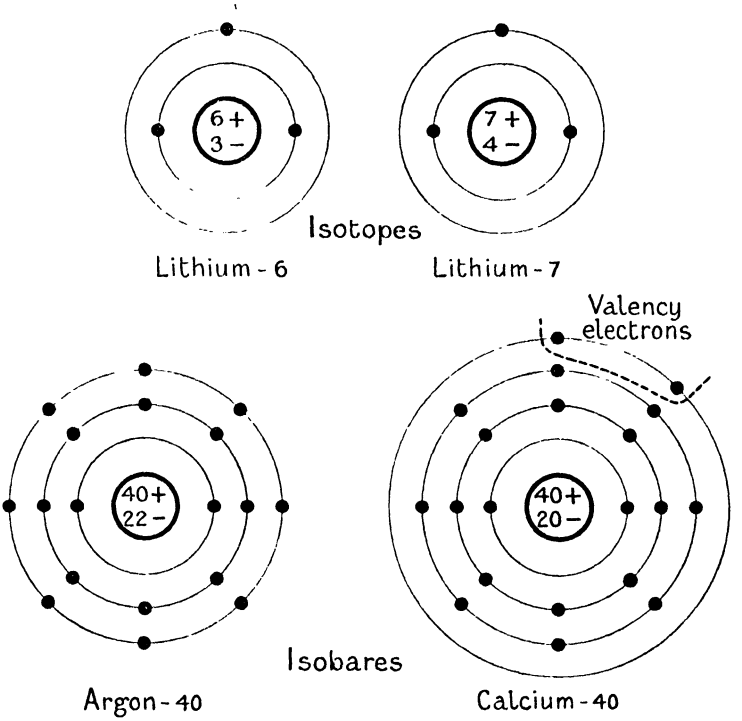


FIG. 25.

whereas calcium, with an atomic number 20, has 20 intra-nuclear electrons. In the outer sphere of the atom, using the Bury model, each system has three identical electronic groups holding in all 18 electrons; but the extra two electrons of the calcium system find a footing in a new outer sphere which has no counterpart in the argon system; and thus the divalency of calcium is expressed in the model.

Before terminating this chapter, it may be well to glance at one or two points which were suggested in the preceding sections.

The chemical theory of the model atom, built up by the work of Rydberg, G. N. Lewis, Langmuir, and Bury, has now reached a stage where it is satisfactory without having become too intricate. G. N. Lewis has given us the conception of two electrons shared in common by two atoms in order to represent what is generally termed a " single bond." * By a combination of Lewis's cubic atom with a spherical arrangement of shells with different radii, the Rydberg atomic number series and the abnormalities of the B Sub-groups of the Periodic Table have found a satisfactory expression. Whether the whole truth has been reached is still problematical; but certainly present-day ideas cannot be far off the mark.

G. N. Lewis [1] has drawn attention to certain cases in which the octet rule seems to be disobeyed. For example, in PCl_5 the phosphorus atom is apparently attached to five chlorine atoms, and each bond implies the sharing of a pair of electrons; so that no less than ten electrons must be placed around the central atom of the pentachloride. The sulphur atom of SF_6 must, on the same reasoning, have a dozen electrons grouped about it. Lewis has tentatively suggested an increase in the number of the valency shells of the atom to account for this; but the question is still an open one. Bury's model atom seems to yield the best results in this case.

Another question raised by Lewis [2] is connected with variable valency. In 1911, Crymble [3] drew attention to the fact that the elements may be grouped into three classes: (1) those of invariable valency, such as the alkali metals; (2) those which change their valency in steps of two units, such as tin, which forms $SnCl_2$ and $SnCl_4$, and thallium, which yields TlCl and $TlCl_3$; and (3) those which change their valency by single-unit stages, such as iron, which yields $FeCl_2$ and $FeCl_3$. Crymble, from a very complete examination of the absorption spectra of metallic ions, was able to show that elements of non-variable valency are practically diactinic in dilute solution; whereas elements which change their valency by two units at a time show

* Langmuir has christened this a " covalency "; but Lewis doubts the necessity of a fresh name.

[1] G. N. Lewis, *Valence*, pp. 101 ff. (1923).

[2] *Ibid.*, p. 60 (1923).

[3] Crymble, *P.*, 1911, **27**, 68.

general absorption; and those which change their valency one unit at a time show selective absorption.

In Lewis's view, compounds exhibiting colour are those in which the electrons are loosely held; so that his ideas at this point come into line with Crymble's experimental work, with which Lewis evidently was not acquainted.

Enough has now been said to give some idea of the lines upon which chemical speculation has been moving as regards the structure of the outer region of the atom. By its very nature, the problem is one which can hardly be approached experimentally with our present practical equipment; so we are forced in our reasoning to rely upon our judgment of probabilities and to select for ourselves the atomic model which is most congenial to our tastes. The ultimate cause of the stability of the inert gas atoms is beyond our ken; but we can certainly with safety assume that arrangements of 2, 10, 18, 36, 54, and 86 electrons are distinguished by their markedly stable character. Beyond that stage, it seems best to bear in mind the fact that the truth, when discovered, is generally simple in the scientific field; and that very probably the finally accepted model of the atom will be distinguished by its severe lack of adornment with subsidiary hypotheses.

CHAPTER XIV

RECENT STAGES IN THE ROLL-CALL OF THE ELEMENTS

HAFNIUM

1. *Element No.* 72

IN the field of inorganic chemistry, no region has been more fruitful in disappointed hopes than the rare earth group of elements. Although, as is now known, there are places for only sixteen elements between barium and tantalum, Mellor [1] has catalogued no fewer than seventy announcements of new elements in this part of the elemental sequence. Of these, twenty referred to materials which subsequently proved to be mixtures; fifteen remained without confirmation; and some of the remainder were found, on further investigation, to deal with elements already known.

In any other section of the Periodic Table, this record would be discreditable; but the conditions in the rare earth group are so peculiar and the investigation of it is beset by so many pitfalls that it would not be surprising had the number of erroneous reports been much greater. The isolation of one rare earth from it congeners is at best a tedious and lengthy process; whilst, even when the separation has been carried out, a further difficulty is encountered when an attempt is made to establish the homogeneity of the product. Traces of unremovable impurities may interfere with the work of the spectroscope; and thus the finest instrument in the rare earth chemist's hands may prove ineffective.

The history of Element No. 72 has furnished yet another example of the difficulties encountered in this field; but No. 72 has a claim to distinction lacking to all its congeners, since for the first time in chemistry, the X-ray spectrum was employed in the process of discovery.

[1] Mellor, *Treatise on Inorganic and Theoretical Chemistry*, vol. 5, pp. 504–5 (1924).

In 1911, Urbain [1] described the results of an attempt made by him to isolate the element lutecium from the mineral gadolinite. In fractionating the mixed nitrates of ytterbium and lutecium, he obtained from the mother-liquor a white rare earth which he believed to be new. The chloride of the element he found to be more volatile than lutecium chloride and less volatile than scandium chloride; whilst in basicity the new material was said to lie between the same two elements, being more basic than scandium and less basic than lutecium. His determination of the element's magnetic susceptibility suggested that it was four times weaker than that of pure lutecium; and his spectroscopic examination revealed lutecium lines as well as others which he attributed to the new material. On the basis of these investigations, he christened the substance "celtium."

About ten years later, Dauvillier,[2] in the course of a detailed study of the K and L series of X-ray spectra derived from Urbain's oxides of ytterbium and lutecium, observed two very feeble lines which he believed to be due to a trace of Urbain's "celtium." From the frequencies of the lines, Dauvillier inferred that "celtium" had the atomic number 72, so that in the elemental sequence it would fall into place immediately before tantalum.

In 1923, however, the whole problem was thrown into a condition of doubt. Coster and Hevesy [3] stated that while making an X-ray spectral examination of certain zirconium ores they had observed six lines which could be ascribed only to Element No. 72, since two of them agreed within one unit of wave-length with the values obtained theoretically by interpolation on a Moseley graph.

Coster and Hevesy criticised the previous work on Element No. 72 on the following grounds. In the first place, they believed that this element would not be a true rare earth congener, but would resemble zirconium in its properties, just as tantalum is the analogue of vanadium and columbium. It would thus be a quadrivalent metal and not a trivalent element like the "celtium" of Urbain. In view of the faintness of the lines observed by Dauvillier, they threw doubt on the evidence derived from magnetic susceptibility, on the ground that the

[1] Urbain, *Compt. rend.*, 1911, **152**, 141.
[2] Dauvillier, *Compt. rend.*, 1922, **174**, 1347.
[3] Coster and Hevesy, *Nature*, 1923, **111**, 79.

percentage of " celtium " present in the sample examined must have been extremely minute. In conclusion, they claimed the prerogative of christening this new representative of No. 72; and to it they gave the name Hafnium, from Hafniae (one of the names of Copenhagen).

This marked the opening of a rather lengthy controversy; but as chemical polemics are best enjoyed in the original literature, it will be sufficient to refer [1] the reader to that mine of interest for the full details and to confine ourselves to the chief arguments of the protagonists.

Urbain and Dauviller [2] claimed that the lines observed by Coster and Hevesy in the X-ray spectra of zirconium minerals had previously been observed by them in the case of ytterbia; but it was at the same time admitted by Urbain that " celtium " had been incorrectly described as being intermediate in properties between lutecium and scandium. It was contended, however, that it is not impossible for a quadrivalent element to present itself in the mother-liquors of rare earth fractionations, since thorium molybdate, for instance, is isomorphous and miscible with cerous molybdate.[3]

To this Coster and Hevesy [4] replied, apparently conclusively, that hafnium is easily separable from the rare earths by means of oxalic acid; and it should therefore have been absent from the preparation which, according to Dauvillier, contained the element No. 72. As regards the arc spectrum of " celtium," it has been pointed out that the optical spectrum of hafnium does not contain the lines ascribed by Urbain to " celtium "; but that the majority of Urbain's " celtium " lines are to be found in the spectrum of lutecium.[5]

On the face of the evidence at present available, it seems that Coster and Hevesy have established their priority in the dis-

[1] In favour of celtium: Dauvillier, *Compt. rend.*, 1923, **176**, 676; de Broglie and Cabrera, *ibid.*, 433; Urbain, *Chemistry and Industry*, 1923, 42, 764; Anon., *ibid.*, 784; Brauner, *ibid.*, 884; Dauvillier, *ibid.*, 1182. In favour of hafnium: Hansen and Werner, *Nature*, 1923, **111**, 322, 461; Coster and Hevesy, *ibid.*, 462; King, *ibid.*, 1923, **112**, 9; Hevesey, *Ber.*, 1923, **56** [B], 1503.

[2] Urbain, *Compt. rend.*, 1923, **176**, 469; Urbain and Dauvillier, *Nature*, 1923, **111**, 218.

[3] Zambonini, *Atti R. Accad. Lincei*, 1923 (v.), **32**, i., 518.

[4] Coster and Hevesy, *Nature*, 1923, **111**, 252, 462.

[5] Hansen and Werner, *Nature*, 1923, **111**, 461.

covery of Element No. 72; and as, further, all our knowledge of its chemical character is due to them, it appears reasonable that No. 72 should be christened hafnium in accordance with their proposal.

2. *The Sources of Hafnium*

After the discovery of a new element, it is often found that the previously unknown body is much more widely distributed in nature than might have been expected; and hafnium has been no exception to this rule. In its case, there can be little surprise at this state of affairs; for the search for element No. 72 had been almost exclusively confined to the rare earth sources, whereas its chemical character, as is now known, makes it an associate of the Group IV elements. In practice, the zirconium ores have proved to be the most fruitful sources of the new element.

An examination of some anomalous zircon minerals by Hadding's method of X-ray analysis [1] established the presence of hafnium in malacon and alvite.[2] A more extensive investigation of nearly thirty zirconium ores [3] has shown astonishingly large percentages of hafnium in some of these materials. The hafnium content of the specimens was determined by comparing the intensity of the hafnium X-ray lines with the intensity of the line due to a known quantity of tantalum which had been added to the specimens before examination. It was found that the secondary zirconium minerals such as alvite, cyrtolith, nægeite, and malacon, may yield zirconium preparations containing anything up to 30 per cent. of hafnium. Common zirconium minerals such as zircon may contain up to 6 per cent. of hafnium oxide. The natural oxides of zirconium contain much lower percentages, baddeleyite, for instance, yielding only 1·8 per cent. of hafnium oxide. Eudialyte, eucolite, and catapleite are poor in hafnium.

Thorium minerals which are free from zirconium appear to contain no hafnium, since thorianite, orangeite, and thorite showed no traces of the new element. The same is true for titanium minerals such as rutile and ilmenite.

[1] Hadding, *Z. anorg. Chem.*, 1922, **122**, 195.
[2] Goldschmidt and Thomassen, *Norsk Geologisk Tidsskrift*, 1923, **7**, 61.
[3] Hevesy and Jantzen, *J.*, 1923, **123**, 3218.

Hevesy and Jantzen reported a curious parallelism between the hafnium content and the radioactivity of zircons with large percentages of uranium or thorium, which is shown in the following figures:

	Activity.	Relative Hafnium content.
Cyrtolite	3·8	9
Alvite (from Risör)	3·6	10
Alvite (from Kragerö)	1·2	8
Zircon	0·16	1·7

On the basis of their analyses, Hevesy and Jantzen estimate that the actual hafnium content of the earth's crust probably lies between 1/100,000 and 1/300,000.

It may be pointed out that in at least one case, baddeleyite, the mineral had already been chemically analysed; but the hafnium present had been treated as zirconium, owing to the general similarity between the two elements.

3. *The Separation and Properties of Hafnium*

A separation of hafnium from zirconium can be carried out either by taking advantage of the difference in basicity between the two oxides or else by utilising the different solubilities of the salts of the two metals. At 20° C., the solubility of zirconium potassium fluoride is 2·6 per cent., whilst the solubility of the corresponding hafnium salt is nearly 3 per cent. In the case of hafnium ammonium oxalate and hafnium ammonium sulphate, the solubilities are greater than those of the corresponding zirconium salts; whereas hafnium oxychloride is less soluble than zirconium oxychloride. Hafnium being more basic than zirconium, the latter element is precipitated first when converted into a basic salt. In order to purify concentrated preparations of hafnium from admixed zirconium, the oxychlorides of the two elements are dissolved in alcohol and ether is added, which throws down the basic salt $Zr_2O_3Cl_2.5H_2O$, since this is less soluble than the corresponding hafnium compound.

The properties of hafnium lie much closer to those of zirconium than to those of thorium. The precipitation of a zirconium phosphate from a strongly acid solution, a reaction which in the past has been used to identify zirconium, is now paralleled in the case of hafnium. Hafnium phosphate, in fact, appears to

be the least soluble of all the known phosphates.[1] Hafnium also resembles zirconium in infusibility, in its power of electronic emission, and in the high power of light emission exhibited by its oxide.[2]

Accurate measurements of the hafnium X-ray spectrum have been made,[3] and fourteen lines of the L series have been identified. In the optical spectrum,[4] fifty-two lines have been identified as originating with hafnium in the region 2,500–3,500 Å.U. Many of these lines had previously been attributed to zirconium.

Early attempts [5] to determine the atomic weight of hafnium yielded a result of approximately 180 on the assumption that the preparation contained about 6 per cent. of zirconium. A later result, derived from the isomorphism of $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$, is $179 \pm 5{\cdot}4$.

Illinium *

The detection of hafnium was marked off from all earlier discoveries of new elements by the fact that in it, for the first time, X-ray spectroscopy was brought into play as the main instrument during the earlier stages of the research. The discovery of illinium is likewise unique, though on a different account. Illinium's isolation has completed the roll of the rare earth elements and has thus closed one of the most intricate chapters in the history of chemical investigation.

On the basis of his investigation of the X-ray spectra of the elements, which was described in Chapter III, Moseley [6] pointed out that an unknown rare earth element was to be expected, which would have the atomic number 61 and would be situated between neodymium and samarium in the natural order

[1] Hevesy, *Chem. Ztg.*, 1923, **47**, 345.

[2] Coster and Hevesy, *Chemistry and Industry*, 1923, **42**, 258.

[3] Zácek, *Z. Physik*, 1923, **15**, 31 ; Coster, *Phil. Mag.*, 1923, **46**, 956.

[4] Hansen and Werner, *Nature*, 1923, **111**, 322, 618.

[5] Coster, *Physics*, 1923, **15**, 31.

* In writing this narrative, I have been indebted to Professor B. S. Hopkins's own accounts of the work, which are to be found in *The Scientific American*, 1927, **136** (2), 87 ; *J. Franklin Inst.*, 1927, **204**, 1 ; and in his lecture, *Completing the Periodic Table*, delivered at Columbia University in 1927, printed by the Columbia University Press (1927).

[6] See Soddy, *Ann. Reports*, 1914, **11**, 279, for information supplementing Moseley's papers in the *Phil. Mag.*

of the elements. In 1917, Eder [1] in the course of some work on the arc spectrum of samarium discovered certain lines which might indicate the presence of a new element; and in 1922, Hadding [2] found reason to suspect a new element in the mineral fluocerite which he subjected to X-ray examination. Neither of these investigations produced anything definite. In 1921, Brinton and James,[3] while investigating the rates of hydrolysis of rare earth carbonates, found a regularity in their curves connecting the volume of carbon dioxide and the time; but this regularity was broken between neodymium and samarium—at the point where Moseley predicted that the undiscovered element would lie.

Early in 1919, a plan of co-operation was arranged by the United States Bureau of Standards and the Chemical Department of the University of Illinois, the object of which was the mapping of the arc spectrum lines of certain rare elements, especially those belonging to the rare earth group. The University furnished the samples for examination and the Bureau carried out exact measurements of the lines in the red and infra-red regions of the spectrum. In publishing the work on neodymium and samarium, it was pointed out [4] that in addition to 1500 lines in each of the spectra there were 130 faint lines common to both spectra:

"These lines are of unknown origin and may belong to the missing element of order number 61, coming between Nd and Sa. . . . When the tabulated wave-lengths for neodymium and samarium were intercompared, it was found that many lines, for the most part faint, were common to the spectra of both. It has not been possible to identify them with the spectra of known elements and, therefore, they have been brought together in a separate table. While it would be a hasty conclusion to regard these lines as characteristic of a new element, yet the idea seems plausible in view of the fact that the present accepted scheme of the periodic table of elements requires a new element of atomic number 61 coming between neodymium and samarium. Eder has published similar lists of unidentified lines which he suggests

[1] Eder, *Sitzungsber. k. Akad. Wiss. Wien*, 1917, IIA, 125.
[2] Hadding, *Z. anorg. Chem.*, 1922, **122**, 195.
[3] Brinton and James, *J. Amer. Chem. Soc.*, 1921, **43**, 1446.
[4] *U.S.A. Bureau of Standards Paper*, No. 442, pp. 201 ff.

may belong to elements not yet isolated, but none of the lines of our table agree with those in his lists."

These results led to work being started at Illinois University upon the concentration and identification of the unknown material which gave rise to these faint lines. Extensive fractionation of neodymium and samarium materials was carried out, the double magnesium nitrates being employed ; and X-ray examination of the products was made by Yntema * at Yale University. After two years' work, the result was the addition of five arc spectrum lines towards the violet, and the conclusion was drawn that if element No. 61 was present, it could only be in a proportion of less than one part in a thousand of the material.[1]

Better results followed the adoption of the bromates [2] as fractionating material.[3] In this method, the samarium salt crystallised at the less soluble end, whilst the neodymium salt concentrated in the more soluble fractions. At wave-length 5816 Å.U. a faint line made its appearance and grew stronger as the fractionation proceeded, while the characteristic absorption lines of both neodymium and samarium grew weaker. Later, another line was detected at 5123 Å.U., which likewise grew more marked as the process continued. These lines had been concealed by the broad and persistent absorption bands of neodymium and samarium.

Now when the most prominent absorption lines of the rare earth elements are plotted according to their wave-lengths, it is found that there is a relationship between the positions of the characteristic absorption bands of adjacent elements.[4] From element No. 59 to element No. 64 there seems to be a definite drift towards the short-wave end with increase in the atomic number, so that gadolinium (No. 64) has its absorption band in the ultra-violet. The two bands at 5816 Å.U. and 5123 Å.U. fit neatly into this scheme, if they are attributed to element No. 61.

The next stage in the investigation took the form of building

* Dr. Yntema was then working as a Fellow of the National Research Council.

[1] Yntema, *J. Amer. Chem. Soc.*, 1924, **46**, 37.

[2] James, *J. Amer. Chem. Soc.*, 1914, **36**, 2060 ; 1926, **48**, 2871 ; 1927, **49**, 132.

[3] Harris and Hopkins, *J. Amer. Chem. Soc.*, 1926, **48**, 1585.

[4] Yntema, *J. Amer. Chem. Soc.*, 1926, **48**, 1598 ; Harris and Hopkins, *ibid.*, 1585.

in the Illinois laboratory a glass X-ray tube with water-cooled electrodes. The cathode was made of aluminium; and the target was of copper, into a recess in which the rare earth oxide was fused in order to overcome the difficulty of retaining the material on the target during the electronic bombardment. By means of this tube, and by using three different calcite crystals as diffraction gratings to avoid any possible constant error, determinations of the wave-lengths of the L_{α_1} and L_{β_1} lines of the material's X-ray spectrum were made with the most rigid care to avert even any sub-conscious influences on the part of observers. As a result,[1] the L_{α_1} line was found at wave-length 2·2781, whilst the line L_{β_1} was detected at wave-length 2·0770, the samarium L_{α_2} and the neodymium L_{α_1} being used as controls. The maximum deviation from the wave-length calculated for element No. 61 was less than 0·0004 Å.U. in the case of the L_{α_1} line, and in the single determination made of the position of the L_{β_1} line only the same very minute discrepancy was observed. These results had been foreshadowed by earlier work on some material supplied by Hopkins to the University of Iowa for examination [2]; and they have been confirmed by later workers,[3] who have determined the positions of lines belonging to the K-series.

The discoverers suggested "the name of Illinium * with

[1] Harris, Yntema, and Hopkins, *J. Amer. Chem. Soc.*, 1926, **48**, 1594.

[2] Lapp, Rogers, and Hopkins, *Physical Rev.*, 1925, **25**, 106.

[3] Cork, James, and Fogg, *Proc. Nat. Acad. Sci.*, 1926 (December), p. 696; Meyer, Schuhmacher, and Kotowski, *Naturwiss.*, 1926, **14**, 771.

* Aclaim that the element should be termed Florentium in honour of Florence was put forward by Rolla and Fernandes. The facts seem to be these. The ublication by the Bureau of Standards of the wave-lengths of 130 new lines observed in the spectra of material supplied by Illinois University (see above) was dated January 6th, 1922. The detection of five extra lines in the ultra-violet spectrum was made public by Yntema in a publication dated September 29th, 1923. Early in 1922, Rolla began work on a small quantity of didymium material obtained from Brazilian monazite, which he fractionated as double thallium sulphate. He obtained evidence of the existence of a new element in the form of X-ray absorption spectra of the K-series. During the course of June 1924, Rolla, instead of publishing his results, consigned them in a sealed package to the care of the Reale Accademia dei Lincei. Meanwhile the American investigators had been following up the line of their earlier publication. In November 1925, Lapp, Rogers, and Hopkins identified the La_1 line of element 61 in the spectrum of the Illinois preparations, and on April 26th, 1926, Harris and Hopkins sent in their papers: *Element No.* 61: *Part I—Concentration and Isolation in Impure State; Part II—X-ray Analysis.* These communications were published by the American Chemical Society on June 5th, 1926. The

symbol Il for this element, in honour of the State of Illinois and our University."

Rhenium (Dvi-Manganese)

In Group VII of his Periodic Table, Mendeléef left two vacant spaces under manganese for unknown elements which he provisionally termed eka-manganese and dvi-manganese. These correspond to elements 43 and 75 in the atomic order.

In June, 1925, Noddack, Tacke, and Berg [1] published an account of some investigations on platinum ores from which they had obtained a volatile oxide. This they believed to be the highest oxide of element No. 75, to which they gave the name rhenium. From columbite a product was isolated which contained 5 per cent. of the element; and the evidence for the material's identity was strengthened by measurements of X-ray spectra. Further measurements [2] of the X-ray spectra have been made by other workers; but the matter is complicated by the fact that Noddack states [3] that in his opinion some of these investigators never obtained No. 75 at all, whilst an investigation of native platinum is declared to have resulted in completely negative results so far as No. 75 is concerned.[4]

Only the briefest account of the search for rhenium can be given here, since so many different minerals (each demanding

contents of Rolla's sealed package were not made public by him until November 1926: five months after the Illinois workers had published their complete results, and a year after Lapp, Rogers, and Hopkins had communicated their earlier X-ray work to the American Physical Society. According to the etiquette governing such cases, there seems no doubt that the element should receive the name Illinium. Any one with a morbid craving for chemical controversy will find the following references of interest: Brunetti, *Atti R. Accad. Lincei*, 1926, (vi), **4**, 515, 518; *Z. anorg. Chem.*, 1927, **160**, 237; Rolla and Fernandes, *Atti R. Accad. Lincei*, 1926, (vi), **4**, 498; *Gazzetta*, 1926, **56**, 435, 862; *Z. anorg. Chem.*, 1926, **157**, 371; 1927, **160**, 190; *Nature*, 1927, **119**, 637; Brauner, *ibid.*, 1926, **118**, 84; Noyes, *ibid.*, 1927, **119**, 319; *Z. anorg. Chem.*, 1927, **168**, 264.

[1] Noddack, Tacke, and Berg, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, **19**, 400.

[2] Druce, *Chem. News*, 1925, **131**, 373; Loring and Druce, *ibid.*, 337 Loring, *ibid.*, 1926, **132**, 101; Dolejsek and Heyrovsky, *Nature*, 1925, **116**, 782; Polland, *Compt. rend.*, 1926, **183**, 737; Beuthe, *Z. Physik*, 1926, **46**, 873; 1928, **50**, 762; Wennerlöf, *ibid.*, 1928, **47**, 422.

[3] Noddack, *Z. angew. Chem.*, 1927, **40**, 250; *Chem. Met. Eng.*, 1926, **1**, 109; *Ergebnisse d. exakt. Naturwiss.*, 1927, **6**, 335.

[4] Zvjaginstsev, Korsunski, and Seljakov, *Nature*, 1926, **118**, 262.

special treatment) were utilised in the work. For details, the reader may refer to Noddack's summary.[1]

From theoretical considerations, it was believed that rhenium would most probably be found in conjunction with molybdenum, tungsten, ruthenium, and osmium; and the initial search was made among ores of these elements. Since the probable percentage of rhenium in its natural sources was assumed to be minute, the object kept in view was to concentrate all the new element in a single preparation derived from a number of different minerals. The guiding clue used in this procedure was the theoretical forecast of the properties of rhenium which was drawn up on the basis of its position in the Periodic Table and its relationships with elements in adjacent places.

When the rhenium had thus been concentrated, the preparation containing it was heated in a stream of oxygen in order to isolate the volatile oxide; and thereafter X-ray spectroscopy was utilised to investigate the product. Optical spectroscopy seems to have furnished little help in the matter.

The next stage in the research was to discover a mineral or minerals which contained rhenium in quantity sufficient to repay working up. The final results led to the conclusion that rhenium is most plentiful in certain columbites, gadolinites and alvites from various quarters of the globe. The mineral content of element No. 75 is, however, extraordinarily small. For instance, in the columbites examined, the concentration of rhenium lay between $0{\cdot}5\times10^{-7}$ and 2×10^{-7}.

Finally, the rhenium-rich portions of a number of different preparations were lumped together, yielding a mass of about 0·67 gr. in weight. This was strongly heated with potassium nitrate, and extracted with water. The solution was treated with ammonium chloride to precipitate silicic and titanic acids; and after filtration was treated with concentrated sulphuric acid and boiled until all oxides of nitrogen were removed. Sulphuretted hydrogen was then led into the acid solution, which was left to stand for two days. The sulphide precipitate which was thrown down weighed 0·135 gr. and contained about 1·5 per cent. rhenium. It was strongly heated for a long time in a stream of oxygen, whereby most of the rhenium oxide sublimed along with molybdenum oxide. In order to remove the molybdenum,

[1] Noddack, *Ergebnisse d. Exakt. Wissenschaft.*, 1927, **6**, 333.

advantage was taken of the solubility of $Mo(CNS)_5$ in ether. The carefully sublimed mixture of oxides was dissolved in 5 per cent. sulphuric acid, treated with potassium thiocyanate, and then twice extracted with ether. Only a slight amount of rhenium passed into the ether. The aqueous solution, containing mainly rhenium, vanadium, and arsenic, was precipitated with sulphuretted hydrogen, and the sulphides were then reduced in a current of hydrogen, whereby a portion of the arsenic was removed. Further heating in a current of oxygen yielded a yellow sublimate, which appears to be a higher oxide of rhenium, contaminated with a little arsenic and molybdenum. The total rhenium content, reckoned as metal, amounted to about 0·0016 gr.

The following appear to be the main chemical properties of rhenium and its compounds.[1]

When the sulphide is heated in a current of hydrogen, a heavy black powder is produced which is either the metal itself or a lower sulphide. This powder burns in a stream of oxygen to form an oxide which is deposited on a cold surface in the form of a white powder with a yellow superficial layer. It is more easily volatile than MoO_3 and has a different crystalline form. This oxide dissolves readily in dilute hydrochloric acid, producing a colourless solution, which yields neither precipitate nor coloration when treated with caustic potash, caustic soda, ammonia, or sulphuric acid. Sulphuretted hydrogen acts slowly on the solution of the hydrochloride, yielding a grey precipitate, which is probably rhenium sulphide. On shaking rhenium hydrochloride solution with ether, the rhenium passes into the ether layer, apparently in the form of oxychloride. On the other hand, if a solution of the rhenium oxide in sulphuric acid be treated with potassium thiocyanate and then shaken with ether, the rhenium remains in the aqueous layer and does not pass into the ether as molybdenum would do.

Masurium

According to Noddack, Tacke, and Berg,[2] element No. 43 occurs, in small quantities, in sperrylith, gadolinite, fergusonite,

[1] Noddack, *Ergebnisse d. Exakt. Wissenschaften*, 1927, **6**, 333; *Z. physikal Chem.*, 1927, **125**, 264; *Z. Elektrochem.*, 1928, **34**, 627.

[2] Noddack, Tacke, and Berg, *Sitzungsber., Preuss. Akad. Wiss. Berlin*, 1925, **19**, 400.

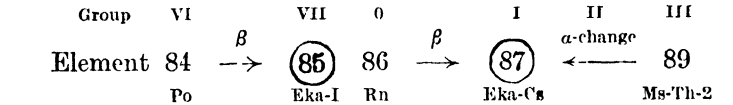
and zircon. Some lines in the X-ray spectrum have been measured and the results agree fairly well with the values calculated for element No. 43. The investigators have suggested the name *masurium* for this congener of manganese.

Elements 85 and 87

After the elements described above have been inserted, the present Periodic Table still contains two blank spaces: No. 85, which should contain eka-iodine, and No. 87, which should be occupied by eka-caesium.

Loring and Druce,[1] during an examination of pyrolusite, detected certain lines which they ascribed to eka-caesium and another unknown element; but the matter evidently requires further investigation.

The problem of elements 85 and 87 has been attacked on a much broader basis by Hahn [2] and by Hevesy.[3] A glance at the following scheme will make clear the possibilities in the case:



It is evident that No. 87 might arise as the result of an α-ray change in element 89, or as a consequence of a β-ray change in element 86. Element No. 85 might be produced by a β-ray change in No. 84; but evolution through an α-ray change may be neglected, since the hypothetical parent in this case would be No. 87, which certainly does not exist in quantity sufficient to produce a detectable amount of No. 85.

The suggestion that eka-caesium results from an α-ray change in atoms of element 89 has been tested by Hahn in the case of mesothorium-2, which is one of the isotopic forms of No. 89. Hahn added a caesium compound to a strong mesothorium preparation and then by chemical treatment removed all the known radio-elements from the mixture. If any product corresponding to the atomic number 85 were produced from the mesothorium-2, it would remain with the caesium, just as

[1] Loring and Druce, *Chem. News*, 1925, **131**, 321, 337; Loring, *ibid.*, 371; 1926, **132**, 101; *Nature*, 1926, **117**, 448.

[2] Hahn, *Naturwiss.*, 1926, **14**, 159.

[3] Hevesy, *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1926, **7**, No. 11, 1

radium concentrates along with barium; and the conditions of experiment were such that a radioactive eka-caesium could have been detected so long as its half-life period was at least two hours and the number of mesothorium-2 atoms disintegrating reached 10^{-4}. Hahn failed to discover any trace of the sought-for element.

Hevesy attempted to prove the emission of α-particles from mesothorium-2; but his results show that less than one in every 200,000 atoms of mesothorium-2 can be undergoing the α-ray change, if indeed any such change occurs at all.

This seems to establish that eka-caesium does not arise from an α-ray change in mesothorium-2; but these results are not applicable to the remaining alternative: that No. 87 is produced by an α-ray change in actinium, which has the atomic number 89 also.

The other possible derivation of eka-caesium—by a β-ray change in radon—seems excluded by further work of Hevesy, who found no trace of any radioactive alkali during an examination of an active deposit from 100 millicuries. This, of course, still leaves the possibility that eka-caesium may be produced by β-ray changes in thoron or actinon.

Hevesy's preliminary experiments to detect a trace of eka-iodine (No. 85) as a product of the short-lived isotopes of element 84 were also fruitless.

CHAPTER XV

ACTIVE HYDROGEN

1. *The Discovery of* X_3

WHEN some solids are bombarded with cathode rays, gases are liberated; and examination of the gas mixture by positive ray analysis established the presence of helium, neon, and a third substance to which the name X_3 was provisionally given by Sir J. J. Thomson.[1] Platinum, palladium, aluminium, copper, zinc, iron, nickel, silver, gold, lead, graphite, diamond dust, lithium chloride and other metallic salts, all yielded the unidentified gas when subjected to cathode ray bombardment. The presence of mercury seemed to diminish the yield of the so-called X_3, so far as could be judged from the intensity of the line in the mass spectrum.

Since X_3 evidently is a particle in which the ratio of mass to charge is 3, only two explanations of its nature are possible if it be assumed that the maximum number of charges per particle is limited to a small integer. The particle of X_3 must be either (1) a carbon atom carrying four electrical charges; or (2) a molecule containing three hydrogen atoms and carrying a unit charge.

At the time of the discovery of X_3, conservative opinion inclined to the former explanation, for it was well known that carbon compounds are retained by glass under conditions which might normally be expected to preclude their appearance.[2] Further, the existence of a monovalent element in the form of a triatomic grouping was quite inexplicable on the theory of valency which was then current.

On the other side, however, there was a considerable amount of evidence. Thomson showed that whenever X_3 was detected,

[1] Thomson, *Rays of Positive Electricity*, p. 116 (1913).
[2] Collie and Patterson, *Proc. Chem. Soc.*, 1913, **29**, 217.

ordinary hydrogen was also present. Further, when various compounds were bombarded after recrystallisation the yield of X_3 was greatest in the case of deliquescent salts or from hydroxides, both of which types are possible sources of hydrogen.

The properties of X_3 were examined by Thomson with the following results. When mixed with hydrogen, X_3 is not markedly photosensitive; but when a mixture of X_3, hydrogen and oxygen is exposed to a magnesium flash, the X_3 is destroyed. This suggests that X_3 combines with oxygen even more readily than hydrogen does. Like hydrogen, X_3 was found to have the power of passing through a palladium wall; but its rate of diffusion was lower than that of hydrogen. In the absence of oxygen, X_3 could be heated to a high temperature without vanishing. No new optical spectrum could be detected for X_3, for a mixture of it with hydrogen shows only the normal hydrogen spectrum.

On the strength of this evidence, Thomson put forward the suggestion that the so-called X_3 was really a new form of hydrogen, H_3, the hydrogen analogue of ozone.

2. *The Action of α-Particles on Hydrogen*

The work of Thomson was concerned with positive ray measurements, and the quantity of X_3 obtained by him seemed incapable of treatment by any other method. Four years later, however, the subject was brought into closer touch with chemistry by the investigations of Duane and Wendt.[1] They observed that when hydrogen is exposed to bombardment by α-particles from radon, a contraction takes place, part of which may be ascribed to the gas being driven into the walls of the containing vessel. The remaining hydrogen, however, acquires properties which differentiate it from the ordinary form of the element. It reduces sulphur to hydrogen sulphide, phosphorus to phosphine, arsenic to arsine; and in neutral solutions of potassium permanganate it produces a precipitate of manganese dioxide.

This new form of hydrogen is unstable; and in about a minute it reverts to the ordinary type of the element. It is thus much less stable than ozone.

[1] Duane and Wendt, *Physical Rev.*, 1917, **10**, 116; Lind, *J. Amer. Chem. Soc.*, 1919, **41**, 545.

3. *The Preparation and Properties of Triatomic Hydrogen*

A much simpler method of preparing active hydrogen was soon devised.[1] Carefully purified hydrogen at a pressure of 2 to 8 cms. was passed through a glass spiral which could be cooled by liquid air, then into a discharge tube of the ordinary vacuum tube pattern with two electrodes, then through a second glass spiral and through a tube packed with glass wool, until finally it traversed a tube containing coarsely ground crystallised sulphur. After leaving the sulphur tube it was drawn into a flask in which moist lead acetate paper was suspended. The electrodes of the discharge tube were sometimes connected with the terminals of a large induction coil; in other experiments they were joined to the poles of a 2,200-volt alternating current transformer.

When no discharge was passing, hydrogen was allowed to travel through the apparatus for an hour; and during this period no blackening of the test-paper was seen. This blank experiment proves that the hydrogen used was unable to attack the sulphur and yield hydrogen sulphide.

As soon as the discharge was applied, however, the paper was darkened by the formation of lead sulphide, which shows that the hydrogen had been activated by the discharge to such an extent that it readily combined with the solid sulphur at ordinary temperatures. The efficiency of the new method over the older one with α-rays was proved by the fact that in the discharge method one minute sufficed to darken the lead paper as much as it had been discoloured after eight hours of experimenting with the α-ray method.

Two possible causes of this reducing action of the hydrogen might be suggested, apart from an actual alteration of the gas into a new molecular type: on the one hand, there might be a slight heating effect due to the passage of the discharge; and, on the other hand, the action on the sulphur might be due to hydrogen ions and not to molecular hydrogen. To dispose of the first suggestion, the glass spiral through which the gas passes after leaving the discharge tube was immersed successively in boiling water, an ice-water mixture, a freezing mixture at about

[1] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 930; compare Smallwood and Urey, *ibid.*, 1928, **50**, 620.

—20° C., and liquid air. In all of these except the last, the hydrogen retained its special activity and showed unchanged avidity for the sulphur in the apparatus. Liquid air, however, seemed to condense the active gas and stop the flow of it into the sulphur tube. As ordinary hydrogen would pass unchecked through a liquid air bath; this seems to prove that the active form of hydrogen is molecularly different from the normal form and is much more readily condensed by cooling agents.

The second suggestion—that the action is due to ions of hydrogen—was tested in two different ways. In the first place, the activated gas was made to pass between two electrodes which were connected with the opposite poles of an 800-volt battery. This treatment would remove a large number of gaseous ions had such been present; but in practice it was found that the electrical field had no perceptible influence on the hydrogen's activity. In the second place, the hydrogen from the discharge tube was tested for ions by means of the ordinary emanation electroscope after it had passed through the electrical field; but the experiments showed that no ions could be detected.

These facts are sufficient to prove that the activation of the hydrogen cannot be put down to heating effects or to the influence of ionisation in the gas; and the fact that cooling in liquid air removes the activity tends to show that the active form of hydrogen is something quite different from the normal form of the element.

A further series of experiments showed that this active form of hydrogen can conveniently be obtained by passing hydrogen through an ozoniser connected with a high-tension transformer yielding 20,000 volts.[1] When active hydrogen is obtained by this method, it is found to yield ammonia if brought into contact with pure nitrogen.

Since all the foregoing methods of preparing active hydrogen involve processes in which ionisation of the gas may occur, Wendt and Landauer hoped to obtain active hydrogen by using ultra-violet light as an activating agent. It was found, however, that under the Schumann light ordinary hydrogen is not transformed into the active variety. Activation by a hot wire [1] was observed; but the explanation of this phenomenon

[1] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 511.

is not yet quite clear, though probably it is connected with a thermal emission of ions by the heated metal.

In this connection, it is necessary to deal with another side of the phenomenon, viz. the contraction in volume which is sometimes observed when hydrogen is electrically treated. In 1910, Usher [1] exposed a mixture of nitrogen and hydrogen to the action of α-rays from radon and found that the diminution in the volume of the gas was much greater than could be accounted for by the amount of ammonia produced by the radioactive discharge. For example, 1·602 c.c. of gas showed a contraction amounting to 0·24 c.c., although only 0·006 c.c. of ammonia was formed. Usher's experiment was repeated and confirmed by Wendt and Landauer.[2] A similar phenomenon was observed by Collie and Patterson,[3] who found that when hydrogen gas was sparked under reduced pressure with aluminium or copper electrodes a very large contraction in volume occurred, amounting in one case to 3·6 c.c. out of an initial volume of 4·6 c.c.

Since the polymerisation of molecular hydrogen to triatomic hydrogen must result in a contraction of the gaseous volume:

$$3H_2 = 2H_3$$

Wendt and Landauer [4] re-investigated the influence of electrical discharges on the volume of hydrogen; and their results confirm those of Collie and Patterson. Marked contractions were observed as a result of passing a discharge through a hydrogen atmosphere at various temperatures; and it is of special interest to note that at the boiling-point of liquid oxygen (−180° C.) the contraction was more than one-third of the entire original volume. This suggests that the contraction is due to the polymerisation of the hydrogen to a variety which is condensable at −180° C.

At this point it may be convenient to summarise the properties of triatomic hydrogen, so far as they are known at present. In the first place, the triatomic nature of the substance may be inferred from the fact that contraction occurs during its production, which points to a polymerisation process; and this, taken in conjunction with the fact that mass spectroscopic

[1] Usher, *J.*, 1910, **97**, 400.
[2] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 930.
[3] Collie and Patterson, *P.*, 1913, **29**, 22, 217.
[4] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510.

analysis has revealed nothing corresponding to H_4, H_5, or higher molecular groupings of hydrogen atoms, whereas the H_3 parabola is frequently found, appears to establish the triatomic formula on a firm basis, since there seems to be no alternative. In view of the analogy of ozone, Wendt and Landauer have suggested the name *hyzone* for the triatomic variety of hydrogen.

Triatomic hydrogen reduces sulphur, arsenic, phosphorus, nitrogen, and potassium permanganate. It is catalytically decomposed by finely divided platinum, nickel, copper, lead, antimony, and cadmium; but it is not affected by contact with silver, mercury, tin, bismuth, molybdenum, zinc, or aluminium.

At the temperature of liquid oxygen, triatomic hydrogen is condensed.

Glass wool permits triatomic hydrogen to pass across it without any diminution in the activity of the gas.

Triatomic hydrogen is unstable and reverts to the normal diatomic form in about a minute. It is not less stable at ordinary pressures than it is at low pressures.

There seems to be some evidence in favour of the idea that the secondary spectrum of hydrogen is connected with the formation of the triatomic form.

4. *Other Varieties of Active Hydrogen*

In recent years the number of observations made upon activated hydrogen has been surprisingly large; and only a very brief account of them can be given in the restricted space available here.

Langmuir [1] found that when filaments of tungsten, platinum, or palladium are raised to high temperatures in an atmosphere of hydrogen under low pressure, the hydrogen slowly disappears. This disappearance is explained by the metals dissolving the gas and forming a solution in which the hydrogen is present as single atoms and not as diatomic molecules. These isolated atoms of hydrogen then diffuse out of the metal; but under the low pressure in the containing vessel they do not readily reunite to form molecular hydrogen.

[1] Langmuir, *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 225; *J. Amer. Chem. Soc.*, 1912, **34**, 860; Langmuir and Mackay, *ibid.*, 1914, **36**, 1708; Langmuir, *ibid.*, 1915, **36**, 417.

Apart from any theory, the facts are as follows. The gas is strongly adsorbed by the glass walls of the containing vessel and is retained by glass wool plugs into which it is passed.[1] It has quite abnormal properties, which it retains for a long time when it is in the adsorbed condition. At room temperature it reacts with oxygen or phosphorus vapour; and it reduces the layers of platinum or tungsten oxide which are found in electric lamp bulbs. In the gaseous state, under a pressure of less than 0·02 mm., it is stable for some hours; but it disappears rapidly when mixed with excess of hydrogen.

In 1916, Burt and Edgar [2] observed that when hydrogen was exploded with excess of oxygen, brown stains appeared on the walls of the vessel. These stains were believed to be oxide of mercury; and they disappeared again when a mixture of oxygen with excess of hydrogen was exploded in the vessel. The explanation of the latter phenomenon appears to lie in the formation of active hydrogen, for Venkatramaiah [3] found that when three volumes of hydrogen were mixed with one volume of oxygen and exploded, the residual hydrogen reduced potassium permanganate to manganate, ferric chloride to ferrous chloride, potassium nitrate to nitrite, arsenious acid to arsine, and alkaline indigotin to indigo-white. Further investigation [4] showed that this active form of hydrogen could be obtained by the continuous burning of oxygen in hydrogen, from a high tension arc in hydrogen, by heating hydrogen in the arcs of various metals, and by the liberation of hydrogen from certain metallic hydrides by the action of water.[5] It is also produced when a silent electric discharge acts upon a mixture of oxygen with excess of hydrogen.[6]

Active hydrogen is apparently produced by the action of sulphuric or hydrochloric acid upon magnesium under certain conditions,[7] and also by electrolysing solutions of caustic potash or sulphuric acid with a very high current density.[8] The

[1] Freeman, *J. Amer. Chem. Soc.*, 1913, **45**, 927.

[2] Burt and Edgar, *Phil. Trans.*, 1916, (*A*), **216**, 393.

[3] Venkatramaiah, *Proc. Sci. Assoc. Maharajah's Coll. Vizianagram*, July 10, 1921; *Nature*, 1920, **106**, 46.

[4] Venkatramaiah, *J. Amer. Chem. Soc.*, 1923, **45**, 261.

[5] Venkatramaiah, *Proc. Sci. Assoc. Maharajah's Coll. Vizianagram*, December, 1922.

[6] Venkatramaiah, *ibid.*, 1923.

[7] Grubb, *Nature*, 1923, **111**, 600.

[8] Grubb, *ibid.*, 1923, **111**, 671.

hydrogen so produced reacts with nitrogen to form ammonia, and its activity persists even after the gas has been passed over glass wool, which shows that this form of hydrogen is more akin to Wendt and Landauer's variety than to Langmuir's monatomic hydrogen. The life of the active form discovered by Grubb is not greater than two minutes, a figure which agrees with the Wendt-Landauer results much better than with Langmuir's data. Grubb's results have been confirmed by other workers.[1]

When a continuous discharge is passed through a vacuum tube containing hydrogen at low pressure, a spectrum is emitted which is termed the primary hydrogen spectrum. If a condenser be inserted in the circuit, so that the discharge becomes an oscillating one, the character of the emission changes and a spectrum is emitted which is known as the secondary hydrogen spectrum. A considerable amount of controversy has taken place as to the origin of this alteration in the spectrum, and the suggestion has been made that dissociation of the hydrogen may lie at the root of the matter; but the question cannot be regarded as settled yet.

On examining the spectrum of hydrogen in long vacuum tubes, Wood [2] observed that both spectral types could be seen, the primary Balmer spectrum appearing in the central portion of the tube, whilst the secondary spectrum was emitted at the ends of the tube. If at least a fifth of a second was allowed to elapse after the discharge had passed, and if then the switch was closed, there was a flash of the secondary spectrum throughout the whole tube which lasted for about one-fiftieth of a second. Wood found that if hydrogen were withdrawn from the central portion of the tube, it had peculiar properties; for on passing it over certain substances, such as fractured glass, metals, and some oxides, it raised them to the temperature of incandescence.

Active hydrogen drawn off from the central part of a discharge tube has been further investigated.[3] It was found to reduce

[1] Venkatramaiah and Rao, *Nature*, 1923, **112**, 57.

[2] Wood, *Phil. Mag.*, 1921, (vi), **42**, 729; 1922, **44**, 538; Dorsch and Kallman, *Z. Physik*, 1929, **58**, 80; Smallwood, *J. Amer. Chem. Soc.*, **51**, 1985.

[3] Bonhoeffer, *Z. physikal. Chem.*, 1924, **113**, 199, 492; 1925, **116**, 391; Boehm and Bonhoeffer, *ibid.*, 1926, **119**, 385; Bonhoeffer and Harteck, *ibid.*, 1928, **139**, 164; 1929, [B], **4**, 113; **5**, 292; *Naturwiss.*, 1929, **17**, 182, 321; *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1929, 103; *Z. Elektrochem.*, 1929, **35**, 621; Taylor and Hill, *Z. physikal. Chem.*, 1929, [B], **2**, 449; Klemenc and Patat, *ibid.*, **3**, 289.

certain metallic oxides, halides, and sulphides ; whilst it converts sulphur, arsenic, and phosphorus into the corresponding hydrides. With oxygen it yields hydrogen peroxide ; and from the halogens the corresponding acids are produced. Carbon monoxide and carbon dioxide yield traces of formaldehyde. Oleic acid is reduced by it. This active form of hydrogen is rapidly altered by hydrogen chloride, hydrogen bromide, hydrogen sulphide, and methyl chloride, the reaction giving rise to molecular hydrogen :

$$H+HCl=H_2+Cl$$

With mercury, it is believed that a mercury hydride is formed. Wood's active hydrogen luminesces in the ultra-violet region (3064 Å.) ; and it gives visible luminescence when brought into contact with mercury, zinc sulphide, anthracene, vapours of the alkali metals, and sundry other materials.

It is believed that Wood's active hydrogen is simply atomic hydrogen ; and that the incandescence observed when it passes over rough glass surfaces, etc., is due to a catalytic reformation of molecular hydrogen. Its normal life-period is about a fifth of a second ; and its activity is destroyed immediately at the temperature of liquid air.

When hydrogen is cooled with liquid air, the tint of the emitted light in a discharge tube is found to alter.[1] Now, Wendt and Landauer[2] observed the spectrum of the hydrogen in their discharge tube during the experiments made by them on the contraction of the gas during electrical discharge ; and they noticed in the case of liquid-oxygen cooling that the light emitted by the tube underwent a series of interesting changes. Beginning with the usual lavender tint, the colour of the light first showed an intensification of the red. For half a minute it was brick-red ; then it changed rapidly through orange to yellow, becoming finally a bright greenish-yellow. Examination of the light by means of a visual spectroscope revealed the fact that the primary hydrogen spectrum was much weakened, whilst the secondary spectrum was brilliantly displayed.

On shutting off the current for a few minutes and then once more closing the circuit, the emitted light is still found to be greenish-yellow as before, showing that the material which emits

[1] Lemon, *Astrophys. J.*, 1912, **35**, 109.

[2] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510.

it has not altered markedly during the interval. This is probably to be ascribed to the cooling effect.

For further information, the original papers must be consulted.[1]

5. *Possible Forms of Hydrogen*

The change which has come over the face of chemistry in the last ten years can hardly be better exemplified than by an examination of the present state of our knowledge of hydrogen. Little more than a decade back in the history of the subject, hydrogen presented no particular difficulties to the inquirer of that period. It was known to exist in three forms: molecular hydrogen, H_2; the hydrogen ion, which was regarded as a hydrogen atom carrying one positive charge of electricity; and "nascent hydrogen," which was generally assumed to be a series of isolated hydrogen atoms. In valency questions hydrogen was used as the unit, since it was assumed to be definitely monovalent and incapable of uniting with more than a single other atom.

The experimental work and the speculations which have been dealt with in earlier chapters of this book have altered all this. On the theoretical side, a clearer conception has arisen of the nature of the hydrogen atom and of the possible variations in the character of the materials which are grouped under the head of "hydrogen"; whilst the experimental advances have greatly increased our knowledge of the behaviour of the hydrogen system under different conditions. Some points remain to be cleared up; but there seems every reason to believe that in a short time even these matters will have been illuminated by further experiment.

It seems of interest, therefore, to bring together the various pieces of information which have been acquired and to indicate those points which are still obscure.

In the first place, the resemblances which hydrogen shows to the alkali metals on the one hand and to the halogens on the other, can be accounted for on the modern theory of valency

[1] Hemptinne, *Ann. Soc. Sci. Bruxelles*, 1927, **47**, B, i., 143; Elliott, *A.*, 1927, 187; Glockler, Baxter, and Dalton, *J. Amer. Chem. Soc.*, 1927, **49**, 58; Glockler, *Science*, 1926, **64**, 505; *Nature*, 1927, **121**, 93; Lunt, *ibid.*, 357; Elliott, *ibid.*, 985; Poljakov, *Naturwiss.*, 1928, **16**, 131; Schwab and Seuferling, *Z. Elektrochem.*, 1928, **34**, 654.

without any great difficulty. If hydrogen be regarded as a system containing a single proton round which a single electron revolves, then the possible electronic changes in that system are limited to three. In the first place, the system may give up its electron to an exterior system; or it may share its electron with a second system; or, finally, it may assimilate an extra electron from an exterior system. For each of these cases a chemical parallel can be found.

Take first the case in which the hydrogen system parts with its electron. On the theory of valency of G. N. Lewis, the alkali metals have a single electron in their outermost spheres, whilst the halogen atoms have an outer sphere containing seven electrons. When lithium fluoride ionises, the electron of the lithium atom leaves this system and attaches itself to the fluorine system, the outermost sphere of which then contains eight electrons and becomes analogous to the electronic system of neon; while by the same operation the electronic system of lithium reverts to the helium form with two electrons in the outermost existing sphere. When the two systems fall apart, there is an excess of one negative charge on the fluorine grouping —the nuclear charge being 9 and the electronic charge being 8— and one excess positive charge on the lithium group—its nuclear charge being 3 and its electronic charge being now 2. Exactly the same reasoning can be applied to the case of the combination between hydrogen and fluorine, except that in this instance the extreme point is reached at which there are no electrons whatever left in the hydrogen system, which thus consists of one proton with its single positive charge. The formation of the hydrogen ion is evidently parallel to the ionisation of the alkali metals, since in both cases there is no electron left in the outermost sphere of the atom.

Turn now to the case of electron-sharing. The carbon atom of methane, CH_4, has an outer sphere containing four electrons. If four extra electrons be added to this grouping, the system will revert to the inert gas type which contains eight electrons in the outer sphere. These four electrons could be supplied from four hydrogen systems, provided that the electrons are counted as belonging to both systems at once.* Each hydrogen system

* This provision is necessary in order to distinguish the case from the ionisation of lithium fluoride, since actual experiment shows that methane, CH_4, does not ionise.

would contain its own electron; whilst by bringing these four systems into the outermost sphere of the carbon atom the latter system would be raised to the electronic octet which is the analogy of the neon system. It must be frankly admitted that this conception necessitates the further postulate that a system of this type does not yield ions, which is a point that requires some satisfactory explanation. However, in the present place, we are concerned only with seeing whether a picture of the mechanism can be produced, and the explanation may possibly come in due time.

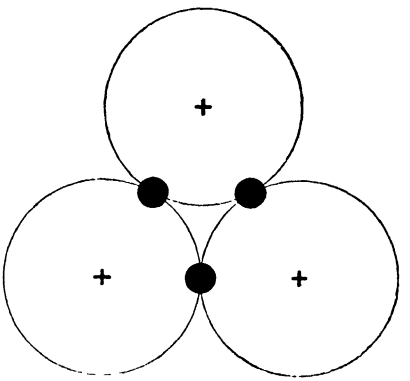


FIG. 26.

It seems highly probable that the existence of triatomic hydrogen can be accounted for on analogous lines. If the circles in Fig. 26 represent the electronic spheres of three hydrogen atoms, and if the three electrons be distributed as shown, then each electron is shared by two systems, and each of the three hydrogen systems is a "pseudo-inert gas" system akin to the helium type.

There still remains a final possibility: that the hydrogen system may acquire an extra electron. In this case, the outermost sphere of the atom would contain two electrons * and would thus be analogous to the inert gas grouping of helium; whilst at the same time, owing to the extra electron, the system as a whole would acquire a negative charge. This arrangement appears to throw light upon the affinity of hydrogen for the metals. Take the case of lithium hydride as an example. Here there is the lithium atom with one electron in its outermost sphere; and this electron, as already mentioned, can be transferred to other atoms in order to bring their outermost electronic groupings to an inert gas type—as in the case of lithium fluoride which was described above. Assume, now, that the outermost

* This state of affairs, of course, occurs in the case of the methane molecule; but in that system the electron pairs are shared between the hydrogen and the carbon systems.

electron of the lithium atom is transferred to a hydrogen atom. The hydrogen system now contains one proton and two electrons, so that it carries one surplus negative charge—just like the fluorine ion; whilst simultaneously the lithium atom has an excess positive charge, since it has three protons and two electrons in its system. If this pair of atoms now splits apart in ionisation, it will be resolved into a positive lithium ion and a negative hydrogen ion; and this, it may be recalled, is exactly what is found by experiment in the electrolysis of lithium hydride.

Thus the modern theory of electronic valency allows us to picture * the various possible arrangements of the hydrogen system in a satisfactory manner, though up to the present we have no explanation of the different behaviours of these systems in practice.

There now remains for consideration the problem of identifying, so far as is possible, the various modifications of the hydrogen system with which chemists are acquainted at the present time.

In the first place, there is molecular hydrogen, H_2. This is the normal form of the element; and its properties are too well known to need description here.

Next, there is the ionic form of hydrogen which appears in the reactions of acids. This, so far as can be seen, is a single proton, the simplest chemical material with which we are acquainted.

Triatomic hydrogen's identity also seems beyond doubt; and the available evidence suggests that Grubb's active hydrogen may belong to this category.

The monatomic hydrogen of Langmuir seems to be an extreme example of what is usually termed "nascent hydrogen." Under the normal conditions of preparation, the form of hydrogen which we call "nascent" is obtained in high concentration; and if

* Mental confusion between a representation and an explanation is unfortunately commoner in science than it should be. A representation may show *how* a thing behaves; but it furnishes no explanation of *why* such behaviour is to be expected. A painting of a donkey eating thistles is a representation of how a certain process takes place; but it certainly could not be regarded as an explanation of the ass's avidity for these apparently unappetising vegetables. In the same way, our pictures of model atoms probably are quite good representations of the sub-microscopic world; but it would be a mistake to regard them as explanatory of the forces which are at work in that sphere. They may furnish us with the key of the problem, but they are not in themselves the key.

it be composed of single atoms, they must undergo such frequent collisions that the existence of the monatomic form must be very brief. Under the experimental conditions devised by Langmuir, the chance of combination by collision is greatly reduced; and when frequent collisions are made possible by adsorption on glass wool, the gas seems to lose those properties which suggest the nascent condition. The same reasoning might be applied to Venkatramaiah's active hydrogen, since it is found as a product in chemical reactions from which "nascent hydrogen" might be expected.

It is, of course, possible that the active hydrogens discovered by Venkatramaiah and Grubb are not monatomic forms but are really hydrogen molecules which have undergone energy-change.

To complete this survey, some account must be taken of the hydrogen types which have been detected by means of the mass spectrograph.

In the first place, there is the negative hydrogen particle.* This particle is apparently a grouping composed of one proton and two electrons. It carries a single negative charge. It seems very probable that this form of hydrogen is produced at the positive electrode when lithium hydride or calcium hydride is electrolysed.

Secondly, the mass spectrograph has revealed the existence of a hydrogen molecule carrying one positive charge.† This system of two protons and one electron has not yet been recognised among our ordinary chemical products, though possibly it may be represented by Wood's form of active hydrogen.

In conclusion, attention may be drawn to a possibility in the hydrogen problem, though up to the present there is no experimental evidence forthcoming which suggests the occurrence of the material in nature. If an atomic nucleus existed which contained n protons and $(n-1)$ electrons, the atom would be isotopic with hydrogen, since it would have a positive nuclear charge of one unit. It was at one time suggested that Wendt and Landauer's form of hydrogen corresponded to this hypo-

* A photograph of the parabola produced by particles of this type is shown on Plate III.

† For a photograph of the parabola corresponding to this, see Plate III.

thetical iso-hydrogen; but all the evidence seems to be against the hypothesis.[1]

In the first place, the quantities of energy required in order to condense three normal hydrogen nuclei into a single nucleus of iso-hydrogen would be quite out of proportion to the energy which is actually absorbed during the experimental production of triatomic hydrogen by means of a heated wire or by passing an electrical discharge through an ordinary vacuum tube.

Secondly, if iso-hydrogen existed with an atomic weight of 3, then, since in chemical properties it would be identical with ordinary hydrogen, it should have a molecular weight of 6. But no parabola corresponding to this value has been observed by means of the mass spectroscope.

Thirdly, iso-hydrogen, having the same chemical properties as normal hydrogen, should not show the great reactivity manifested by triatomic hydrogen.

These arguments seem to dispose of the possibility that triatomic hydrogen furnishes an example of hydrogen isotopy.

[1] Wendt and Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510.

CHAPTER XVI

SOME NEW HYDRIDES

A. Boron Hydrides

1. *The Preparation of the Boron Hydrides*

It is curious to find that early attempts to prepare hydrides of boron were not very successful; for, once the correct method was devised, boron proved itself to be capable of forming a longer series of hydrogen compounds than any other elements except carbon and silicon. Wöhler and Deville [1] failed to obtain boron hydride from aluminium boride and hydrochloric acid; and the attempt of Moissan [2] met the same fate. Gustavson [3] was also unable to isolate any hydride resulting from the interaction of sodium amalgam and boron trichloride at 150° C., though a silicon hydride can be obtained by an analogous reaction.

Slightly better results attended the researches of Jones and Taylor,[4] Sabatier,[5] Ramsay and Hatfield [6]: though in no case was a pure boron hydride isolated by any of these investigators. In most cases the specimens seem to have been contaminated by admixtures of hydrogen silicides. Vournasos [7] obtained some boron hydride by the action of sodium formate on boron; and some solid hydrides, probably mixtures, had been prepared by other workers.[8]

Stock and his collaborators opened up a completely fresh

[1] Wöhler and Deville, *Ann. Chim. Phys.*, 1858, (3), **52**, 88.

[2] Moissan, *Compt. rend.*, 1893, **117**, 423; *Ann. Chim. Phys.*, 1895, (7), **6**, 296; Moissan and Williams, *Compt. rend.*, 1897, **125**, 629.

[3] Gustavson, *Zeit. Chem. Phys. Math.*, 1870, (2), **6**, 522.

[4] Jones, *J.*, 1879, **35**, 41; Jones and Taylor, *J.*, 1881, **39**, 213.

[5] Sabatier, *Compt. rend.*, 1891, **112**, 866.

[6] Ramsay and Hatfield, *P.*, 1901, **17**, 152.

[7] Vournasos, *Compt. rend.*, 1910, **150**, 464, 922.

[8] Reinitzer, *Monatsh.*, 1880, **1**, 792; Lorenz, *Annalen*, 1888, **247**, 246; Winkler, *Ber.*, 1890, **23**, 778.

field and revealed that boron is capable of forming chain compounds analogous to the hydrocarbons.

Magnesium boride, prepared by the interaction of boron trioxide and magnesium, was found to yield volatile boron hydrides when treated with hydrochloric acid (2N to 8N in strength) at 50°–80° C. The gaseous product, however, is a mixture of various hydrides and is further contaminated with silicon hydrides arising from silicon impurity in the magnesium

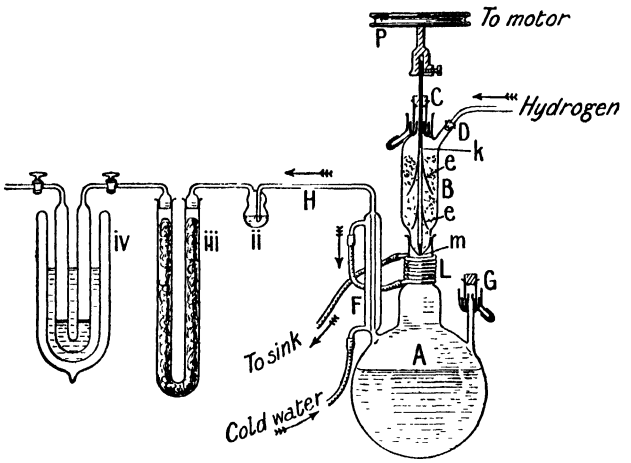


FIG. 27.—Stock's Apparatus for preparing Boron Hydrides.
(*From Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry."*)

employed. A special apparatus was designed,[1] part of which is shown in Fig. 27.

The hydrochloric acid is placed in the flask A, which has an outlet tube H, jacketed with the condenser F. A mercury safety tap is shown at G. The vessel B contains powdered magnesium boride which is kept agitated by the wings *e*, *e* of the stirrer K, which is driven by the pulley P. At C there is a mercury seal. At K there is an opening in the side of the stirrer tube. Hydrogen is slowly passed through the side tube at D, makes its way through the orifice at K, and so passes into the flask A. At *m* there is communication between the flask A and

[1] Stock and Massenez, *Ber.*, 1912, **45**, 3539; Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.

the boride reservoir; and the speed with which the powder descends into A is governed by the speed of the stirrer.

The gaseous products of the reaction, mixed with hydrogen, pass out through the side tube H. At F the condenser frees them from some water; at (ii) they pass through a bubbler of water which enables the speed of flow to be gauged; at (iii) a drying tube of calcium chloride and phosphorus pentoxide is interposed; and finally they are collected in a U-tube cooled by liquid air at (iv). The boride reservoir holds about 100 gr., from which in nine hours a yield of 70 litres of gas is obtained.

The material thus prepared is very complex. It contains the silicon hydride, SiH_4; carbon dioxide; the silicon hydride, Si_2H_6; a boron hydride, B_4H_{10}; another boron hydride, B_6H_{12}; and some other, higher-boiling hydrides of silicon and boron. Separation of these was attained by fractional distillation or fractional condensation with the help of liquid air.

2. *The Properties of the Boron Hydrides*

Diborane, B_2H_6, is the simplest hydride known at present. The best method of preparing it is to heat tetraborane, B_4H_{10}, in a sealed tube. Diborane melts at —165·5° C. and boils at —92° C., so that under ordinary conditions it is gaseous. In the absence of grease or moisture, it is quite stable; and it undergoes no dissociation at temperatures up to 155° C.[1] When heated over an open flame, however, it decomposes. The products of its decomposition are hydrogen, the hydride, $B_{10}H_{14}$, and two other solid hydrides, one of which is colourless and soluble in carbon disulphide, whilst the other is yellow and insoluble in carbon disulphide.[2]

When treated with water or alkali solutions,[3] diborane is immediately decomposed, yielding hydrogen and leaving boric acid or a borate in solution. The initial product seems to be hypoboric acid, which at once breaks up:

$$B_2H_6+6H_2O=2H_3BO_3+6H_2$$

Diborane inflames spontaneously in contact with air, but does not appear to react with hydrogen sulphide. Its reactions

[1] Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.
[2] Stock, Friederici, and Priess, *Ber.*, 1913, **46**, 3353.
[3] Stock and Friederici, *Ber.*, 1913, **46**, 1959.

with the halogens are of considerable interest.[1] It explodes with chlorine, but reacts only slowly with bromine. In each case, half the quantity of halogen employed reappears as halogen acid when the diborane is in excess. With excess of halogen present, boron trichloride, BCl_3, or boron tribromide, BBr_3, is formed and not B_2Cl_6 or B_2Br_6, as might have been expected from the formula B_2H_6 of the hydride. So far as can be seen, the reaction takes place in two stages, in the first of which unstable substitution products of the type $B_2H_4Cl_2$ and $B_2H_3Cl_3$ are formed; and these quickly decompose and rearrange themselves into B_2H_5Cl and B_2H_6 on the one hand, and BCl_3 on the other. Thus the second reaction of the series is the usual one of mutual oxidation and reduction which is so common in chemistry:

$$6B_2H_5Cl = 5B_2H_6 + 2BCl_3$$

Both the monochloride, B_2H_5Cl, and the monobromide, B_2H_5Br, are gases under ordinary conditions. The monochloride is spontaneously inflammable. The monobromide burns with a pale green flame and reacts with water in the following manner:

$$B_2H_5Br + 3H_2O = B_2O_3 + HBr + 5H_2$$

An attempt to prepare tetraborane, B_4H_{10}, by acting on B_2H_4Br with sodium—by analogy with the Wurtz-Fittig reaction for the preparation of butane from ethyl bromide—led to no results.

If the boranes formed a homologous series like the paraffins, the next hydride which might be expected would be triborane, B_3H_8, but up to the present no such substance has been isolated.

Tetraborane, B_4H_{10}, was among the earliest hydrides obtained by Stock and Massenez.[2] It melts at —120° C. and boils at 18° C.; but even when quite pure it decomposes rapidly into hydrogen, diborane, B_2H_6, and two solid hydrides.[3] This reaction is catalysed by ultra-violet light. Curiously enough, tetraborane reacts with ethane, yielding hydrogen, the hydride B_5H_9, and a crystalline compound containing boron, carbon, and hydrogen. With acetylene, tetraborane fails to interact at ordinary temperatures; but at 100° C. a mixture of the two

[1] Stock, Kuss, and Priess, *Ber.*, 1914, **47**, 3115; Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.

[2] Stock and Massenez, *Ber.*, 1912, **45**, 3539.

[3] Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.

explodes. With halogens,[1] tetraborane gives substitution products, like members of the paraffin series in organic chemistry.

With water,[2] tetraborane reacts readily, yielding boric acid and hydrogen:

$$B_4H_{10}+12H_2O=4H_3BO_3+11H_2$$

It is therefore a strong reducing agent. With alkali [3] it yields a hypoborate in the following manner:

$$B_4H_{10}+4KOH=4KOBH_3+H_2$$

The hypoborate thus formed is deliquescent and decomposes slowly. It is a strong reducing agent; and with copper salts it yields copper hydride, whilst with nickel salts it produces nickel boride, NiB_2. The decomposition of the hypoborate seems to take the following course:

$$2KOBH_3+2H_2O=2KBO_2+5H_2$$

This reaction is immediate when acid is present. When the dry hypoborate is heated to 500° C. it breaks up and liberates hydrogen, water, and metallic potassium. The mechanism of the reaction is obscure, but the following has been suggested:

$$5KOBH_3=K_3B_5O_3+2K+2H_2O+11H$$

The substance $K_3B_5O_3$ is a weak reducing agent; and when treated with sulphuric acid, it liberates hydrogen and deposits some hydrides of boron.

The next three hydrides contain five atoms of boron in the molecule; and it will be sufficient to distinguish them by their formulæ instead of adopting names like pentaboron enneahydride, which, after all, merely restate the formulæ in words.

The hydride B_5H_9 was obtained by Stock and Kuss [4] in a pure state by heating tetraborane, B_4H_{10}, to 100° C. and then fractionating the product. It melts at —46·9° C., and under ordinary conditions is a mobile liquid with an extremely unpleasant odour. It appears to be the substance which lends a noxious character to the original mixture of the hydrides in the raw state. It decomposes slowly into hydrogen and a colourless hydride soluble in carbon disulphide but insoluble in water,

[1] Stock, Kuss, and Priess, *Ber.*, 1914, **47**, 3115.
[2] Stock and Massenez, *Ber.*, 1912, **45**, 3539.
[3] Stock and Kuss, *Ber.*, 1914, **47**, 810.
[4] *Ibid.*, 1923, **56**, (B), 789.

which is possibly identical with the hydride obtained from tetraborane's decomposition. Water slowly hydrolyses B_5H_9 with the liberation of hydrogen and boric acid.

Some of its other reactions [1] are peculiar. It refuses to react with hydrogen chloride even in presence of aluminium chloride; but it combines direct with ammonia, yielding a white solid having the composition $B_5H_9(NH_3)_4$. This compound reacts readily with hydrogen chloride, though the parent body will not; the first product seems to be $B_5H_5Cl_4(NH_3)_4$, but further action leads to the formation of $B_5H_2Cl_7(NH_3)_4$. This hepta-chloro derivative, when dissolved in water, yields a strong reducing solution, hydrogen being liberated.

The hydride B_5H_{10} comes next in the series.[1] Its formula is not absolutely established; but it contains more than nine hydrogen atoms and the available evidence seems to indicate B_5H_{10} as the most probable composition. It is obtained by heating tetraborane, B_4H_{10}; and at ordinary temperatures it decomposes, yielding hydrogen and a yellow hydride, insoluble in carbon disulphide but soluble in water, which is probably identical with the second hydride produced in the decomposition of tetraborane.

The hydride B_5H_{11} is found among the decomposition products of diborane, B_2H_6. It is a colourless liquid which rapidly decomposes at ordinary temperatures, yielding a solid hydride with the formula $B_{10}H_{14}$, as well as hydrogen.[1]

The hydride B_6H_{10} is obtained [2] by working up the residues in the preparation of tetraborane, B_4H_{10}, so that possibly it is a decomposition product of tetraborane. It is a colourless, spontaneously inflammable liquid with a disagreeable odour. Its sensitiveness to water is greater than that of tetraborane; and its instability sometimes leads to dangerous explosions.

At one time it was supposed that a hydride B_6H_{12} existed; but recent investigation [3] seems to have established that it is really a mixture of various hydrides.

The hydride $B_{10}H_{14}$ is obtained by heating diborane, B_2H_6, for forty-eight hours at 120° C. or by heating tetraborane, B_4H_{10},

[1] Stock and Siecke, *Ber.*, 1924, **57**, (B), 562.
[2] Stock and Massenez, *Ber.*, 1912, **45**, 3539.
[3] Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.

to 100° C. for four hours. As has already been mentioned, the resulting product is a mixture of three hydrides, but as $B_{10}H_{14}$ can be sublimed in vacuo whilst the other two hydrides are non-volatile, a separation is possible.[1] If the heating during the preparation of $B_{10}H_{14}$ be too prolonged, the yield is reduced[2] owing to the decomposition of the hydride into two other hydrides which are supposed to be B_5H_9 and B_5H_{10}. At 600°–700° C., $B_{10}H_{14}$ decomposes into its elements. It is a solid, soluble in alcohol, ether, benzene, and especially readily in carbon disulphide, but insoluble in water.[1]

It must be borne in mind that the yields of these hydrides are extraordinarily poor, so that the investigation of their properties has been beset with more than normal difficulties.

3. *The Structures of the Boron Hydrides*

From the data in the foregoing section, it is clear that boron sometimes behaves like carbon in its hydride-formation, but that in other cases it functions as a trivalent element. It may therefore be expected that it will furnish one set of hydrides closely allied in structure to the paraffins, and also a second series built up on the basis of both tri- and quadrivalent boron.

Stock[3] has formulated the structures of the commoner boron hydrides on this basis; and the following examples will suffice to indicate his results:

$B_2H_6 = BH_3.BH_3$
$B_4H_{10} = BH_3.BH_2.BH_2.BH_3$
$B_5H_9 = BH_3.BH.BH.BH.BH_3$
$B_5H_{11} = BH_3.BH_2.BH.BH_2.BH_3$
$B_6H_{10} = BH_3.(BH)_4.BH_3$
$B_{10}H_{14} = BH_3.(BH)_8.BH_3$

He has also put forward suggestions as to the nomenclature of the group, but as these are somewhat complicated, they need not be described here.

[1] Stock, Friederici, and Priess, *Ber.*, 1913, **46**, 3353.
[2] Stock and Kuss, *Ber.*, 1923, **56**, (B), 789.
[3] Stock, *Ber.*, 1926, **59**, (B), 2226.

B. Silicon Hydrides

1. *Nomenclature*

The silicon hydrides form a regular series akin to the homologous series of organic chemistry; and Stock [1] has taken advantage of this to devise a nomenclature for the silicon group which is even more simple than the carbon terminology. Just as the members of the paraffin series differ from each other by the methylene group —CH_2—, the silicon hydrides increase by —SiH_2— as the series is ascended. Stock terms them all "*silanes*"; and he distinguishes between them by means of a prefix. Thus SiH_4 is *monosilane*; Si_2H_6 is *disilane*; Si_3H_8 is *trisilane*; Si_4H_{10} is *tetrasilane*, and so forth.

Corresponding to the ethylene series, C_2H_4, C_3H_6, C_4H_8, etc., there would be a series of *silenes*. Thus Si_2H_4 would be *disilene*; Si_4H_8 would be *tetrasilene*. The silicon analogues of the acetylenes, C_2H_2, C_3H_4, etc., would be designated *silins*, with the customary prefix to indicate the number of silicon atoms in the molecule; *e.g.* Si_2H_2 would be described as *disilin*.

Radicles derived from the silanes by removal of one hydrogen atom are named by replacing the termination *ane* of the parent's name by *yl*, just as is done in the case of the paraffins. Thus the radicle —SiH_3 derived from monosilane is called *monosilyl*, and —Si_2H_5 is known as *disilyl*. When a silicon and a carbon radicle are joined together in a chain, the name of the compound is derived from those of the parents. Thus $SiH_3.CH_2.CH_3$ would be named either *ethyl-monosilane* or *monosilyl-ethane*.

When two silyl radicles are linked through an oxygen atom, the name is obtained by placing the suffic *oxan* after the abbreviated title of the radicle: thus $SiH_3—O—SiH_3$ is termed *disiloxan*.

2. *The Preparation of the Silanes*

Monosilane was discovered in 1857 by Wöhler and Buff [2] among the products of the action of hydrochloric acid upon aluminium contaminated with silicon. Disilane was first pre-

[1] Stock, *Ber.*, 1916, **49**, 108; 1917, **50**, 169.

[2] Wöhler and Buff, *Annalen*, 1857, **103**, 218; Moissan and Smiles, *Compt. rend.*, 1902, **134**, 569.

pared by Moissan and Smiles,[1] who obtained it by treating magnesium silicide with hydrochloric acid. These were the only hydrides of silicon known until 1915, when the work of Stock and his collaborators [2] extended the field so that it now includes a regularly ascending series of homologous compounds which form a close parallel to the hydrocarbons.

Magnesium silicide is the starting material from which all the silanes hitherto obtained can be prepared; but since some members of the series are spontaneously inflammable, a special apparatus was devised [3] in order that the preparation and fractionation of the mixed products could safely be carried out. It was found that the best results were obtained when powdered magnesium silicide was added to excess of hydrochloric acid, and not *vice versâ*. The gases resulting from the reaction were cooled in liquid air; and by fractional vaporisation of the liquefied material an almost complete separation of the various members of the series was accomplished with ease.

3. *The Properties of the Silanes*

Monosilane,[3] SiH_4, can be distilled off practically pure from the crude mixture of liquefied gases generated from hydrochloric acid and magnesium silicide, if the temperature be raised to —120° C. When dilute, the gas has an odour recalling that of antimoniuretted hydrogen; but in strong concentration it has a disagreeable smell and produces headache.

At ordinary temperatures it is very stable, as is shown by the fact that it is found among the decomposition products when trisilane or tetrasilane is passing through a dull red quartz tube. At a red heat, however, monosilane decomposes into silicon and hydrogen. It is much the most stable of all the silanes.

A peculiarity in its behaviour has been observed with regard to spontaneous inflammability, for in this respect it seems to behave erratically. Although at times perfectly pure specimens of monosilane take fire and explode with a loud noise, depositing brown flocky material, at other times it fails to go off, especially in the case of small bubbles. If it is mixed with trifling quantities of the other silanes, it almost invariably explodes in air.

[1] Moissan and Smiles, *Compt. rend.*, 1902, **134**, 569, 1549.
[2] For a summary of this work, see Stock, *Z. Elektrochem.*, 1926, **32**, 341.
[3] Stock and Somieski, *Ber.*, 1916, **49**, 111.

At ordinary temperatures, monosilane is only slowly decomposed by water—about 20 per cent. in 24 hours.* The reaction takes the course shown below :

$$SiH_4+2H_2O=SiO_2+4H_2$$

With alkali, a similar reaction occurs :

$$SiH_4+2NaOH+H_2O=Na_2SiO_3+4H_2$$

Dry ammonia, concentrated sulphuric acid, alcohol, ether, benzene, carbon disulphide, chloroform, and carbon tetrachloride are without action upon monosilane, though it dissolves to some extent in the organic solvents.

The action of diluted oxygen at low temperatures [1] upon monosilane has been studied ; but the results have not been very encouraging. Free hydrogen is liberated and a number of solid substances such as polymeric siloxan, $(SiH_2O)_n$, and silicoformic anhydride, $[(SiHO)_2O)]_n$. Taken in conjunction with the liberation of hydrogen, the presence of these substances suggests that the primary oxidation reaction is :

$$SiH_4+O=SiH_2O+H_2$$

This production of hydrogen seems to give a clue to the difference between the quiet spontaneous ignition of impure phosphine in air—wherein no hydrogen is liberated—and the explosive violence of the spontaneous inflammation of monosilane.

The most remarkable reaction of monosilane is that with hydrogen chloride or hydrogen bromide.[2] In presence of aluminium chloride (or bromide), the reaction takes the following course :

$$SiH_4+HCl=SiH_3Cl+H_2$$
$$SiH_4+2HCl=SiH_2Cl_2+2H_2$$

This behaviour of monosilane differentiates it completely from the hydrocarbons with which it shows so many analogies ; for the halogen hydrides have no action upon the corresponding carbon derivative, CH_4. Curiously enough, however, the product of the foregoing reaction, chloro-monosilane, SiH_3Cl, behaves analogously to methyl chloride, CH_3Cl, in one respect :

* This reaction is catalysed by acid and alkali. In quartz vessels it goes extremely slowly (Stock and Somieski, *Ber.*, 1918, **51**, 989).

[1] Stock and Somieski, *Ber.*, 1922, **55**, (B), 3961.

[2] *Ibid.*, 1918, **51**, 989 ; 1919, **52**, 695 ; 1920, **53**, 759.

for with zinc methyl it yields methyl-monosilane, $SiH_3.CH_3$, exactly as ethane, $CH_3.CH_3$, can be prepared from methyl chloride and zinc methyl:

$$2SiH_3Cl+Zn(CH_3)_2=2SiH_3.CH_3+ZnCl_2$$
$$2CH_3.Cl+Zn(CH_3)_2=2CH_3.CH_3+ZnCl_2$$

By the discovery of this reaction, it has been possible to extend the series of mono-alkyl derivatives into a new class and to place $CH_3.SiH_3$ alongside the already known substances such as $CH_3.NH_2$, $CH_3.PH_2$, $CH_3.AsH_2$, $CH_3.OH$, and $CH_3.SH$.

Disilane,[1] Si_2H_6, can be obtained practically pure in the second fraction of the crude gases from magnesium silicide and hydrochloric acid, after cooling in liquid air. It is finally freed from contamination by repeated fractional distillation. Disilane, like monosilane, is a colourless gas with a disagreeable odour. It is quite stable, since only at 300° C. does it decompose, yielding a mixture of brown liquids and solids. Even when electric sparks are passed through it, disilane shows a remarkable stability.

In contrast to the behaviour of monosilane, disilane never fails to ignite spontaneously in air; and the report of the explosion appears to be remarkably loud. As in the case of monosilane, brown flocky materials are formed in the reaction.

Disilane's reaction with water resembles that of monosilane. In twenty-four hours, about 25 per cent. of the material is decomposed according to the equation:

$$Si_2H_6+4H_2O=2SiO_2+7H_2$$

The reaction with alkali is also analogous to that of monosilane:

$$Si_2H_6+4NaOH+2H_2O=2Na_2SiO_3+7H_2$$

Like monosilane, disilane is soluble in benzene and carbon disulphide. Alcohol readily dissolves it and the solution gives off some gaseous material. Concentrated sulphuric acid, dry ammonia, and dry hydrogen chloride seem without marked action. Disilane acts as a reducing agent upon solutions of salts like ferric chloride, potassium permanganate, mercuric chloride, and copper sulphate, the reduction being probably due to the nascent hydrogen liberated by the interaction between the disilane and the water of the solution.[2]

[1] Stock and Somieski, *Ber.*, 1916, **49**, 111.
[2] *Ibid.*, 1922, **55**, (B), 3961.

A somewhat extraordinary result [1] is observed when disilane is mixed with chloroform or carbon tetrachloride. A violent reaction takes place, flames being evolved and a heavy deposition of brown solid materials occurs. This phenomenon is the more surprising when it is remembered that monosilane dissolves in chloroform and carbon tetrachloride without reacting on them.

Like monosilane, disilane reacts with halogen hydrides [2] in presence of catalysts yielding hydrogen and a halogen substitution product:

$$Si_2H_6+HBr=Si_2H_5Br+H_2$$

Trisilane,[1] Si_3H_8, is found in the fraction of the crude gas which distils over after the mono- and disilane have been removed. It is a mobile, colourless liquid, with much less stability than either of the lower silanes and thus resembling the boranes. On heating, it breaks down finally into silicon and hydrogen, monosilane being apparently formed as an intermediate product in the decomposition.

Like disilane, it inflames spontaneously in air with a bright flame and a loud report.

Its behaviour with water recalls that of the lower silanes. About 18 per cent. of it decomposes in twenty-four hours in contact with water. The reaction appears to take the following course:

$$Si_3H_8+6H_2O=3SiO_2+10H_2$$

Trisilane is rapidly decomposed by alkali solutions, the reaction here also being analogous to these of the lower silanes:

$$Si_3H_8+6NaOH+3H_2O=3Na_2SiO_3+10H_2$$

Trisilane resembles disilane rather than monosilane in its behaviour with chloroform and carbon tetrachloride; for it explodes with both these reagents. It has been found [3] that the explosion occurs only in presence of oxygen, the merest trace of which suffices to start the action. Possibly the reaction between the silane and oxygen produces a local rise of temperature which starts the other reaction. In the case of chloroform, it

[1] Moissan and Smiles, *Compt. rend.*, 1902, **134**, 1549; Stock and Somieski, *Ber.*, 1916, **49**, 111.

[2] Stock and Somieski, *Ber.*, 1920, **53**, 759.

[3] Stock and Stiebeler, *Ber.*, 1923, **56**, (B), 1087.

is supposed that the reaction occurs mainly in accordance with the following equations :

$$Si_3H_8+4CHCl_3=Si_3H_4Cl_4+4CH_2Cl_2$$
$$Si_3H_8+5CHCl_3=Si_3H_3Cl_5+5CH_2Cl_2$$

This reaction illustrated the superiority of silicon over carbon in the power of attracting chlorine.

Tetrasilane,[1] Si_4H_{10}, is a colourless liquid of medium refractive power, and shows a close resemblance to trisilane in many properties. At room temperature it decomposes fairly rapidly; and its breakdown on heating is very like that of trisilane. The reactions with water and alkali seem to be analogous to those of the lower silanes; and it inflames spontaneously in air with a loud report. With chloroform and carbon tetrachloride its behaviour is similar to that of trisilane.[2]

Since the corresponding carbon compound, butane, C_4H_8, occurs in two isomeric forms, an attempt was made to isolate an isomeric tetrasilane; but apparently only one variety could be obtained.[2]

Pentasilanes,[2] Si_5H_{12}, apparently exist in isomeric forms, but very little investigation of them has yet been made.

Hexasilanes,[2] Si_6H_{14}, also appear to exist in more than one form, but this seems to be the extent of our knowledge at present.

In order that the difficulties of this investigation may be appreciated, it is only necessary to consider the approximate yields of the various silanes. Using 100 gr. of magnesium silicide (or at least the material which was employed by Stock and his collaborators) the yields of the different substances were: monosilane, 1·6 grs.; disilane, 1·1 grs.; trisilane, 0·5 gr.; and tetrasilane, 0·3 gr.

C. Germanium Hydrides

A hydride of germanium was first prepared by Voegelen,[3] who reduced germanium chloride by means of zinc and sulphuric acid. Twenty years later, Paneth and Schmidt-Hebbel[4] obtained the

[1] Stock and Somieski, *Ber.*, 1916, **49**, 111.

[2] Stock, Stiebeler, and Zeidler, *Ber.*, 1923, **56**, (B), 1695.

[3] Voegelen, *Z. anorg. Chem.*, 1902, **30**, 325.

[4] Paneth and Schmidt-Hebbel, *Ber.*, 1922, **55**, 2615; Paneth, Matthies, and Schmidt-Hebbel, *ibid.*, 785; see also Schenck, *Rec. trav. chim.*, 1922, **41**, 569.

hydride by acting on a solution of germanium in sulphuric acid with zinc or magnesium. The only compound detected by these workers was the simple monogermane, GeH_4. Muller and Smith [1] employed this hydride-formation as a refined test for small quantities of germanium.

In 1924, our knowledge of the subject was considerably extended by Dennis, Corey, and Moore,[2] who adapted Stock's method to the case of germanium. By acting upon a magnesium-germanium alloy with dilute hydrochloric acid, they obtained a mixture of at least three germanium hydrides, to which the names monogermane, GeH_4; digermane, Ge_2H_6; and trigermane, Ge_3H_8, have been given.

Monogermane, GeH_4, is a gas at ordinary temperatures. Its boiling-point is given as —125° C. by Schenck [3] and as —90° C. by the later workers, Corey, Laubengayer, and Dennis.[4] Its melting-point is —165° C. It is a stable compound, for samples kept in the gaseous state for a year showed no appreciable decomposition. On heating the hydride to 280° C., decomposition was observed; and a germanium mirror was formed in the tube.[4]

Digermane, Ge_2H_6, melts at —109° C. and boils at 29° C. It is a clear liquid. On heating to 214° C. it begins to decompose; and, ten degrees higher, it deposits a heavy germanium mirror. On exposure to air, it turns yellow and is finally changed to a dark-brown solid. It is not usually spontaneously inflammable in air; but on one occasion it was observed to ignite when air was rapidly admitted into a burette containing the hydride. When brought near a flame it ignites with almost explosive violence and burns with great rapidity, a reddish-brown material being deposited. With oxygen, it does not usually react with any marked eagerness; no reaction was observed when the oxygen was admitted to contact with the hydride, and only after ten minutes was a white substance deposited. With water, digermane's action is equally sluggish; only after some minutes was any action noticeable. A white substance formed in the water layer and gradually darkened

[1] Muller and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909.
[2] Dennis, Corey, and Moore, *J. Amer. Chem. Soc.*, 1924, **47**, 657.
[3] Schenck, *Rec. trav. chim.*, 1922, **41**, 569.
[4] Corey, Laubengayer, and Dennis, *J. Amer. Chem. Soc.*, 1925, **47**, 112.

in colour to light brown. Some gas was observed at the interface between the two liquids. When a 33 per cent. sodium hydroxide solution was substituted for water, a combustible gas of unknown nature was evolved at the liquid interface. Monogermane does not show this reaction, which thus forms a distinction between monogermane and digermane. With carbon tetrachloride, digermane reacts slowly, though heat is evolved when the two liquids are mixed.

Trigermane, Ge_3H_8, melts at —105·6° C. and boils at 110·5° C. It is a colourless mobile liquid which rapidly changes to a white solid on exposure to air. Its behaviour with oxygen, with water, and with carbon tetrachloride, was exactly similar to that of digermane. With caustic soda solution, however, it behaved like monogermane, showing no signs of reaction. Its thermal decomposition begins at 194° C., and a heavy mirror is formed at 208° C.

D. Tin Hydride

In the case of the boranes and silanes, interest naturally centres round the parallelism between those two groups of hydrides and the hydrocarbons. The hydrides which will be described in the remainder of this chapter contain no linked chains; their importance lies in a different field. Not so long ago it was tacitly assumed that increasing atomic weight rendered an atom less capable of furnishing a gaseous hydride; and the apparent non-occurrence of bismuth hydride was taken as a proof that antimony marked the extreme limit in weight of the atom which could furnish a volatile hydride. Recent investigations have upset this dogma; and it is now possible to make a general survey of the hydrides of even the heavier elements and so draw some inferences about hydrides in general.

Tin hydride is an example of the danger of accepting negative evidence on a problem, even when the evidence appears to be strong. Just over a century ago, Kastner [1] asserted that this hydride existed; but attempts by other workers to obtain the compound resulted in failure; and as late as 1902, the discoverer of germanium hydride [2] stated that his attempts to prepare tin hydride had been unsuccessful and that the existence

[1] Kastner, *Grundzüge der Physik und Chemie* (1821).
[2] Voegelen, *Z. anorg. Chem.*, 1902, **30**, 325.

of such a substance was improbable. Yet in less than twenty years the compound was obtained by one of the simplest of reactions.

The first successful attempt was made by Paneth and Fürth,[1] who prepared the gas by the action of 4N hydrochloric acid upon a magnesium-tin alloy. Later investigation [2] has proved that the hydride can readily be obtained by acting with metallic magnesium on solutions of tin sulphate or of stannous chloride in hydrochloric acid. It can also be produced, though in minute yield, by passing a spark discharge between tin electrodes in a hydrogen atmosphere; and by electrolysing a dilute solution of tin in sulphuric acid with a lead cathode.[3]

When prepared by the first of these methods, the hydride was identified in the following manner. A Marsh tube was connected with the generating apparatus; and this tube was heated with a Bunsen burner, as in testing for arsenic by the decomposition of arsine. A ring of metallic deposit formed in the tube close to the heated portion and much nearer to it than is found in the case of arsenic or antimony, so that the deposited metal is obviously different from either of these elements.

After cooling the tube, various tests were applied to the metallic mirror, all of which tended to prove the presence of tin. Cold concentrated nitric acid had little action on the film, which proved it could not be composed of arsenic, antimony, or bismuth, since their mirrors are easily removed by nitric acid. Yellow ammonium sulphide destroys the tin mirror, like those of arsenic and antimony; but this distinguishes it from the bismuth mirror, which is only deepened in tint by the action of ammonium sulphide. More characteristic still is the behaviour of the tin mirror when treated with a 1 per cent. gold chloride solution. Purple of Cassius is immediately produced. When mercuric chloride solution is introduced into the tube, the tin mirror attacks it and produces a white precipitate of calomel, which serves to distinguish the mirror from those of antimony and bismuth.

These tests seem sufficient to establish the existence of tin hydride; and, in view of the formulæ of the other volatile

[1] Paneth and Fürth, *Ber.*, 1919, **52**, 2020.

[2] Paneth, Johannsen, and Matthies, *Ber.*, 1922, **55**, (B), 769.

[3] Paneth, Matthies, and Schmidt-Hebbel, *Ber.*, 1922, **55**, (B), 775; Paneth, *Z. Elektrochem.*, 1923, **29**, 97.

hydrides of this group, CH_4, SiH_4, GeH_4, it seems reasonable to assume that SnH_4 is the proper formula for the compound.

In conclusion, it seems worth while pointing out that tin hydride cannot be prepared [1] from the well-defined sodium-tin alloy, Na_4Sn; for from this material not a trace of SnH_4 was obtained.

E. Lead Hydride

The application of radioactivity methods in the discovery of bismuth hydride, with which the next section of this chapter will deal, led to the application of analogous processes in the search for a hydride of lead; but as the results were not altogether conclusive by this method and as another process gave better effects, it will be sufficient to deal here with the latter mode of preparation.[2]

The process depends upon a sputtering of a lead electrode by means of a heavy current and an almost simultaneous liberation of hydrogen by electrolysis of a sulphuric acid solution. By these means, extremely finely divided lead is brought into contact with nascent hydrogen. The apparatus was so contrived that the lead electrode just touched the level of the sulphuric acid solution, which is variable. The closing of the circuit leads to evolution of hydrogen, which drives the liquid electrolyte out of contact with the lead electrode. A discharge through the gaseous space then follows; and the current is interrupted at this point. The electrolyte then flows upward to the electrode again; and the process is repeated. Thus, with proper arrangements for breaking the circuit, it is possible to produce a rapid rotation of sputtering and electrolysis intervals.

The gases obtained from this apparatus were passed into a Marsh tube heated by a Bunsen burner, special precautions being taken against the passage of fine particles of metallic lead into the tube. A metallic mirror was formed in the tube close to the heated section.

The possible nature of this deposit seems to be limited to arsenic, antimony, bismuth, tin, and lead, since these are the only likely materials giving gaseous hydrides and mirror deposits.

[1] Paneth, Johannsen, and Matthies, *Ber.*, 1922, **55**, (B), 769.

[2] Paneth and Norring, *Ber.*, 1920, **53**, 1693; Paneth, *Radio-elements as Indicators* (1928)

The fact that the mirror is deposited close to the heated zone makes it unlikely that arsenic and antimony can be present in it; but something more definite was required as a test.

Yellow ammonium sulphide intensifies the tint of the mirror. This proves that arsenic, antimony, tin, and tellurium are absent, since mirrors of these materials are soluble in ammonium sulphide. The lead mirror, however, shows the same character as bismuth, which also darkens with ammonium sulphide; so a further series of tests is required.

When the sulphide mirror obtained in the last test is treated with hydrogen peroxide, the colour changes from brown to white, which indicates the formation of lead sulphate from the lead sulphide; and the brown sulphide can be regenerated by a second treatment with yellow ammonium sulphide, provided the action of the hydrogen peroxide has not been allowed to go too far. This test satisfactorily excludes all the elements except bismuth, but unfortunately a bismuth mirror will show a somewhat similar series of colour-changes.

The crucial test was applied as follows. A tiny piece of iodine was placed before the mirror; and on warming the tube and applying a small flame, the grey mirror was changed into the yellow of lead iodide. Ammonia was then blown through the tube; and the deposit apparently vanished, reappearing once more when the tube had been exposed to air for a short time. Since under the same conditions a bismuth mirror gives a faint rose colour with iodine and changes in tint to yellow with ammonia without disappearing, this test seems to prove conclusively that the mirror is really formed of metallic lead.

No analysis of the hydride has been made, owing to the minute quantities in which it is formed; but it seems reasonable to ascribe the formula PbH_4 to it, and thus bring it into line with the other hydrides of the same group.

F. Bismuth Hydride

The discovery of bismuth hydride [1] brings into view a new weapon in the chemist's armoury: the radioactive indicator. In his earliest work on bismuth hydride, Paneth [2] assumed that

[1] For a general account, see Paneth, *Radio-elements as Indicators* (1928).

[2] Paneth, *Ber.*, 1918, **51**, 1704.

the compound might be formed only in minimal yields, and that therefore one of the chief difficulties would lie in its detection. Now, radioactivity measurements are very much more delicate than any chemical process when small quantities of material are concerned; so much so, in fact, that the electroscope will prove the existence of traces which no chemical reaction could detect. If, then, measurements of radioactivity can be substituted for purely chemical methods, it should be possible to establish the existence of the slightest yields of gaseous hydrides.

Now, in the case of bismuth, such an application is made possible owing to thefact that bismuth has four isotopes, Radium-C, Thorium-C, Actinium-C, and Radium-E, all of which are chemically indistinguishable from ordinary bismuth and all of which have radioactive properties. If bismuth forms a gaseous hydride, then all its four isotopes will also exhibit hydride formation; and their hydrides, being radioactive compounds, will be readily detectable in the minutest quantity by electroscopic measurements. They will, in fact, act as indicators showing whether or not ordinary bismuth is capable of hydride formation.

Using the necessary precautions, Paneth deposited some thorium-C upon magnesium foil and then allowed dilute hydrochloric acid to act upon the metal. The gas evolved from the reaction was examined in an emanation electroscope and found to be radioactive. As the radioactivity could be due only to thorium-C (since all precautions were taken to prevent mechanical transfer of any spray into the electroscope), this gave very good grounds for supposing that a volatile hydride of thorium-C had been formed; and if thorium-C yields a gaseous hydride, then non-radioactive bismuth must also do so, since bismuth and thorium-C are identical in all chemical properties.

By means of electroscopic measurements, it was found possible to determine the rate of decomposition of the hydride in the following way. As the hydride decomposes, thorium-C is thrown out in the form of fine solid particles which can be stopped by a glass-wool filter. Measurements of the activity of a fixed volume of the gas were made at intervals, and from the decline in activity, the quantity of trapped thorium-C could be estimated. In this way it was found that at ordinary temperature in a hydrogen atmosphere 80 per cent. of the hydride de-

composed in 50 minutes, showing that it is very unstable.* With a rise in temperature, the decomposition proceeds even more rapidly, for the amounts left undecomposed after passing through a heated tube were: at 160° C., 35 per cent.; at 250° C.. 9 per cent.; at 350° C., 6–7 per cent.

The gas was found to be condensable by cooling with liquid air. On passing it through a tube locally heated to redness, a deposit of thorium-C was found just beyond the heated portion, just as arsenic and antimony are deposited in the parallel tests.

Encouraged by these results, Paneth and Winternitz [1] treated a bismuth-magnesium alloy with acid; and were able to detect in the gas evolved some bismuth hydride, which they identified by the reactions of the deposit made by it in a Marsh tube. The mirror gave all the ordinary reactions for bismuth; and Paneth and Winternitz were even able to determine the weight of the deposit, which shows that it is not negligible.

A final test applied by them to their product may be mentioned here, as it is rather unusual: Donau's thermo-luminescence reaction.[2] When some calcium salts containing traces of bismuth are brought into contact with a hydrogen flame, it is found that, just before they begin to glow with the natural heat, they emit a characteristic bluish luminescence. This test is extremely delicate, for by means of it quantities so small as 10^{-10} gr. can be detected.

Recent work [3] has shown that it is not necessary to prepare a bismuth alloy in order to obtain the hydride; for very good yields were got from magnesium foil which had been coated with fused metallic bismuth. No hydride could be detected when the alloy, Na_3Bi, was employed.

* It should be noted that this decomposition in presence of a radioactive material is no criterion of the natural rate of decomposition of bismuth hydride.

[1] Paneth and Winternitz, *Ber.*, 1918, **51**, 1728.

[2] Donau, *Monatsh.*, 1913, **34**, 949; *Arbeitsmethoden der Mikrochemie* (1913), pp. 18 and 30.

[3] Paneth, Johannsen, and Matthies, *Ber.*, 1922, **53**, (B), 769.

G. Polonium Hydride *

The first hint that polonium hydride might be capable of existence is to be found in Lawson's work on the range of α-particles from polonium.[1] With lapse of time, a gradual increase in the ionisation current at a given distance was observed, which seemed to point to the formation of a hydrogen compound.

Paneth,[2] using magnesium foil upon which a film of polonium had been deposited electrolytically, was able to show that when the metal was treated with acid, the gas evolved had radioactive properties. This method was subsequently [3] varied in detail; and further investigations were made on the properties of the hydride.[4]

When polonium hydride is condensed by means of liquid air and then re-vaporised, considerable decomposition occurs. Phosphorus pentoxide produces marked decomposition of the hydride. Oxygen evidently affects the hydride considerably; for when the gas is passed through air-free distilled water, 50 per cent. appears on the further side; whereas when unboiled distilled water is used, only 3 per cent. of the hydride passes through unchanged. Caustic soda and silver nitrate solutions also cause great decomposition of the hydride.

The rate of spontaneous decomposition of polonium hydride is very high: 50 per cent. breaking up in 4 minutes, whereas the corresponding time for bismuth hydride under the same conditions is 25 minutes.

* Polonium is radium-F.

[1] Lawson, *Monatsh.*, 1915, **36**, 845; *Wiener Ber.*, 1915, **124**, 509.

[2] Paneth, *Ber.*, 1918, **51**, 1704.

[3] Paneth and Johannsen, *Ber.*, 1922, **55**, (B), 2622.

[4] For a general account, see Paneth, *Radio-elements as Indicators* (1928).

CHAPTER XVII

THE HYDRIDES AND THE PERIODIC SYSTEM

1. *General* *

WHEN the Periodic Table is examined, it is found that the hydride-forming elements are distributed through it in a manner which suggests a certain underlying regularity in their grouping. Selecting the Mendeléef form of the Table for the sake of easy reference, and omitting the rare earth group, about which there is still some dispute, the following facts come to light.

In Group I, the capacity for hydride-formation is confined to the elements of Group IA (if lithium and sodium be included in this category); whilst the Group IB metals, copper,† silver, and gold, show no inclination to form hydrides.

In Group II, hydride formation is again confined to the sub-Group A, since calcium, strontium and barium are the only hydride-forming members. The Group IIB series, zinc, cadmium, and mercury, yield no hydrides. It is curious that neither beryllium nor magnesium has been found to give a hydride; but it may be recalled that these two elements stand rather by themselves in Group II.

With Group III, an extreme case is reached; for here the initial element boron is the only one capable of hydride formation. All other members of the Group, whether in the A or B sub-Groups, seem incapable of yielding hydrogen compounds.

In Group IV, the hydride-forming capacity passes into the other sub-Group; for titanium, zirconium, and thorium in Group IVA are the only members which do not combine with hydrogen. The typical elements, carbon and silicon and all the remainder, in Group IIB form hydrides.

In Group V, the division is the same. Here the two typical

* An interesting collection of data concerning the properties of some hydrides is to be found in Paneth's *Radio-elements as Indicators*, (1928).

† The evidence in favour of the existence of a stable copper hydride seems insufficient.

elements, nitrogen and phosphorus, and all the elements of Group VB unite with hydrogen.

In Group VI, also, the same division appears. The typical elements, oxygen and sulphur, as well as the members of sub-Group B, yield hydrides, while chromium, molybdenum, and tungsten fail to combine with hydrogen.

A similar state of affairs appears in Group VII, since all the halogens combine with hydrogen, whereas manganese yields no hydride.

In Group VIII, the available information seems to show that though some of the elements can take up hydrogen—just as copper and tantalum are reported to do—the products are not true chemical compounds, but must be regarded either as alloys of hydrogen and the metal or as solutions of hydrogen in the metal, whichever term be preferred.

If, for the sake of convenient description, we include beryllium and magnesium in Group IIB and regard the typical elements of Groups IV, V, VI, and VII as belonging to the sub-Groups B in each case, then the following rule holds good.* The capacity for hydride formation is exhibited on the left-hand side of the Table in sub-Groups A; when Group III is reached, anomaly appears (since even boron does not yield the expected hydride BH_3); and thereafter, the power of hydride-formation passes into the sub-Groups B to Group VII, after which it ceases.

Group III thus appears as a sort of no-man's-land in the centre of the Table; and it seems worth while to examine the characters of the hydrides formed by the elements to the right and left of it, in order to see whether this division in the distribution corresponds to any difference in type between the hydrides ranged on either side.

The relevant portion of the Periodic Table lying to the right of the no-man's-land of Group III is shown below:

Group:	III	IV	V	VI	VII	0
	B	C	N	O	F	Ne
	—	Si	P	S	Cl	A
	—	Ge	As	Se	Br	Kr
	—	Sn	Sb	Te	I	Xe
	—	Pb	Bi	Po	—	Rd

* The rare earth elements are omitted from this survey, as there is as yet no generally accepted arrangement of them in the Periodic Table.

Now Paneth [1] has pointed out that all these elements occupying the final four places before the occurrence of one of the inert gases, yield easily-volatile hydrides; and as has been seen in the previous chapter, boron must be added to this list, since its hydrides also are volatile. Thus all hydrides formed from elements to the right of Group III are volatile; and most of them are actually gaseous at ordinary temperatures. Water is the only exception to this rule among the simpler hydrides; and its peculiarity may be due to the readiness with which it associates.

On the other hand, when the hydrides of Group I and Group II elements are examined, it is found that they are all solids of comparatively high melting-point; so that the frontier-line of Group III obviously corresponds to something quite definite as a line of cleavage between two different types of hydride.

As will be seen in a later section of this chapter, the behaviour of the hydrogen atoms in the hydrides of Groups I and II suggests an explanation for these remarkable facts; but the peculiarity of the Group III elements still awaits a satisfactory solution. There is no impossibility in making three hydrogen atoms combine with a metallic atom, for in the rare earth group Muthmann and others [2] have prepared a number of compounds like LaH_3.

Another peculiarity comes to light when the problem of hydride formation is considered in relation to the atomic volume curve. So far as the Long Periods are concerned, it seems to be the rule that non-hydride-forming elements are to be found in the troughs of the curve, *i.e.* the region from scandium to gallium in the first Long Period; from yttrium to indium in the second Long Period; and from tantalum to thallium in the third Long Period. But, curiously enough, when the corresponding lowest regions of the first two sections of the curve are examined (corresponding to the two Short Periods) it is found that the troughs here are occupied by elements especially marked out by the number of hydrides which they form. Thus in the trough of the first Short Period appear boron and carbon; whilst silicon occurs in the trough of the second Short Period.

[1] Paneth, *Ber.*, 1920, **53**, (B), 1710.

[2] Muthmann and Kraft, *Annalen*, 1902, **325**, 261; Muthmann and Beck, *ibid.*, 1904, **331**, 58.

It is useless to attempt to draw any connection between the numerical value of the atomic volume of an element and its power of hydride formation; for hydrides are formed by cæsium (which has the largest atomic volume of all) and by carbon (which has the lowest atomic volume in the series); and within the range between these two elements the atomic volumes of the hydride-forming and non-hydride-forming elements seem to be distributed without any particular regularity.

2. *The Preparation of the Hydrides*

All the known hydrides can be obtained by direct union of hydrogen with the appropriate element; but in actual practice only metallic hydrides are so prepared; for in all other cases except the hydrocarbons the hydride is most easily produced by the action of acid on a metallic derivative or a salt of the element which it is desired to combine with hydrogen.

The most recent investigations of the metallic hydrides [1] have shown the following to be the best methods in Group I. If a rapid stream of hydrogen be led over the surface of the metal at such a temperature (above 350° C.) that a yellow glow is produced, the hydride is driven over in the form of a white cloud which can be precipitated electrically and trapped by means of glass wool. In the cases of sodium and potassium hydride it was found advantageous to add some metallic calcium to the metal. The hydrides of rubidium and cæsium were obtained by mixing the alkali carbonate with metallic magnesium and passing hydrogen for some days across the mixture, which was kept at 650° C. in the case of rubidium, and 580°–620° C. in the case of cæsium. It should be noticed that since the hydride, when formed, is soluble in the remaining metal, the process is not simply one of straightforward combination between pure metal and hydrogen; apparently the formation of a eutectic mixture influences the progress of the reaction. This factor may serve to explain the fact that whereas the action with the alkali metals is slow, in the case of the alkaline earth metals it proceeds so rapidly as to reach the stage of incandescence. Curiously enough, lithium seems to resemble the alkaline earth metals more than its normal congeners, the alkali metals, so far as hydride formation goes.

[1] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 762, 900

In Group III, boron is the only element which yields hydrides; and, as was mentioned in the foregoing chapter, these are prepared by decomposing a metallic boride with acid. Boron, therefore, shows no resemblance to its predecessors in Groups I and II, but is linked by this reaction to the elements of the later Groups.

In Group IV, the hydrides can be prepared in various ways. In the case of carbon, a direct union of the elements can be attained by passing hydrogen over sugar-charcoal in a heated porcelain tube,[1] the yielding rising to 95 per cent. of the theoretical value. Silicon hydrides, as has already been mentioned, are best prepared by decomposing magnesium silicide with acid. Tin hydride, it will be remembered, was obtained by a process analogous to the production of arsine in Marsh's test. In the case of hydride of germanium, yet another method may be adopted, for GeH_4 can be formed by reducing germanium chloride by means of sodium amalgam.[2] Thus the Group IV elements offer no less than four different methods by which hydride-formation can be brought about: (1) direct union of the elements by heating; (2) decomposition of a compound of the element with acids; (3) action of nascent hydrogen on the metallic element; and (4) reduction of a chloride by means of nascent hydrogen.

In Group V, the typical element nitrogen shows the greatest versatility of all the members, so far as hydride-formation is concerned. Ammonia can be obtained: (1) synthetically from nitrogen and hydrogen by catalytic action; (2) by reduction with nascent hydrogen; and (3) by the decomposition of ammonia derivatives. In the case of the remaining elements of the Group which form hydrides, only the second and third methods can be usefully employed. Marsh's test is an example of the second method; and the equations below show the application of the third method to all the elements concerned:

$$Mg_3N_2+6H_2O=2NH_3+3Mg(OH)_2$$
$$Ca_3P_2+6H_2O=2PH_3+3Ca(OH)_2$$
$$Mg_3As_2+6H_2O=2AsH_3+3Mg(OH)_2$$
$$Zn_3Sb_2+6H_2O=2SbH_3+3Zn(OH)_2$$
$$Mg_3Bi_2+6H_2O=2BiH_3+3Mg(OH)_2$$

[1] Bone and Coward, *J.*, 1910, **97**, 1219.
[2] Voegelen, *Z. anorg. Chem.*, 1902, **30**, 325.

Among the hydride-forming elements of Group VI, oxygen is marked out from its congeners by the enormous number of reactions by which its hydride can be produced and also by the fact that it enters so frequently into the preparation of the other hydrides. All the Group VI hydrides can be prepared by the direct union of elements; but there is a regular gradation in the ease with which the combination takes place, which is reflected in the fact that the heats of formation of the compounds descend from oxygen to tellurium, the hydride of the latter being a markedly endothermic substance. All the hydrides can be obtained by the action of nascent hydrogen upon the second element of the hydride; but as a practical method this is valuable only in the case of tellurium. As in Group V, the hydrolysis of certain metallic derivatives yields the best results for H_2S, H_2Se, and H_2Te; but the reaction only goes satisfactorily when acid is present to attack the hydroxide formed in the process.

For the preparation of the halogen hydrides of Group VII, a number of methods are employed. The direct union of the elements is the most obvious one; and the yield is largely governed by the temperature at which the reaction proceeds, since it falls off as the temperature rises. A second method consists in allowing one component of the hydride to act upon a compound of the other, as in the reduction of a halogen derivative with nascent hydrogen or the action of the halogens upon water. Hydrolysis of the halides of certain elements or organic compounds like acetyl chloride forms a third method of preparing the hydrides of Group VII:

$$PCl_3+3H_2O=H_3PO_3+3HCl$$
$$CH_3.CO.Cl+H_2O=CH_3.CO.OH+HCl$$

Finally, the halogen halides can be obtained by heating double compounds like HF.KF, or by acting on a metallic halide with a non-volatile mineral acid such as sulphuric or phosphoric acid.

3. *The Properties of the Hydrides*

The properties of the hydrides must now be described; and in order to compare the various groups with each other, it will be convenient to begin with the alkali metal hydrides and proceed across the Table to the halogen derivatives step by step.

All the alkali metal hydrides are white crystalline solids ; [1] and it has been shown that the crystalline structure of lithium hydride is analogous to that of sodium chloride.[2] Of the five hydrides, that of lithium is the most stable, while cæsium hydride is the least stable.[3] For example, lithium hydride is not attacked by dry hydrogen chloride or chlorine at ordinary temperatures,[4] whereas rubidium hydride under the same conditions reacts readily.[5] These hydrides react rapidly with water or alcohol, yielding the corresponding hydroxide or ethylate :

$$LiH+H_2O=LiOH+H_2$$
$$LiH+C_2H_5OH=LiOC_2H_5+H_2$$

This easy evolution of hydrogen renders these hydrides good reducing agents. Even more curious are the reactions of the hydrides with carbon dioxide and sulphur dioxide ; in the first case, a formate is produced, whilst in the second a hyposulphite is formed :

$$KH+CO_2=H.CO.OK$$
$$2KH+2SO_2=K_2S_2O_4+H_2$$

Coming now to the hydrides of the alkaline earth metals, the same gradation in stability is again detectable, since calcium hydride is the most stable and barium hydride the least stable of the three.[6] All these hydrides are white solids with a crystalline fracture. Like the Group I hydrides, the members of the calcium set are readily attacked by water at ordinary temperatures, hydrogen being liberated :

$$CaH_2+2H_2O=Ca(OH)_2+2H_2$$

so that this group of hydrides likewise shows strong reducing powers. With chlorine, calcium hydride reacts only on heating, just as lithium hydride does ; and it seems that in many ways lithium hydride bears a strong resemblance to the hydrides of the Group II elements.[6] In one respect, however, the alkaline earth metal hydrides stand by themselves ; for they yield the

[1] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 762.

[2] Bijvoet and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 26 ; Bijvoet, *Rec. trav. chim.*, 1923, **42**, 859.

[3] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 762.

[4] Guntz, *Compt. rend.*, 1896, **122**, 245 ; **123**, 694.

[5] Moissan, *Compt. rend.*, 1903, **136**, 587, 1177.

[6] Ephraim and Michel, *Helv. Chim. Acta*, 1921, **4**, 900.

well-known reaction of nitride-formation when heated in a nitrogen atmosphere:

$$3BaH_2 + N_2 = Ba_3N_2 + 3H_2$$

With carbon dioxide, however, they behave exactly analogously to the hydrides of Group I, yielding formates:

$$CaH_2 + 2CO_2 = (H.COO)_2Ca$$

but in this case a number of by-products seem to be formed in addition to the salts.

Group III is anomalous in at least two respects. In the first place, only a single element, boron, forms hydrides at all; and in the second place, the hydride which might be expected, BH_3, seems to be incapable of existence. With Group III, also, we enter that region of the Table where the elements form a series of hydrides instead of only a single hydrogen derivative like lithium and calcium. There is no need to recapitulate the general properties of the boranes, as they have been fully described in the foregoing chapter; but it seems worth while to point out that with Group III the series of gaseous hydrides begins, in contradistinction to the solid hydrides of Groups I and II.

The following table contains the melting and boiling points of the various hydrides of carbon, silcon, and germanium which show parallelism in their formulæ:

Substance.	Formula.	Melting-point.	Boiling-point.
Methane	CH_4	−184°	−164°
Monosilane . . .	SiH_4	−185°	−112°
Monogermane . .	GeH_4	−165°	− 90°
Ethane	C_2H_6	−172°	− 84°
Disilane	Si_2H_6	−132·5°	− 15°
Digermane . . .	Ge_2H_6	−109°	+ 29°
Propane	C_3H_8	−187·8°	− 45°
Trisilane	Si_3H_8	−117·4°	+ 53°
Trigermane . . .	Ge_3H_8	−106·5°	+110·5°
n-Butane . . .	C_4H_{10}	−135°	+ 1°
Tetrasilane . . .	Si_4H_{10}	− 90° (approx.)	+109°

From the above figures, it is evident that the boiling-points of the paraffins are lower than those of the corresponding silanes; and that these in turn boil lower than the germanium analogues.

The figures for the melting-points show some deviation from this rule in the case of the carbon compounds; but it seems doubtful if the melting-points of the paraffin series have been accurately determined; so possibly these apparent anomalies are due to incompleteness in our knowledge.

The hydrides of Group IV suggest a number of problems to which there are as yet no solutions. Descending the Group from carbon to germanium, it may be recalled that methane, CH_4, is unaffected by water; monosilane, SiH_4, is rapidly decomposed by water; whilst monogermane, GeH_4, instead of being more easily attacked, as might be expected, turns out to be unexpectedly stable when brought into contact with water. Sufficient information about the hydrides of tin and lead is not available at present; but it will obviously be of great interest to know how they behave.

Then, again, we are quite in the dark as to the origin of catenating power in this particular group of elements. Carbon has long been marked out as possessing the power of chain-formation in a pre-eminent degree; but recent work has shown that boron, if not so fertile in hydrides as its neighbour, is yet by no means negligible in this respect; whilst the other neighbouring element, nitrogen, also exhibits a certain capacity for chain-making. So long as these were the only elements which could reasonably be termed highly catenating, it was possible to suppose that at least non-metallic character and chain-forming power went hand-in-hand. Now, however, with the discovery of the germanes and the possibility of complex lead and tin hydrides awaiting detection, it is no longer feasible to dissociate metallic character and chain-formation. Nor is it any longer possible to suppose that the catenating power is associated with small atomic volume, as might have been inferred from the case of carbon, which has the greatest chain-forming capacity and also the lowest atomic volume of all the elements; for the atomic volume of germanium is certainly greater than those of a number of elements which form no chain-compounds. The only hint which seems to throw light on the problem lies in the fact that, so far as can be seen, the elements which are pre-eminent in chain-formation have the power of combining readily with both chlorine and hydrogen; and their chlorine compounds in the highest state of valency do not ionise like ordinary salts.

In Group IV lie the hydrides which contain the greatest number of hydrogen atoms united with one atom of another element; and as we advance across the Table there comes a step-by-step decline in the number of hydrogen atoms in the hydrides: CH_4, NH_3, H_2O, and HF.

In Group V, ammonia exemplifies a new type of hydride which is capable of attaching to itself extra groups of atoms, *e.g.* in the formation of ammonium hydroxide and ammonium chloride. This quality is strongest in the elements of low atomic weight and fades out gradually as the group is descended. For some unknown reason, the introduction of alkyl groups instead of the hydrogen atoms of the hydrides has the effect of strengthening this power of addition; neither arsine, AsH_3, nor stibine, SbH_3, unites with hydrogen chloride; but trimethyl-arsine, $(CH_3)_3As$, and trimethyl-stibine, $(CH_3)_3Sb$, unite readily with methyl iodide to form respectively tetramethyl-arsonium iodide, $(CH_3)_4AsI$, and tetramethyl-stibonium iodide, $(CH_3)_4SbI$. The trialkyl derivatives of bismuth, however, do not yield quaternary derivatives of this type.

As regards chain-forming capacity in purely hydrogen derivatives, nitrogen is the only element in Group V which need occupy our attention. In hydrazine, $H_2N—NH_2$, two nitrogen atoms are linked in a straight chain; and in azoimide, N_3H, there seems to be a ring of three nitrogen atoms. The higher hydrides of phosphorus have not been sufficiently investigated to make it worth while considering them.

With ammonia in Group V, a second new hydride property is encountered; for in the liquid state ammonia has a marked power of dissociating electrolytes, so that a series of ammonolytic reactions can be placed in parallel with the hydrolytic reactions associated with water.

In Group VI, the hydrides exhibit the same phenomena as those of Group V, with respect to the power of adding on extra groups of atoms. The first hydride of the series, water, is able to form addition-compounds with many salts; but hydrogen sulphide, hydrogen selenide, and hydrogen telluride show no noticeable aptitude in this direction. When, however, alkyl groups are substituted for the hydrogen atoms in the hydrides, a marked increase of addition-power is observed. The oxonium salts,[1]

[1] Collie and Tickle, *J.*, 1899, **75**, 710.

the sulphonium,[1] selenonium,[2] and telluronium[2] derivatives all contain four radicles or atoms attached to the central atom of oxygen, sulphur, selenium, or tellurium.

Chain-formation is at a low ebb in the hydrides of Group VI. Apart from the cases of hydrogen peroxide, HO—OH, and hydrogen persulphide, HS—SH (if they really have these structures), there seems no sign of catenating power in this group, unless the very debatable case of the polysulphides be brought in.

The hydrides of Group VI, however, possess a new property which has not appeared in their immediate predecessors, viz. the power of dissociating into ions, even water itself showing some slight dissociation.

In the hydrides of Group VII this property is accentuated, since all the halogen hydrides are markedly acidic. It is unnecessary to describe this Group, as it is so well known; but it is worth pointing out that here also the stability is least in the member of highest molecular weight.

The following table serves to bring out the differences between typical hydrides of the various Groups when they are acted upon by water:

Group.	Hydride.	Results of Water's Action.
I	LiH	$LiOH$ and H_2
II	CaH_2	$Ca(OH)_2$ and H_2
III	B_2H_6	H_3BO_3 and H_2
IV	SiH_4	SiO_2 and H_2
V	NH_3	NH_4OH
VI	H_2O	Feeble ionisation
VII	HCl	Strong ionisation

Inspection of this table suggests a fresh point of interest. The facts indicate that six of the hydrides given in the table can be grouped in pairs: lithium and calcium hydrides both yield basic hydroxides and hydrogen; boron and silicon hydrides give rise to acidic oxides and hydrogen; whilst the hydrides of Groups VI and VII ionise in aqueous solution. Ammonia stands apart from all the rest, since although it yields a basic hydroxide, it gives off no hydrogen. Now nitrogen in Group V has some affinities with boron in Group III; and just as boron stands

[1] Oefele, *Annalen*, 1864, **132**, 82.
[2] Scott, *Proc. Chem. Soc.*, 1904, **20**, 156.

apart from all the other elements in the peculiarity of its hydride, so nitrogen is to some extent unique in the properties of its hydride, since it is the only member of its group which yields salts such as ammonium chloride, which are stable in presence of water.

4. *The Rôle of Hydrogen in the Hydrides*

A point of considerable interest is revealed when a comparison is made between the actions of water upon the hydrides and the halides of boron or silicon.

$$\text{(i)}\quad SiH_4+2H_2O=SiO_2+4H.H$$
$$SiCl_4+2H_2O=SiO_2+4H.Cl$$
$$\text{(ii)}\quad B_2H_6+6H_2O=2H_3BO_3+6H.H$$
$$2BCl_3+6H_2O=2H_3BO_3+6H.Cl$$

Inspection of these equations reveals at once a certain analogy between the two sets of compounds, since the only difference lies in the fact that in one case hydrogen is liberated and in the other hydrogen chloride is set free. If, for the sake of argument, molecular hydrogen be regarded as hydride of hydrogen, then the two sets of reactions are absolutely parallel. This suggests that possibly hydrogen is akin to the elements of the halogen group instead of to the metals. Some further evidence on the point seems worthy of consideration.

If hydrogen be an analogue of the metallic elements, then the metallic hydrides should have to some extent like intermetallic compounds; but, on the other hand, if hydrogen belongs to the halogen group, then these hydrides ought to resemble the halides of the metals.[1]

The most evident property of the intermetallic compounds is their power of conducting electricity; whereas in the solid state the metallic halides are extremely poor conductors. Now Moissan [2] found that calcium hydride in a compact layer 5 cm. in thickness, behaved as a non-conductor of electricity. A study of lithium hydride [3] has proved that it is a close analogue of lithium chloride in crystalline form, heat of formation, atomic heat, molecular volume, colouring by ultra-violet light, and other

[1] Compare Lowry, *Chemistry and Industry*, 1923, **42**, 43.
[2] Moissan, *Compt. rend.*, 1903, **136**, 591.
[3] Nernst, *Z. Elektrochem.*, 1920, **26**, 323.

properties. The X-ray analysis has shown [1] that its crystal structure is analogous to that of sodium chloride, the lithium atom playing the part of the sodium and the hydrogen replacing the chlorine in the crystal lattice. When treated with mercury, lithium hydride behaves like a salt, since it undergoes decomposition instead of passing into solution like an intermetallic compound. The electrical conductivity of the hydride ranges it among the salts and not with the alloys.[2] When dissolved in the eutectic mixture of sodium and potassium chlorides, calcium hydride undergoes electrolysis and liberates hydrogen at the anode in the quantity required by Faraday's Law.[3] Lithium hydride shows an analogous behaviour on electrolysis.[4] The electrolysis of lithium chloride is thus paralleled by the electrolysis of lithium hydride; and in the case of the hydride the hydrogen is liberated at the pole where the acidic portion of a salt usually makes its appearance.

These facts seem to establish that hydrogen in the hydrides of Groups I, II, III, and IV behaves like a halogen and not like a metallic atom; and in the last of these Groups, it may be pointed out, there are no metallic analogues for the hydrides. For example, CCl_4 and CH_4 are quite stable; but CNa_4 is unknown; whilst from silicon it is possible to prepare $SiCl_2$ and SiH_4, but $SiNa_4$ has never been obtained.

[1] Bijvoet and Karssen, *Proc. Akad. Wetensch. Amsterdam*, 1923, **25**, 26; Bijvoet, *Rec. trav. chim.*, 1923, **42**, 859.

[2] Moers, *Z. anorg. Chem.*, 1920, **113**, 179

[3] Bardwell, *J. Amer. Chem. Soc.*, 1922, **44**, 2499.

[4] Peters, *Z. anorg. Chem.*, 1924, **131**, 140.

CHAPTER XVIII

THE DONNAN EQUILIBRIUM

1. *Congo-red*

CONGO-RED, the disodium salt of diphenylbisazonaphthylamine-sulphonic acid :

$$\begin{matrix}NH_2\\NaSO_3\end{matrix}\!\!\diagdown\!C_{10}H_5\!-\!N:N\!-\!C_6H_4\!-\!C_6H_4\!-\!N:N\!-\!C_{10}H_5\!\!\diagup\!\!\begin{matrix}NH_2\\SO_3Na\end{matrix}$$

is a reddish-brown powder, which dissolves in water to produce a red solution, and is capable of dyeing cotton direct. In view of its high molecular weight—696—it it not surprising to find that such a substance forms colloidal solutions and diffuses only very slowly, if at all, through parchment paper membranes. This last property renders it possible to determine the osmotic pressure produced in a given solution of Congo-red by using an osmometer with a parchment paper diaphragm.

Bayliss [1] carried out a series of experiments in this field by placing a solution of Congo-red acid inside the osmometer and adding dilute sodium hydroxide solution to the outside water every twenty-four hours until this water retained a slight permanent alkalinity. The water in the outer vessel was then repeatedly changed until no further rise in osmotic pressure was registered on the gauge.

The results were surprising. The maximum osmotic pressure so obtained was between 88 and 97 per cent. of the value calculated on the basis that Congo-red exists in solution in the form of simple, undissociated, and non-aggregated molecules. Though possible, this seemed hardly probable ; and, as will be seen immediately, the assumption that Congo-red is undissociated in solution is one which must be dismissed from consideration.

Another point of interest came to light in Bayliss's experi-

[1] Bayliss, *Proc. Roy. Soc.*, 1909, **81**, *B*, 345.

ments. The osmotic pressure of Congo-red solution is lowered by the presence of sodium chloride, sodium hydroxide, and carbonic acid.

Some further work in the field was carried out by Biltz and Vegesack [1]; but it threw no fresh light on the subject; and some of it has been subjected to unfavourable criticism by Donnan and Harris.[2]

A short time after Bayliss's investigations, the Congo-red problem was attacked by Donnan and Harris [2] on a broader basis, for in their work they included electrical measurements as well as determinations of osmotic pressure.

They were able to show that when Congo-red solution and pure water are separated by a parchment paper membrane, the Congo-red solution has an osmotic pressure approximating to that calculated on the basis of single, undissociated molecules of Congo-red—in complete accordance with the results obtained by Bayliss. The material used by Donnan and Harris was Grübler's Congo-red, which contained about 30 per cent. of sodium chloride as an impurity. This naturally was removed by dialysis. In the experiments, it was found that the osmotic pressure rose quickly at first, though the velocity of the increase diminished as time went on. After four or five days, the osmotic pressure reached a maximum and then began slowly to diminish. On changing the external water, a further rise of pressure was observed, followed by a slow fall; and succeeding changes of the external water produced a like phenomenon, though the increase of the pressure became rapidly smaller with each successive change of the external water. The following table illustrates these facts. In it, the asterisks indicate changes of the external water:

Time in hours.	Difference of mercury levels in osmometer (mm.).	Time in hours.	Difference of mercury levels in osmometer (mm.).
24	88·5	282	125·0
73	105·0	306*	124·0
96	107·5	314	125·0
144	108·0	330*	122·0
234*	105·0	356*	123·0
240	119·0	401	121·0
258	123·0	450	115·0

[1] Biltz and Vegesack, *Z. physikal. Chem.*, 1909, **68**, 367; 1910, **73**, 481; compare Donnan and Harris, *J.*, 1911, **99**, 1554.

[2] Donnan and Harris, *J.*, 1911, **99**, 1554.

After about 48 hours' dialysis, it was noted that the contents of the osmometer had a muddy-brown appearance. The muddy-brown solution is unaffected by sodium chloride ; but the addition of a trace of sodium hydroxide reconverts the colour of the solution to the normal bright red. The change to the muddy-brown colour was found to be more rapid at high temperatures.

Donnan and Harris inferred that the tint was due to the formation of a very fine colloidal suspension ; and they concluded that during the osmosis a slow hydrolysis of the Congo-red salt was taking place, accompanied by the dialysis of the liberated sodium hydroxide through the membrane and by the conversion of the nascent Congo-red acid into colloidal material. To test this idea, an N/800 sodium hydroxide solution was substituted for the pure water in the external vessel ; whereupon it was found that not only was precipitation in the osmometer averted, but, further, a perfectly definite and constant osmotic pressure was obtained.

These results indicate that the precipitation is linked with a dialysis of sodium hydroxide through the membrane into the outer cell ; and such sodium hydroxide can be generated only by hydrolysis of the Congo-red salt in the inner vessel.

The following table shows the effect of placing solutions of sodium hydroxide and of sodium chloride in the outer vessel :

NaOH	Osmotic pressure.	NaCl	Osmotic pressure.
N/100	37·0 mm. Hg.	N/25	82 mm. Hg.
N/200	57·7 ,,	N/50	131 ,,
N/400	76·3 ,,	N/100	191 ,,
N/800	96·0 ,,	N/200	259 ,,
N/1200	104·6 ,,	Pure water	365 ,,
Pure water	114·5 ,,		

Obviously the presence of the sodium hydroxide or sodium chloride in the outer vessel tends to diminish the dialysis of sodium ions through the membrane in practice, just as the theory suggested.

Bayliss's observation on the influence of carbonic acid also finds its explanation ; for any carbonic acid present in the external water will combine with the alkali which comes outward through the membrane ; and in this way the hydrolysis of the

Congo-red salt within the membrane will be increased, as will also the precipitation of the liberated Congo-red acid.

We must now turn to the results obtained in the measurements of conductivity. An initial difficulty was found in obtaining the disodium salt of Congo-red completely free from sodium chloride, with which the technical material was admixed, whilst simultaneously avoiding any appreciable hydrolysis of the Congo-red salt. This was overcome; and solutions of Congo-red were obtained practically free from sodium chloride. An examination of these yielded the following results, along with which we give the figures for N/50 sodium chloride solution, both for 25° C.:

Congo-red concentrations in grams per 100 c.c.	Specific conductivity $\times 10^3$	Molar conductivity.
2·485	3·664	102·0
1·2425	2·046	114·6
0·6212	1·125	126·0
0·3106	0·626	140·2
0·1553	0·352	157·7
0·0776	0·189	169·3
0·0388	0·102	182·8
	N/50NaCl 2·328	116·4

These figures prove that the Congo-red sodium salt behaves as a highly dissociated salt. Combined with the normal value of the osmotic pressure—which seems to indicate that no dissociation has occurred—they suggest a paradoxical state of affairs in which a dissociated substance acts as if it were undissociated. Or, as an alternative, that the Congo-red salt is first gathered into aggregates (thus reducing the osmotic pressure) and that then these aggregates undergo ionic dissociation to the exact degree necessary to re-establish the theoretical osmotic pressure. This last hypothesis is obviously too fantastic to require much consideration.

A more feasible solution of the problem is to be found in the so-called "membrane-hydrolysis." Owing to the properties of the semipermeable membrane, sodium ions in company with hydroxyl ions diffuse outwards into the external vessel, whilst an insoluble phase (free acid, acid salt, or some more complex material) becomes either aggregated or thrown out of solution within the dialyser.

The facts which have been described above are sufficient

to prove that the osmotic pressures observed do not correspond with an ordinary state of osmotic equilibrium, inasmuch as diffusible sodium ions are arrested, in their diffusion across the membrane, by potential differences, and do actually pass through, to a certain extent, in company with hydroxyl ions. When Congo-red is present on one side of the membrane, sodium chloride distributes itself in unequal concentrations on the two sides of the membrane. A reversible ionic equilibrium is produced, in which the concentration of sodium chloride is higher on the side of the membrane opposite to that on which the Congo-red lies.

Further investigations by Donnan and Allmand [1] were made on the distribution of potassium chloride between two compartments separated by a copper ferrocyanide diaphragm, when one of the compartments contained potassium ferrocyanide. These experiments established that at equilibrium the concentration of potassium chloride is higher in the compartment free from potassium ferrocyanide. Another series of experiments [2] was concerned with the equilibrium concentrations of solutions of potassium ferrocyanide ; sodium and potassium ferrocyanides ; and sodium and calcium ferrocyanides across a copper ferrocyanide membrane. In addition, a liquid membrane was examined ; the liquid being amyl alcohol and the electrolytes being potassium chloride and lithium chloride.* In general, the results are in accordance with the theory of membrane equilibria proposed by Donnan, though in the case of the copper ferrocyanide membrane and potassium ferrocyanide solution, a discussion of the distribution data in connection with E.M.F. measurements suggests that the phenomena are not quite so simple as the theory would indicate.

2. *The Theory of Membrane Equilibria* †

Suppose that a membrane divides the solution of a salt NaA from a solution of equal and constant volume containing a

[1] Donnan and Allmand, *J.*, 1914, **105**, 1941.

[2] Donnan and Green, *Proc. Roy. Soc.*, 1914, (*A*), **90**, 450 ; Donnan and Garner, *J.*, 1919, **115**, 1313.

* Lithium chloride gives rise to double molecules in amyl alcohol solution.

† In this section, Donnan's own simplified treatment of the subject (*Chemical Reviews*, 1925, **1**, 73) has been followed to a great extent. See also Donnan, *Z. Elektrochem.*, 1911, **17**, 572.

salt KA; and let it be assumed that both salts are completely ionised. If the membrane is permeable to all the three ions, a state of equilibrium will be attained, evidently, when there is a uniform distribution of each ion throughout the whole system. But if the membrane be chosen so that it is freely permeable by the metallic ions but impermeable to the anion A, the system is no longer a free one, but becomes subject to two conditions of restraint: (1) the inability of the A ions to traverse the membrane; and (2) the restraint conditions of equimolar quantities.

Taking these two restraints into account, the initial and the final (equilibrium) states of the system can be represented as below; the vertical lines stand for the membrane. The initial concentrations of the salts are c_1 for NaA and c_2 for KA. During the progression towards equilibrium, x sodium ions traverse the membrane in one direction, and an equal number of potassium ions cross it in the opposite direction.

Initial State (I)		*Equilibrium State* (II)	
c_1 Na^+	K^+ c_2	(c_1-x) Na^+	Na^+ x
c_1 A^-	A^- c_2	x K^+	K^+ (c_2-x)
		c_1 A^-	A^- c_2
(1)	(2)	(1)	(2)

Now consider the system symbolised in II above and imagine that while we transfer a small quantity (δn) of sodium ions from the compartment (1) to the compartment (2)* we simultaneously transport an equal quantity (δn) of potassium ions from the compartment (2) across the membrane into compartment (1). As we make no alteration in the electrical character of the system by these shifts, electrical work terms do not enter into the problem.

Applying the usual expression to this case, and calling the change in the free energy of the system δF, we have

$$\delta F = RT\left[\delta n \log \frac{[Na^+]_1}{[Na^+]_2} + \delta n \log \frac{[K^+]_2}{[K^+]_1}\right] \quad . \quad (1)$$

where $[Na^+]_1$ represents the amount of Na ions in compartment (1) of the system, $[K^+]_2$ represents the amount of K ions in

* That is, from left to right across the membrane.

compartment (2), and so forth. At equilibrium, there will be no change in the free energy of the system, so that $\delta F=0$; and therefore the expression in the large square bracket is also zero. This implies that

$$\frac{[Na^+]_1}{[K^+]_1}=\frac{[Na^+]_2}{[K^+]_2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But at equilibrium, $[Na^+]_1=(c_1-x)$; $[K^+]_1=x$; $[Na^+]_2=x$; and $[K^+]_2=(c_2-x)$. Substituting these values in the above equation (2) we obtain

$$\frac{(c_1-x)}{x}=\frac{x}{(c_2-x)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and by solving this for x we find the value of x when the system is in equilibrium :

$$x=\frac{c_1c_2}{c_1+c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By inserting this value in the expression (II) for the two compartments we get the following symbol for the state of affairs at equilibrium :

(1)		(2)	
$\frac{c_1^2}{c_1+c_2}$	Na^+	Na^+	$\frac{c_1c_2}{c_1+c_2}$
$\frac{c_1c_2}{c_1+c_2}$	K^+	K^+	$\frac{c_2^2}{c_1+c_2}$
c_1	A^-	A^-	c_2

Mere inspection of the values indicated in the left-hand " compartment " (1) will show that

$$\frac{[Na^+]_1}{[K^+]_1}=\frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the right-hand " compartment " (2) yields the expression

$$\frac{[Na^+]_2}{[K^+]_2}=\frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

also. Thus an equal distribution of the potassium and sodium ions in either compartment implies that $c_1=c_2$; and only when this condition is fulfilled at equilibrium do we get a uniform arrangement of the ions.

A numerical example will bring out clearly the magnitude of the changes which occur in such systems before they reach equilibrium. In the case of the salts NaA and KA, suppose that $c_1=1$ and that $c_2=10$. Then the initial state of the system can be represented thus:

1	Na^+	K^+	10
1	A^-	A^-	10

whilst at equilibrium the condition of things will be symbolised by

$\frac{1}{11}$	Na^+	Na^+	$\frac{10}{11}$
$\frac{10}{11}$	K^+	K^+	$\frac{100}{11}$
1	A^-	A^-	10
(1)		(2)	

from which it is evident that 9·09 per cent. of the potassium ions originally present in compartment (2) have diffused into compartment (1); whilst 90·9 per cent. of the sodium ions originally present in compartment (1) have diffused into (2). In other words, the fall of a relatively small percentage of potassium ions down a concentration gradient has been sufficient to pull a high percentage of sodium ions up a concentration gradient.

The foregoing paragraphs have dealt with the simplest example of the Donnan equilibrium; but we may now examine some further instances, each of which presents a fresh problem.

Suppose that in the example we have just given, a divalent calcium ion be substituted for the potassium ion, what will be the effect? It is evident that the second condition of restraint will apply here; and it demands that for every calcium ion passing across the membrane in one direction, *two* sodium ions must be transported through the membrane in the opposite direction, so that the electrical state of the two compartments remains the same throughout.

If this postulate be conceded, the expression for the equilibrium conditions becomes:

$$\delta F=RT\left[\delta n\, 2\log\frac{[Na^+]_1}{[Na^+]_2}+\delta n\log\frac{[Ca^{++}]_2}{[Ca^{++}]_1}\right]=0 \quad . \quad (7)$$

from which it can be inferred that

$$\frac{[Ca^{++}]_1}{[Ca^{++}]_2}=\left(\frac{[Na^+]_1}{[Na^+]_2}\right)^2 \quad . \quad . \quad . \quad . \quad (8)$$

Hitherto the electrical factor has been left out of account, but something must now be said about it. Reverting to the original example of the two salts KA and NaA, let us consider the transfer of a small quantity (δn) of potassium ion from the KA compartment through the membrane to the other compartment. As there is complete freedom of passage for the K ions through the membrane in either direction, a simple diffusion should lead to equal distribution of K ions on both sides of the membrane. As we have seen, this is not what occurs in practice. In order to account for the results, we must assume that a potential difference exists between the solutions in the two compartments.

Let ϵ be the excess of the positive potential of solution (1) above that of solution (2); then the variational criterion of equilibrium becomes:

$$\delta n \, \mathrm{RT} \log \frac{[\mathrm{K}^+]_2}{[\mathrm{K}^+]_1} - \mathrm{F}\delta n\epsilon = 0 \quad . \quad . \quad . \quad (9)$$

and we have

$$\epsilon = \frac{\mathrm{RT}}{\mathrm{F}} \log \frac{[\mathrm{K}^+]_2}{[\mathrm{K}^+]_1} \quad . \quad . \quad . \quad . \quad (10)$$

This has been found in fair agreement with the experimental results in the case of a copper ferrocyanide membrane separating two solutions of potassium ferrocyanide of different strengths.

In concluding this survey of the Donnan equilibrium, it may be well to emphasise once more the two assumptions on which the theory depends. These two assumptions are:

1. The existence of equilibrium; and
2. The existence of *certain constraints* which restrict the free diffusion of one or more electrically charged or ionised constituents.

If these postulates be granted, then the equations derived from the theory will hold either for simple molecules which have become ionised by a loss or gain of electrons or for colloid units which have acquired an electrical charge by adsorbing ions. The "constraints" demanded by the theory may originate in various ways. For example, if certain ions are restrained from diffusion by a membrane, the electrical charges on them may influence the free passage across the membrane of other ions which normally can traverse the membrane with ease. Or again,

the adsorption of certain ions at the surface of a solid wall might impose a " restraint " on other ions which would interfere with the mobility of other ions.[1]

3. *Applications of Donnan's Theory*

Since semipermeable membranes are widely distributed in living tissues, it is clear that in physiology and biochemistry the Donnan equilibrium will furnish a certain guidance. It has, in fact, been utilised to account for a considerable number of experimental results in these fields ; [2] but even a brief summary of this branch of the subject would demand more space than is available here. All that can be done is to direct attention to one or two applications of the theory which will show that it can be utilised even in cases where no semipermeable membrane, in the usual sense, is present.

Procter and Wilson [3] have utilised Donnan's ideas in order to account for the mechanism of tanning in the following manner. When tannins dissolv in water they form colloidal sols ; and the tannin aggregates acquire negative charges which may be produced either by combination with a negative ion or by actual ionisation of the tannin itself. The surface layer of solution immediately surrounding the particles is assumed to contain a certain concentration of positive ions held by the attraction of the tannin negative charges.

Let the concentration of tannin particles be $[T^-]$ and the concentration of the positive ions in the surface later be $[M^+]$, and let some electrolyte MN be added to the solution. Then in the bulk of the solution, $[M^+]=[N^-]$; but in the surface layer there will be a certain concentration of M^+ held to the tannin by electrochemical attraction, as well as some M^+ and N^- which are not so held. Thus at equilibrium, there is an unequal distribution of the ions of the electrolyte ; and the constraint demanded by Donnan's theory is supplied by the electrostatic retention of the positive ions in the surface layer of the colloid particles.

When equilibrium is established, no work will be done during a small reversible change made at constant temperature and

[1] Compare J. A. Wilson, *J. Amer. Chem. Soc.*, 1916, **38**, 1982 ; J. A. and W. H. Wilson, *ibid.*, 1918, **40**, 886.

See, *inter alia*, Loeb, *Proteins and the Theory of Colloidal Behaviour* (1922).

[3] Procter and J. A. Wilson, *J.*, 1916, **109**, 1327.

pressure. Suppose that this change is the transfer of δn moles of M^+ and N^- from the bulk of the solution to the surface layer. Then we have

$$n\mathrm{RT}\log\frac{[M^+]_1}{[M^+]_2}+\delta n\mathrm{RT}\log\frac{[N^-]_2}{[N^-]_1}=0$$

where $[M^+]_2$ represents the concentration of M^+ in the bulk of the solution, and $[M^+]_1$ its concentration in the surface layer We then have

$$[M^+]_2\times[N^-]_2=[M^+]_1\times[N^-]_1$$

Thus if only binary electrolytes are present, the products of concentration of any pair of diffusible and oppositely charged ions will be equal in the surface layer and bulk of solution.

To simplify the expressions we are about to derive, let us rechristen the various factors.

In the bulk of the solution, let x represent the concentration of positive or negative ions. *In the surface layer*, let y be the concentration of negative, diffusible ions; and let z be the concentration of positively charged ions bound by the electrochemical attractions of the tannin. Then, of course, $(y+z)$ represents the total concentration of positive ions in the surface layer.

Instead of $[M^+]_2\times[N^-]_2=[M^+]_1\times[N^-]_1$ we can write

$$x^2=y(y+z)$$

The non-uniform distribution of the ions in the surface layer and bulk of the solution will result in a difference of potential which, as was pointed out in the previous section, can be expressed by

$$\epsilon=-\frac{\mathrm{R}\,.\,\mathrm{T}}{\mathrm{F}}\log\frac{[N^-]_2}{[N^-]_1}$$

$$=-\frac{\mathrm{R}\,.\,\mathrm{T}}{\mathrm{F}}\log\frac{x}{y}$$

But by solving the equation $x^2=y(y+z)$ for y in in the usual manner, and then dividing x by the result, we get

$$y=\frac{-z+\sqrt{z^2+4x^2}}{2}$$

and

$$\frac{x}{y}=\frac{2x}{-z+\sqrt{z^2+4x^2}}$$

so that the expression for the potential difference becomes

$$\epsilon = \frac{R \cdot T}{F} \log \frac{2x}{-z+\sqrt{z^2+4x^2}}$$

Now since z represents the concentration of positive ions held by electrostatic attraction to the negatively charged colloid, it is clear that there is a maximum possible value for z. On the other hand, the factor x represents the concentration of positive or negative ions in the bulk of the solution, and it may therefore be increased out of all proportion to z. Thus the expression, by increase of x, will tend towards a limiting value which is represented by

$$\epsilon = \frac{R \cdot T}{F} \log \frac{2x}{\sqrt{4x^2}} = 0$$

Thus the potential difference between surface layer and bulk of solution will diminish as the concentration of electrolyte in the solution is increased.

When this difference of potential is made sufficiently small, by the addition of electrolytes, a condition is established which is favourable to the coalescence of the colloid particles, and consequently in these circumstances the tannin will be precipitated.

We must now turn to the other factor in the tanning process, viz., the hide itself, which is also a colloidal material.

A study of colloid jellies [1] leads to the conclusion that in their case also the distributions of ions in the solution and the jelly are different; and hence a potential difference must exist between the jelly and the surrounding solution.

When a hide is immersed in an acid solution, a highly ionisable salt of collagen is formed, in which the collagen is positively charged. The potential difference between the colloid and the surrounding medium can be expressed in the formula

$$\epsilon = \frac{R \cdot T}{F} \log \frac{-z+\sqrt{4x^2+z^2}}{2x}$$

[1] Procter, *J.*, 1914, **105**, 313; Procter and J. A. Wilson, *J.*, 1916, **109**, 307.

in which ϵ obviously has a sign opposite to that which it has in the case of tannin.* Therefore, if a hide is immersed in a slightly acid solution of tannin, the above reasoning suggests that when the (negatively charged) tannin particles approach the (positively charged) hide surface, electrical neutralisation takes place and the co-precipitation of the two colloids is the result. In simpler language, the hide becomes tanned.

The Donnan theory thus leads to the following conclusions as regards the tanning process. The rate of tanning will be a maximum for a given concentration of liquor when the potential differences are of opposite signs and the absolute value of each is a maximum. As the concentration of electrolytes in the solution is increased, the potential differences between the solution on the one hand, and on the other, the jelly phase of the hide or the surface layer of the tannin particles will decrease, leading to a lowering of the rate of tanning. But if the concentration of electrolytes be sufficiently increased, the tannin will precipitate alone, while the collagen shrinks to a hard mass. In alkaline solutions, both colloids have negative charges and consequently cannot combine. If lime be added to the system, the negatively charged tannin particles are neutralised by the calcium ions, and a calcium compound of tannin is precipitated.

Another case in which the Donnan equilibrium has been brought into the question may be mentioned. It has been used to account for the influence of acids and salts on the swelling of gelatine.[1] In this case the gelatine jelly is regarded as an elastic framework built up from gelatine molecules; and it is assumed that molecules of water, acids, etc., can diffuse into the network. Hydrogen ions react chemically with the gelatine molecules and lead to ionisation of the gelatine; but the tenacity of the molecular network prevents free movement of the gelatine particles; and hence the "constraint," demanded as a postulate by Donnan, makes its appearance.

The effect of this constraint is to hinder the free diffusibility of an equivalent amount of anions of the free acid; and, as a

* In *alkaline* solution, the hide substance reacts with the formation of ionisable salts, the collagen becomes negatively charged, and then ϵ has the same sign as in the case of tannin.

[1] Procter, *J.*, 1914, **105**, 313; Procter and J. A. Wilson, *J.*, 1916, **109**, 307; Procter, *J. Amer. Leather Chem. Assoc.*, 1911, 23, 270; 1916, 399; J. A. Wilson, *J. Amer. Chem. Soc.*, 1916, **38**, 1982; Tolman and Stearn, *ibid.*, 1918, **40**, 264.

result of this, there is unequal distribution of ions between the gelatine phase and the surrounding aqueous solution and an increase in the osmotic pressure of the gelatine solution against the external solution, an increase which does not arise from the gelatine molecules and ions in the actual network.

CHAPTER XIX

SOME FLAME REACTIONS

1. *Introductory*

THE study of flames has led to an enormous amount of research work, especially in recent years, and it would be impossible in the scope of a chapter to present even a summary of the whole field.[1] Our attention must perforce be confined to the phenomena observed when certain salts are admitted into flames; and even here it is possible to give only the merest outline of the results obtained. It is hoped, however, that a short summary [2] may serve its purpose in directing attention to an interesting field in which much still remains to be elucidated and which demands no very complicated apparatus for its investigation.

As an illustration, let us choose the well-known Marsh's test for arsenic. Every chemist is acquainted with the method employed and the results obtained in that test; but how many of us have taken the trouble to speculate upon what happens in the course of the operation? Yet very little thought will suggest a number of questions which most of us pass over without noticing the possible complexities of the problem.

The essentials of Marsh's test are a hydrogen flame containing arsine, and a cold surface upon which the flame impinges. A successful experiment results in the deposition of an arsenic mirror on the cold surface. How does the arsenic come to make its appearance in that particular form under these specific conditions? Are we to assume that at the temperature of the flame the arsine is dissociated into hydrogen and arsenic, and

[1] Reference may be made to Bone and Townend, *Flame and Combustion in Gases* (1927); Wilson, *Electrical Properties of Flames and of Incandescent Solids* (1912); Geiger and Scheel, *Handbuch der Physik*, vol. **14**, chap. 3 (1927).

[2] An historical survey of the subject with references and quotations is given in the introductions to the papers of Bancroft and Weiser, *J. Physical Chem.*, 1914, **18**, 213, 218, 762; 1915, **19**, 310.

that the latter element is simply condensed upon the porcelain plate which we hold in the jet? Or, since flames are known to be conducting media, should we assume that the arsenic is present in the flame as arsenic ions and that the deposition is due to the neutralisation of these ions by charges picked up from the surface of the plate? Or, again, can we reasonably assume that the reaction

$$4AsH_3+3O_2=4As+6H_2O$$

plays a part in the process, so that the deposition is the result of oxidation of the arsine in the outer mantle of the flame which comes in contact with the oxygen of the air in which the flame is burning? Or, even, should we postulate an initial deposition of arsenic oxide which is later reduced by the hydrogen? From his knowledge of the various practical modifications of Marsh's test, a chemist can eliminate some of these suggestions at once as being irreconcilable with facts; but the remaining hypotheses are not so easily sifted.

2. *The Deposition of Elements from Flames*

Though the deposition of arsenic and antimony from a hydrogen flame was known in 1837, it was not until 1873 that a third element was obtained in a similar manner. Salet [1] observed that if a water-cooled platinum tube is inserted into a hydrogen flame, a film of sulphur is deposited on the metal when sulphur dioxide is fed into the flame.

Twenty years later, Smithells [2] examined the behaviour of a copper-impregnated flame with the following results. When a quantity of cupric chloride is introduced into a Bunsen flame, the salt first melts, and then in a few moments it is seen to be surrounded by a brilliant patch of yellow, the exterior parts of which show a reddish tinge. Outside the yellow zone, a bright blue colour appears; and still further out, the flame in tinted green.

When a porcelain basin filled with cold water is placed in the flame, different results were noted according to the part of the flame which impinged on the cold surface. From the yellow zone, a deposit was formed which was red in colour. This

[1] Salet, *Ann. chim. phys.*, 1873, (4), **28**, 45.
[2] Smithells, *Phil. Mag.*, 1895, (5), **39**, 127.

material could be burnished and it yielded red fumes when treated with nitric acid. In fact, it answered all the tests for metallic copper. Smithells therefore attributed the yellow luminosity to the incandescence of minute particles of metallic copper. The deposit obtained from the blue part of the flame was quite different. When freshly formed, it was very pale in colour; and when it was breathed on, it turned white. It was identified as cuprous chloride contaminated with traces of cupric salt. From the green part of the flame, a deposit was obtained which was almost black and showed the physical and chemical properties of cupric oxide.

Smithells investigated the matter by means of his flame separator; and the results were explained by him as follows. In the inner cone of the flame, the temperature is high, and the products are largely free hydrogen and carbon monoxide. In this region the cuprous chloride is reduced to metallic copper; but the flame temperature is not high enough to give the copper spectrum. The copper and hydrochloric acid produced in this zone are carried upwards. Some of the metal is deposited on the inner wall of the outer tube of the separator; whilst the rest passes up to the outer flame cones, where it is oxidised by air to cuprous oxide. At the same time cuprous chloride is formed by the action of the hydrochloric acid. Thus the green tint of the outer zone can be explained.

The foregoing is sufficient to show how complex may be the state of affairs in a flame which is observed daily in most laboratories; and it seems surprising that so interesting a subject should not have attracted many more investigators than it has done.

We may now turn to the results obtained by Bancroft and Weiser [1] who attacked the problem on a much broader basis. Their apparatus was very simple. A hard glass tube was drawn out into a jet which fitted into a hole drilled in the side of a Bunsen burner. Dry salts were placed in the glass tube, which was then heated; whilst a slow current of air passed through it and carried the volatilised salt into the tube of the Bunsen and so into the flame. A water-cooled tube of Berlin porcelain served as a cool surface upon which the flame was allowed to impinge. Most of the salts were examined in the Bunsen flame;

[1] Bancroft and Weiser, *J. Physical Chem.*, 1914, **18**, 213.

but in some cases a hydrogen or an oxy-hydrogen flame was required. The following table is given by Bancroft and Weiser to summarise the results obtained by them :

Vapours introduced into Flame.	Flame.	Character of metallic deposit.
$CuCl_2$ . .	Bunsen	Mirror : red colour.
$CdCl_2$ . .	,,	Mirror : very bright metallic.
$SnCl_2$ . .	,,	Mirror : bright metallic with faint tinge like tarnished tin.
$HgCl_2$ . .	,,	No mirror : deposit of particles of mercury mixed with undecomposed salt.
$AgNO_3$.	,,	Mirror : lustrous white.
$Pb(NO_3)_2$.	,,	Mirror : bright metallic with faint tinge of blue.
$Bi(NO_3)_3$.	,,	Mirror : very bright white metallic.
$ZnCl_2$ . .	,,	Mirror : bright metallic.
As_2O_3 . .	,,	Mirror : bright metallic. Also black amorphous powder.
$SbCl_3$ . .	,,	Mirror : bright metallic. Also considerable black powder.
MoO_3 . .	Oxy-hydrogen *	Mirror : bright, lustrous, metallic.
WO_3 . .	Oxy-hydrogen	Mirror : bright, lustrous, metallic.
PCl_3 . .	Hydrogen	Dull reddish phosphorus.
NaCl . .	Hydrogen	Fine particles of Na † or NaOH mixed with undecomposed salt.
KCl . .	Oxy-hydrogen	Fine particles of K † or KOH with undecomposed salt.
SO_2 . .	Hydrogen	Yellow flowers of sulphur.

The work of Bancroft and Weiser obviously represents a great advance in our knowledge, since they showed that the presence of free elements in flames is fairly general and is not confined to the special cases of arsenic, antimony, sulphur, and copper. Probably the most surprising result is the isolation of elemental phosphorus from the heart of a flame fed with phosphorus trichloride.

Bancroft and Weiser pointed out that if the temperature be high enough, all exothermal compounds will decompose ; and that a reducing action on the part of the flame gases is not an essential factor in the problem, though it may help to increase the yield of the deposit obtained.

* From the Bunsen flame and from a hydrogen-air flame molybdenum molybdate was deposited.

† The presence of the actual metal here is not claimed as proved by Bancroft and Weiser. Owing to the ease of oxidation it is clear that proof could hardly be expected. The presence of alkali was established by the phenolphthalein test.

Another factor which may enter into the matter is worth mentioning here. Mitscherlich [1] proved that when a sodium flame is brought over strongly-volatilising ammonium chloride, the yellow colour of the flame almost disappears. Further, when sodium is introduced into a flame of hydrogen burning in chlorine, no coloration of the flame is observed. In these cases, owing to the excess of chlorine present, the dissociation of the sodium chloride present is driven back, in spite of the high temperature of the flame.

The facts which have been given in this section are sufficient to prove that many elements can be withdrawn in a free state from flames; but they cannot be said to establish conclusively the presence of elementary atoms in the flame. It would be just as easy to account for the results by assuming that the metals are present in the flame in the form of ions and that they pick up electrons from the cool surface and are thus collected in atomic form. On the other side it may be pointed out that flames are rich in electrons, and that therefore the ions might easily be neutralised in the flame itself. The point may be settled definitely by future research; but in the meantime, for the sake of conciseness, we shall speak of the elements as though they were present as atoms in the flame.

3. *The Tin Flame*

The facts given in the foregoing section suffice to show that a flame is a laboratory in itself, wherein a whole series of reactions may be taking place simultaneously in different zones. We cannot expect to succeed in isolating many of the products of such reactions; and to gain information with regard to some of them, we must fall back upon a fresh set of phenomena: the emission of spectra from the flame during the progress of the reactions which are going on within it.

Salet [2] observed that when a small quantity of stannous chloride is volatilised in a current of hydrogen, a blue-tinted flame is produced when the hydrogen is ignited. Fumes of stannous oxide are formed, which make the edge of the flame white. The core of the flame is composed of two concentric

[1] Mitscherlich, *Pogg. Ann.*, 1862, **116**, 499; 1864, **121**, 459.
[2] Salet, *Ann. chim. phys.*, 1873, (4), **28**, 5.

cylinders, of which the inner one is blue and the outer one faintly carmine in tint. Now if the flame is cooled by introducing a cold object into it, a red coloration appears in the vicinity of the cold body. If stannous bromide be substituted for the chloride, the inner cylinder is green in tint instead of blue. By using the iodide, the inner region is coloured yellow.

Thus, according to Salet, when different volatile compounds of tin are introduced into the flame of hydrogen, each compound yields three different spectra; but two of these spectra remain constant throughout the series. In the innermost part of the flame, where the temperature is low, a continuous spectrum is emitted which varies with the salts employed; in the middle region, where reduction is possible, the faint carmine spectrum with a small band at $610\mu\mu$ is emitted, which Salet suggested was the primary spectrum of tin; whilst in the outer region, which is the zone of high temperature and combustion, a band spectrum rich in lines is generated, which Salet ascribed to oxide of tin.

Here, then, we have a series of phenomena which, if we can interpret them correctly, should throw light on the state of affairs in each zone of the tin flame. But before going further it may be well to take into account the possibilities involved. Very little reflection will show that these spectra may be regarded as either (*a*) light emitted from definite compounds, or (*b*) light emitted during the conversion of one compound into another—*i.e.* radiant energy liberated during a reaction. These two possibilities must be kept in view throughout the rest of this chapter, and they are specifically mentioned here so as to save continual reference to them.

Bancroft and Weiser [1] have given a more minute description of the appearance presented by a hydrogen flame impregnated with stannous chloride. The small innermost cone is coloured blue and surrounded by a bright red cylinder. Outside this is a cone of light green colour; whilst the upper part of the flame is blue. When stannous bromide is substituted for the chloride, the innermost cone is much more of a blue-green than in the case of the chloride. This blue-green region is surrounded by the red cylinder and this in turn by the light green, as in the chloride flame. The upper portion of the flame is blue, but has more of a greenish tinge than in the case of the chloride. With stannous

[1] Bancroft and Weiser, *J. Physical Chem.*, 1914, **18**, 281.

iodide, the innermost cone is greenish-yellow. All three flames showed the intensification of the carmine tinge noted by Salet when a cold body was introduced into the flame.

Before dealing with the chemistry of the tin flame, we must take into account certain general considerations. Suppose that two reactions are proceeding simultaneously in a flame; and that in Reaction A a red light is emitted, whilst in Reaction B a green light is generated. When the flame is examined as a whole, the eye perceives both types of light simultaneously. Now if, in a certain region of the flame, Reaction A is proceeding much more vigorously than Reaction B, an observer of this region will see mainly red light, since the feeble green tinge will be masked. Conversely, if he examines a region of the flame where Reaction B is proceeding more vigorously than Reaction A, the predominant tint will be green. If in a third region of the flame neither reaction predominates over the other, the flame colour will appear to the observer as a blend of the two colours red and green.

Further, if during a flame reaction some substance is liberated which has selective absorptive power, the light from the flame reactions will be filtered through the absorbing layer of vapour before it reaches the observer's eye; and thus its apparent character will be altered.

Bearing these points in mind, we may now consider the two regions of the tin flame which give rise respectively to the green and carmine luminescences.

Bancroft and Weiser carried out a series of experiments to test whether the two luminescences could be produced outside the tin flame in which they were first observed. It was found that when tin is made to combine slowly with oxygen or with the halogens, green light was emitted and the final product was stannic oxide or a stannic salt. A similar green light was observed when stannous chloride was oxidised to stannic chloride by passing a slow current of chlorine over the stannous salt in the anhydrous state. Further experiments confirmed the idea that the light green luminescence accompanies the transition of stannous tin into stannic tin.

With regard to the carmine luminescence, it is more difficult to obtain data; but the investigations of Bancroft and Weiser seem to have placed the matter beyond doubt. They found

that when a hydrogen flame is made to impinge on a metallic tin surface, the carmine luminescence makes its appearance at the point where the tin is in excess and where the flame has only slight oxidising power. In the strongly oxidising part of the flame, the light green luminescence is clearly seen. Further, at high temperatures, stannic oxide is the stable form and stannous oxide's existence is favoured by lower temperatures. It will be recalled that the carmine luminescence is enhanced by cooling the tin flame and thus making the existence of the stannous oxidation-stage more probable. Finally, by introducing a cold surface into the carmine zone, Bancroft and Weiser obtained an actual deposit of stannous oxide. It might be supposed that the carmine tinge owes its origin to stannous oxide; but Bancroft and Weiser pointed out that metallic tin gives a characteristic arc spectrum in hydrogen; and on this ground they regard the production of the carmine tinge as the result of the oxidation process which converts metallic tin (or tin ion) into stannous oxide (or stannous ion).

These experiments have thus cleared up the matter so far as two zones of the flame are concerned; and we can follow Bancroft and Weiser in their conclusions.

1. The carmine luminescence is due to the reaction $Sn \rightarrow Sn^{\cdot\cdot}$.
2. The green luminescence is emitted during the transition $Sn^{\cdot\cdot} \rightarrow Sn^{\cdot\cdot\cdot\cdot}$.

We must next take up the problem of the innermost cone of the flame. Here, it will be recalled, a change of tint is observed when a chloride, a bromide, or an iodide of tin is introduced into the flame. Bancroft and Weiser believed that the origin of these differences was to be sought in the dissociation of the tin halide, the liberation of the free halogen, and the absorption of light by the halogen vapour. By actual observations of the stannous chloride flame through the vapours of bromine and iodine they found that the external screen altered the tint of the blue flame just as did the introduction of a bromide or an iodide into the flame itself. This accounts satisfactorily for the influence of the halogen in changing the tint of the innermost zone; but that still leaves us to discover what reaction actually leads to the emission of light from the blue-green cone.

In view of the previous evidence, Bancroft and Weiser

postulated that the luminescence must arise during the change from stannous to stannic tin, since it obviously had no kinship with the carmine luminescence produced by the conversion of stannous into stannic tin. To account for such a change in the innermost cone, they postulated that the stannous salt (volatilised into the flame as such or else formed therein by the reduction of stannic salt) does not dissociate entirely in this region, but reacts partly to form tin and stannic salt. Such a process could be hindered by introducing into this region of the flame some reducing agent which would inhibit the production of stannic compounds. An experiment in which formaldehyde vapour was introduced into the stannous chloride flame completely confirmed the hypothesis: for the blue-green luminescence of the inner cone disappeared in presence of the formaldehyde and reappeared when the aldehyde supply was cut off.

4. *The Copper Flame*

When copper chloride is introduced into a Bunsen flame by means of a platinum wire, the following phenomena can be observed. In the immediate vicinity of the bead, a yellowish luminescence is visible; outside this lies a blue coloration; whilst the remainder of the flame is tinted grass-green. If the bead becomes too hot, a diffuse reddish-brown tinge extends up through the flame, being most marked at the flame's edges and tip. If copper bromide is used instead of the chloride, the main difference is a change in the colour of the middle zone from light blue towards greenish-blue; and this change of tint is accentuated when the iodide of copper is utilised instead of the bromide.

Gouy [1] found that by inserting a cold body into the green tract of the flame, the colour could be changed to blue in the cooled region.

If the flame be made strongly reducing, a red luminescence can be produced at the foot of the flame when copper oxide, nitrate, or acetate is introduced; and if the right conditions are hit upon, this red coloration can be made to predominate over the grass-green tinge.[2]

[1] Gouy, *Compt. rend.*, 1877, **85**, 439.
[2] *Ibid.*, **84**, 231; **85**, 439.

Caution is required in dealing with the copper flame, for Lecoq de Boisbaudran [1] showed that by altering the amount of cupric chloride introduced into the flame, the most varied tints might be obtained. It may be taken as fairly certain that two factors are at work here: first, the absorptive power of the dissociation products; and, second, the lowering of the temperature of the flame when excess of cupric salt is introduced into it.

We must now turn to Bancroft and Weiser's explanation of the occurrence of these various tints in the copper flame.[2]

When sample deposits are taken from various parts of the copper flame by means of a cooled tube, it is found that cupric oxide is the main constituent. Bancroft and Weiser failed to obtain cuprous oxide in any degree of purity from any flame. This failure cannot be ascribed to oxidation of a cuprous deposit to the cupric state before withdrawal from the flame could be achieved, for, as has already been pointed out, metallic zinc mirrors can be produced without undergoing oxidation under similar conditions; and Bancroft and Weiser have obtained deposits of the much less stable cuprous chloride. It appears from the results that cupric oxide is the stable oxide under flame conditions.

Now when cuprous oxide was oxidised in a current of oxygen, the luminescence observed was blue in tint; but when copper was sprinkled on a gas flame, a hydrogen flame, or a carbon monoxide flame, the tint emitted was an intense grass-green. From this it follows that the changes involved in the oxidation of copper to the final stable cupric must take the course shown below:

$$\mathrm{Cu} \xrightarrow[\text{Green luminescence}]{} \mathrm{Cu}\cdot \xrightarrow[\text{Blue luminescence.}]{} \mathrm{Cu}\cdot\cdot$$

and it is clear that the green luminescence of the first stage is so powerful that it masks completely the fainter blue light evolved during the oxidation from the cuprous to the cupric state. Further evidence on this point is given by the fact that an excess of copper chloride in a carbon monoxide flame gives a blue tint; but when a jet of hydrogen is allowed to impinge on the flame, the blue is changed to green at the point of contact.

[1] Lecoq de Boisbaudran, *Spectres lumineux*, p. 157.

[2] Bancroft and Weiser, *J. Physical Chem.*, 1914, **18**, 281.

With regard to the reddish luminescence, Bancroft and Weiser point out that this tint appears in two different regions of the flame: at the base in some cases, and also at the edges of the flame. The tinge at the edges of the flame they have shown to be due to the violet-red tint of cupric chloride vapour and also to suspended particles of solid cupric chloride. As to the other region, Bancroft and Weiser found that copper burns in chlorine with a red glow; and they also point out that a reddish luminescence is produced when cathode rays strike cuprous iodide, a process which they consider to lead to the conversion of cuprous ion into cuprous salt.

On the basis of the foregoing, the three tinges of the copper flame should be ascribed to the following changes:

Green luminescence : Copper to cuprous ion
Red ,, : Cuprous ion to cuprous salt
Blue ,, : Cuprous ion to cupric ion or cupric salt.

5. *Alkali Metal Flames*

Bancroft and Weiser's investigations [1] of the results produced by introducing alkali metals into flames may be summarised as follows. Salts of lithium, sodium, and potassium give two spectra: a continuous spectrum and a line spectrum. When hydrochloric acid is introduced into the flame, the intensity of the line spectra is reduced; and in the case of a hydrogen flame burning in chlorine, it falls to zero.

A blue luminescence is obtained from sodium in the following circumstances: when sodium salts are introduced into a flame of hydrogen burning in chlorine; when metallic sodium burns *slowly* in oxygen, chlorine, or bromine; when a sodium salt is fused; when cathode rays impinge on sodium chloride; when the coloured residue obtained in the last process is fused; and when sodium chloride is rapidly precipitated from aqueous solution by alcohol or by hydrochloric acid.

A yellow luminescence is obtained from sodium in the following circumstances: when sodium is introduced into the Bunsen flame; when sodium burns *rapidly* in oxygen, chlorine, or bromine; when positive rays act on sodium chloride. In all these cases there is a faint blue luminescence emitted as well as the yellow tint.

[1] Bancroft and Weiser, *J. Physical Chem.*, 1915, **19**, 310.

Bancroft and Weiser infer from these results that the blue luminescence is due to the transformation of sodium ion into undissociated sodium salt; whereas the yellow luminescence is attributed by them to some stage in the change from sodium vapour to sodium ion.

The absence of the yellow luminescence when sodium burns slowly is accounted for by assuming that the light intensity for the corresponding reaction is very slight when the reaction-velocity is low. The diminished intensity of the line spectra in the hydrogen-chlorine flame or in a Bunsen flame to which hydrochloric acid has been added, is apparently due to the forcing back of the dissociation of the salts in such conditions.

6. *Flames Containing Selenium and Tellurium*

The effect of introducing selenium and tellurium into flames has been studied by Papish [1] and more fully by Weiser and Garrison.[2]

When selenium or a selenium compound was introduced into a flame of hydrogen burning in air, the flame displayed three distinct colours:

1. Blue in the inner region immediately surrounding the cone of unburned gas; and a deeper blue in the outermost shell of the flame.
2. Reddish in the mantle between the two blue regions.
3. Greenish at the tip of the flame.

Similar tinting was observed in the Bunsen flame, with slight differences in the intensity of the light from the four emitting regions.

The blue luminescence has been detected by Weiser and Garrison when selenium burns in excess of oxygen and when selenium is introduced into a flame of hydrogen burning in chlorine. It is also seen when cathode rays impinge upon selenium dioxide. If it be assumed that this blue luminescence is due to the oxidation of selenium, we have a plausible explanation of the occurrence of the blue tint in two regions of the flame. In the inner part of the flame the luminescence is pale, as might be expected from the fact that this region is poor in oxygen;

[1] Papish, *J. Physical Chem.*, 1918, **22**, 430.
[2] Weiser and Garrison, *J. Physical Chem.*, 1919, **23**, 478.

whereas at the outer surface of the flame the blue is strong, for here oxidation will be in full swing. The presence of free selenium in the inner part of the flame, when this has been impregnated with a selenium compound, is easily proved by inserting a cold surface into the flame at this point and obtaining a deposit of elemental selenium.

With regard to the reddish luminescence, Weiser and Garrison suggest that it is partly due to the colour of the vapours in that flame region, partly to purely thermal luminescence, and partly to some stage from electrically neutral selenium vapour to selenic ion; but they put this forward with considerable reservation.

The greenish tinge at the tip of a selenium-fed flame has been observed when selenium is vaporised in a sealed tube. Weiser and Garrison therefore conclude that it is not a true light-emission, but is merely the colour of the vapour of selenium dioxide illuminated by the light of the flame below.

When a hydrogen-in-air flame was impregnated with tellurium or a tellurium compound, the colour-scheme is more complex than any we have yet described, since it consists of no less than four tints. First, green in the inner cone surrounding the unburnt gases; second, an outer mantle of blue which can be modified markedly by the addition of varying amounts of tellurium to the flame; third, a greenish tip; and fourth, a shade of red between the outer blue and inner green regions in the hottest part of the flame. This last colour appears only in some experiments.

It should be borne in mind that while selenium yields only one oxide, SeO_2, tellurium gives the two oxides TeO and TeO_2, each of which corresponds to a series of salts. Now Weiser and Garrison indicate that their experiments with flames point to the emission of the green luminescence being strongest in conditions which favour the production of tellurous compounds; and they conclude that this luminescence is probably due to the passage of a tellurous ion into a tellurous salt. The blue luminescence, on the other hand, makes its appearance in circumstances which favour the formation of telluric compounds; and it is assumed that this luminescence is emitted during the transition from telluric ion to telluric salt. The reddish luminescence is most simply accounted for by recalling the fact that elemental tellurium can be obtained by placing a cold

surface in these flames and that tellurium vapour is golden yellow in tint. Weiser and Garrison hold that the reddish luminescence is to be ascribed to the conjunction of three different causes; the colour of tellurium vapour, thermal luminescence, and chemiluminescence resulting from some stage in the reaction from electrically neutral tellurium vapour to telluric ion. Finally, the green tinge at the flame-tip is supposed to be due to the greenish vapour of tellurium dioxide lit up by the flame below.

CHAPTER XX

EMISSION BAND SPECTRA *

1. *Introductory*

THE term *band spectrum* is used to describe a spectrum which presents a fluted appearance under low resolving power, but which with more powerful instruments is found to consist of groups of fine lines.† In a typical band situated in the visible region, these lines lie closer and closer to each other as we approach one end of the band, and finally they " run together " so that the band terminates in a single line, which is called the *head* of the band.

If the head lies at the long-wave (infra-red) end of the band, the remainder of the lines become sparser and sparser as we pass along the band towards the short-wave (ultra-violet) end; and such a band is said to be *degraded* (or shaded off) towards the short-wave end. On the other hand, if the band head lies at the short-wave end of the band, the lines of the band are more and more widely spaced as we pass towards the red; and such a band is said to be degraded towards the long-wave end.

In a band spectrum there may be a *band-group* containing a number of these band-heads each with its train of attendant

* In the compass of the present chapter, only the merest outline of the subject of band spectra can be given. For fuller information, the reader is referred to the *Symposium on Molecular Structure and Molecular Spectra, Trans. Faraday Soc.*, 1929, **25**, 611; Baly's *Spectroscopy*, Vol. III (1927); *Molecular Spectra in Gases* (Bulletin of the National Research Council, Vol. 11, Part 3, No. 57, published in 1926); Sommerfeld, *Atomic Structure and Spectral Lines* (1923); and Griffith and McKeown, *Photoprocesses in Gaseous and Liquid Systems* (1929). The cognate subjects of fluorescence and phosphorescence are described in Baly's *Spectroscopy*, Vol. II (1927); whilst absorption spectra are dealt with in Henri's *Structure des Molécules* (1925), and will be described in Baly's forthcoming Vol. IV of his *Spectroscopy*.

† The fluted appearance of the benzene spectrum in the Frontispiece to this volume will show the aptness of the term. The spectrum has the appearance of a Corinthian column under illumination from one side.

lines; and the *complete band spectrum* may be built up from a number of band-groups.

If all the bands in a spectrum were isolated from each other, the task of bringing order into the relations between the lines would be comparatively simple, since it would be clear enough that all the lines in one region of the spectrum belonged to a single unit. Unfortunately, in practice, two or more bands may overlap each other, so that the underlying simplicity is lost in the confusion caused by the overlapping; and the various components of the one system have to be disentangled from those of the other systems before we can get a clear field to work in.

But the case of band spectra is even more complex than a mere overlapping of bands would make it. At the present day, it is generally assumed that whilst simple atoms yield the line spectra deal with in Chapter II of this volume, band spectra have their origin in atomic groups. Hydrogen, for example, in addition to the series of lines which have already been described, emits a continuous spectrum which is attributed to radiation from the molecule H_2 and not from either of the component H-atoms. Now under the conditions of spectral observation, the ordinary chemical molecule may be unstable and may be transformed into something which cannot be isolated in the laboratory. For instance, spectra have been observed which are attributed to atomic groups like CH, CN, NH, and OH, none of which can be isolated chemically under normal conditions. Thus at certain points our molecular chemistry may need to be extended into something fresh if we are to cope with the spectra emitted by atomic groupings.

2. *Deslandres' Investigations*

As was mentioned in Chapter II, the year 1885 saw the publication of Balmer's Law relating to the hydrogen spectrum, from which have sprung our current ideas with regard to atomic spectra. Within the same twelvemonth, Deslandres [1] took an equally long step forward in the field of molecular (band) spectra. In view of the complexity of band spectra, as compared with the hydrogen system, the work of Deslandres seems a feat even greater than that of Balmer.

[1] Deslandres, *Compt. rend.*, 1885, **100**, 1259.

From consideration of the experimental data on the subject, Deslandres was able to formulate the following conclusions. In a band spectrum, the lines which spring from a single head form series, and it is possible for more than one series to start from a given band head. The lines in a single series stand in a simple relationship to each other; for if the wave-numbers of consecutive lines in the series be written down, the differences between these wave-numbers form an arithmetical progression.

For example, take part of one of the series in the nitrogen spectrum.

Wave-number of line.	Differences.
256·837	
	15·319
241·518	
	15·001
226·517	
	14·725
211·792	
	14·432
197·360	
	14·109
183·251	

Inspection will show that the differences column contains a rough arithmetical progression, descending step by step with decrements of 0·3 unit.

A system of this kind can be represented by the general expression:

$$\text{Wave-number} = A + bn^2$$

wherein A and b are constant and n increases by successive additions of one unit.

	Differences.
1st term $A+bn^2$	
	$b(2n+1)$
2nd term $A+b(n+1)^2$	
	$b(2n+3)$
3rd term $A+b(n+2)^2$	
	$b(2n+5)$
4th term $A+b(n+3)^2$	

Now, curiously enough, Deslandres detected an analogous system in the arrangement of the band heads of a given spectrum. In other words, the heads of a band-group are distributed in such a way that the wave-number differences between successive band heads lie in arithmetical progression. There is, however,

a further peculiarity to be noted. If the bands are degraded towards the short wave-length end of the spectrum, then the system of band heads will be degraded towards the long wave-length end, and *vice versa*. Thus the law for the band heads is the same as that for the component lines of each individual band in the group, but the shading-off of the band-group is in a direction opposite to that of the lines within each band.

By combining the results for the position of the head of the band and the position of a given line in the band with respect to the head, a number of expressions have been worked out; but at the present day the most convenient one for approximate work is the simple form

$$\text{Wave-number}=A+Bm+Cm^2$$

wherein A, B, and C are constants, and m increases by single units as we pass from line to line.

Since this expression is simply a modified form of the usual equation for a parabola in analytical geometry:

$$y^2-4ax+4a^2=0$$

it appears at first sight as though the wave-numbers of the lines in a band could be treated as the abscissæ of a symmetrical parabolic curve. This, in practice, is not sufficiently accurate; and instead of a symmetrical curve we find that in order to fit the experimental data we have to adopt a curve in which the two branches differ slightly from each other. The necessary correction is obtained by inserting third and fourth power * terms in the equation. For instance, in the case of a band at $\lambda=4280$, which Mulliken [1] has shown to be produced by copper hydride, CuH, Birge [2] finds the best results to be given by using equation (A) for the one branch of the curve and equation (B) for the second branch:

$$(A)=23{,}311{\cdot}080+14{\cdot}6072m-1{\cdot}07834m^2-0{\cdot}001155m^3+0{\cdot}0000138m^4$$

$$(B)=23{,}310{\cdot}976+14{\cdot}4439m-1{\cdot}09105m^2-0{\cdot}003657m^3+0{\cdot}0000138m^4$$

These figures show that although the Deslandres expression serves as a first approximation, the true representation of the relationship between the lines is apt to be more complicated.

* In some cases even a sixth power term is required.

[1] Mulliken, *Nature*, 1924, **113**, 489.

[2] *Molecular Spectra in Gases*, Birge, p. 87.

3. *Energy Changes in Molecules*

Consider the case of a monatomic element such as helium. Here the molecule contains only a single nucleus with its attendant electrons. Such a system can obviously change its energy in three different ways. First, according to the ideas outlined in Chapter II, its electrons may rise and fall among the various possible orbits within the atom, and in so doing they will alter the internal energy of the atomic system to a greater or less extent. Second, the system as a whole may rotate faster or slower, and each change in angular velocity will correspond to an alteration in energy. Third, the system may possess a translatory movement, approaching or receding from a fixed point in space ; and if its motion in this path varies, there will be a corresponding change in the momentum of the system. Thus in the case of the single-nucleus molecule of helium, alterations of energy may be expected from changes in (*a*) electronic motion, (*b*) rotational motion, and (*c*) translational movement.

Turning to the case of a diatomic molecule such as hydrogen, it is evident that it also will possess all of these three types of motion and that a change in any one of them will exert its influence on the energy of the system. But, in addition, the diatomic molecule has a further resource. Since it contains two nuclei, these may approach to or recede from each other ; and during this process there will be a change in the energy of the molecule.*

* An interesting toy can easily be constructed which illustrates the movement of rotation and the relative movements of the two nuclei. Two wooden balls should be procured, with a diameter of about two inches and a weight of about an ounce and a half. In each ball a hole about a quarter of an inch in diameter is drilled about half an inch deep. An ordinary elastic band is then cut to open the ring, the breadth of the band being about a quarter of an inch. One end of the elastic strip thus obtained is placed in the hole drilled in one ball and is then secured in place by driving a wooden plug into the hole till it is level with the surface of the ball. It is best to make all fast with seccotine. The other end of the elastic is similarly attached to the second ball. One ball is then taken in the hand and held close to any rough plane surface such as an unpolished table or a linoleum-covered floor, care being taken to hold the plug downwards. By moving the hand rapidly clockwise in a circle of an inch or two in diameter, the free ball can be made to spin in a circle with the elastic as radius ; and care must be taken that as it rolls round on the table or floor it makes good contact, so that the friction between the ball and the plane surface causes the ball to rotate and twist the elastic band as the rubber in a

Thus any molecule containing more than a single nucleus may exhibit no less than four types of motion: (*a*) translation of the molecule as a whole; (*b*) rotational movement of the molecule; (*c*) relative movements of the nuclei with regard to each other; and (*d*) intra-molecular electronic changes. It is evident that a change in any of these possible motions will have its influence upon the spectrum emitted by the substance under examination; and in some cases two or more of the changes may take place simultaneously, thus complicating the problem.

A translatory movement of a molecule in the line of sight produces the Doppler effect on spectra. If an emitting body is approaching the observer at a high velocity, the radiation from it will appear to increase in frequency as compared with the radiation of the same body when at rest relative to the observer. Conversely, if the emitter recedes from the observer along his line of sight, the frequency of the light will diminish, since the distances between the light-pulses are being increased by the movement of the emitter away from the observer. The result of the Doppler effect is to broaden the lines of a spectrum emitted by a moving body; but the phenomenon is of little chemical interest and need not be dealt with further in this place.

The other three motions, however, have direct relationship with intra-molecular affairs, and it will be convenient to take them up in the order in which they were mentioned above.

toy aeroplane is twisted preparatory to flight. When the twist has become sufficient to draw the two balls almost into contact (say at least fifty turns of the spinning ball), the whirling is stopped and the first ball gently released from the hand. The two balls will then spin round a common centre as the elastic untwists, receding from each other as they do so; and then, over-running the dead point, they will twist the elastic in the opposite direction, drawing nearer and nearer together again. The process will again reverse itself, the elastic untwisting and the balls receding from each other. Thus both the rotation of the system about its centre and the mutual approach and recession of the two massive bodies is neatly illustrated. Care should be taken in carrying out the experiment, as the velocity attained by the balls is sometimes so great as to snap the elastic, and if the experimenter happens to be in the line of the tangent, he will probably be markedly surprised at the amount of energy in the system. Once the knack of spinning the balls has been mastered, it is best to clip the elastic between finger and thumb close to the first ball, while making the winding-up spin, as this saves the band from fraying on the wooden plug during the orbital rotation of the second ball.

4. *Rotation Spectra*

In foregoing chapters of this volume, evidence was adduced to prove that a molecule of, say, hydrogen chloride is an intricate system of protons and electrons. If an attempt were made to work out in detail the effect of rotating such a system of point-masses, the task would be too difficult. For our present purpose, it will be sufficient to take the molecule as a whole and to regard it simply as a rigid body rotating about a fixed axis.

It will be remembered that in the Bohr theory of the hydrogen atom, certain " non-radiating orbits " were selected in accordance with fixed quantum conditions ; and that emission was assumed to take place by the jump of an electron from one of these non-radiating orbits to another. A somewhat similar postulate has to be made when the quantum theory is applied to the case of molecular rotation. Certain rotation conditions are selected which will make the angular momentum of the spinning molecule equal to integral multiples of the fraction $h/2\pi$. A molecule which rotates according to these conditions is assumed to be in a non-radiating state ; but if its rotation changes to a second non-radiating state, the surplus energy thus set free will appear as radiation—or conversely as absorption if the molecule in the first state has less energy than in the second.

Let the moment of inertia of the molecule around its principal axis be denoted by I, and let ω represent the angular velocity. Then we have the following :

$$\text{Angular momentum} = I\omega \quad . \quad . \quad . \quad (1)$$

$$\text{Kinetic energy} = \frac{I\omega^2}{2} \quad . \quad . \quad . \quad (2)$$

But by the postulate which has just been made, the angular momentum must be expressed in integral multiples of $h/2\pi$, so that

$$\text{Angular momentum} = I\omega = \frac{mh}{2\pi} \quad . \quad . \quad . \quad (3)$$

whence

$$\text{Angular velocity} = \omega = \frac{mh}{2\pi I} \quad . \quad . \quad . \quad (4)$$

wherein m may have the values 1, 2, 3 . . . etc.

Now substitute this last value for ω in equation (2) and we find

$$\text{Kinetic energy} = \frac{I\omega^2}{2} = \frac{I}{2} \cdot \frac{m^2h^2}{4\pi^2I^2} = \frac{m^2h^2}{8\pi^2I} \quad . \quad (5)$$

From this the values of the kinetic energy for any of the stationary states can be obtained by substituting the appropriate numerical value of m.

Next assume that the molecule, spinning at such a velocity that $m=m_1$, changes its motion to one in which $m=m_2$. In neither its original nor its final state will it be emitting radiation. But during the change from one state to the other, energy will be emitted, equivalent to the difference between the original and the final kinetic energies possessed by the system. This difference is obviously

$$\text{Difference in kinetic energy} = \frac{h^2}{8\pi^2I} \cdot (m_1^2 - m_2^2) \quad . \quad (6)$$

But this energy will be emitted at some frequency which can be designated as ν; and as energy is radiated in quanta, let us assume that this energy liberated by the molecule will be one quantum, which is $h\nu$.

Hence we have

$$h\nu = \frac{h^2}{8\pi^2I}(m_1^2 - m_2^2)$$

or

$$\nu = \frac{h}{8\pi^2I}(m_1^2 - m_2^2) \quad . \quad . \quad . \quad . \quad (7)$$

Now for the particular type of motion in question, it can be shown mathematically [1] that the quantum number m can change by steps of one unit * only. This is in accordance with what is known as the Principle of Selection. Further, since the wave-number is a positive quantity, m_1 must be greater than m_2 in equation (7). This implies that $m_1=(m_2+1)$; and consequently equation (7) takes the form

$$\nu = \frac{h}{8\pi^2I}[(m+1)^2 - m^2] = \frac{h}{8\pi^2I}(2m+1) \quad . \quad . \quad (8)$$

This expression (8) evidently represents a series of lines spaced

[1] See Sommerfeld, *Atomic Structure and Spectral Lines*, p. 264 ff. (1923)

* See, however, Section 6 of this chapter for recent suggestions as to half-quantum numbers.

equally along the frequency scale with intervals between them corresponding to

$$\nu_1 - \nu_2 = \frac{h}{4\pi^2 I} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From non-spectroscopic evidence, it has been inferred that the factor I has a value of the order of 10^{-40} for light molecules, which would imply that these rotation spectra should make their appearance in the far infra-red; and in practice the study of this group of spectra is carried out by investigating the infra-red absorption spectra of substances.

5. *Rotation-Vibration Spectra*

In the last section, the molecule was considered purely as a rigid body revolving on an axis; but as we have already seen, this simplification of the problem will not suffice to cover more than a small part of the ground. Take the case of a diatomic molecule such as that of hydrogen chloride. Here there are two separate nuclei which mutually repel each other and are held together only by the influence of their associated electrons. If a system of this type pulsates, then owing to the two nuclei moving closer or further apart, disturbances will be set up among the electrons and the whole molecule will be forced into new types of vibration. Fortunately, the masses of the nuclei are vastly greater than those of the electrons; and for practical purposes we can confine our attention to the purely nuclear motions, leaving the concomitant electronic changes out of account for the present.

If the quantum theory be applied to the energy-changes involved in the movements of the nuclei, we shall have to express these changes in terms of quanta. Assume that ν_0 represents the frequency of oscillation of the nuclei. Then the corresponding quantum will obviously be $h\nu_0$ according to Planck's hypothesis. Since energy must be reckoned in integral numbers of quanta, we may suppose that in its initial state the system contains $n_1 h\nu_0$ quanta, whilst in its final state it contains $n_2 h\nu_0$ quanta. Then the change in energy involved in passing from the one state to the other is $(n_1 - n_2)h\nu_0$; and the contribution made to the wave-number by this change in energy is $(n_1 - n_2)h\nu_0$. If this energy appears as radiation of a frequency ν, then we have

$$h\nu = (n_1 - n_2)h\nu_0$$

or simply

$$\nu = (n_1 - n_2)\nu_0 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here, as in the case of m in the previous section, the change $n_1 \rightarrow n_2$ can take place only by leaps of single units, according to Bohr's Correspondence Principle.[1]

Now suppose that this molecule with the vibrating nuclei is rotating as a whole, and assume that the energy liberated in changes in rotation is also liberated at the frequency ν. Then from (8) we have

$$\nu = \frac{h}{8\pi^2 I}(2m+1)$$

Thus each type of movement, the rotational and the vibratory, makes its own contribution to the energy radiated at the frequency ν, and the sum of the two contributions is given by

$$\nu = (n_1 - n_2)\nu_0 + \frac{h}{8\pi^2 I}(2m+1) \quad . \quad . \quad . \quad (11)$$

This equation (11), therefore, includes both types of energy change in its ambit and is thus the expression of a rotation-vibration spectrum.

One or two comments will not be out of place.

In general it is found that the value of ν_0 is considerably greater than that of $h/8\pi^2 I$, so that if $(n_1 - n_2)$ is made a minus quantity, then in equation (11) we might obtain a negative wave-number which would be meaningless. But, on the other hand, owing to this preponderance of ν_0 it is possible to admit negative values of $2m$ into the equation without necessarily getting negative values for ν. Thus the full equation for a rotation-vibration spectrum would be

$$\nu = (n_1 - n_2)\nu_0 + \frac{h}{8\pi^2 I}(\pm 2m+1) \quad . \quad . \quad (12)$$

with the proviso that no values for m, n_1, or n_2 are chosen which would make ν negative in sign.

Now consider the case of an emission in which $(n_1 - n_2) = 1$. The equation (12) then takes the form

$$\nu = \nu_0 + \frac{h}{8\pi^2 I}(\pm 2m+1) \quad . \quad . \quad . \quad (13)$$

and it is clear that this represents a series of lines spaced evenly

[1] See Somerfeld, *Atomic Structure and Spectral Lines*, pp. 417, 577 ff. (1923).

on the wave-number scale, with a difference of $h/4\pi^2 I$ between each pair.

By putting $m=0$, we obtain the position of the so-called *null line*, or zero point, which obviously lies at

$$\nu = \nu_0 + \frac{h}{8\pi^2 I} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and on one side of this will lie a *positive branch* of lines produced by energy transitions in which a term $(m+1)$ becomes m, whilst on the other side of the null line will lie a *negative branch* of lines arising from energy transitions in which a term $(m-1)$ becomes m.

In this connection, an interesting point is brought to light by turning to absorption spectra. Imes [1] photographed the

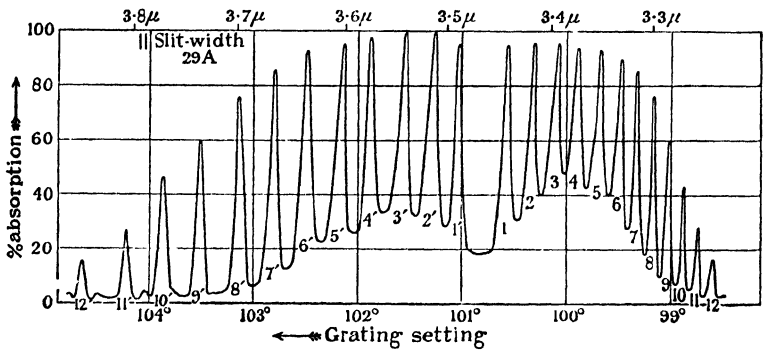


FIG. 28.

absorption spectrum of hydrogen chloride, using a grating which gave great dispersive power. In Fig. 28 the absorption percentage is plotted as the ordinate, the angle of deflection is plotted as the abscissa, and a corresponding scale of wave-lengths is printed at the top of the diagram.

This curve represents the rotation-vibration absorption spectrum of hydrogen chloride; but as it is plotted on the wave-length scale instead of a scale of wave-numbers, the regular spacing of the wave-number plotting is lost. What is of importance to us is the fact that quite obviously one of the "teeth of the saw" is missing (the one which should be situated immediately to the right of abscissa 101°). This is the position which the null line should occupy; and quite evidently this null

[1] Imes, *Astrophys. J.*, 1919, **50**, 251.

line is either so weak as to be immeasurable, or else it does not occur at all in the absorption spectrum.

In Fig. 29 is plotted a typical distribution of lines in a rotation-vibration spectrum of this kind, but here the abscissæ represent wave-numbers, and the regularity of the system is clearly shown.

The theoretical situation of the null line is dotted; and the position of $\nu=\nu_0$ is also shown. This wave-number ν_0 is unoccupied by any line in the experimental spectrum, which is easy to understand, since it does not belong to the series at all.

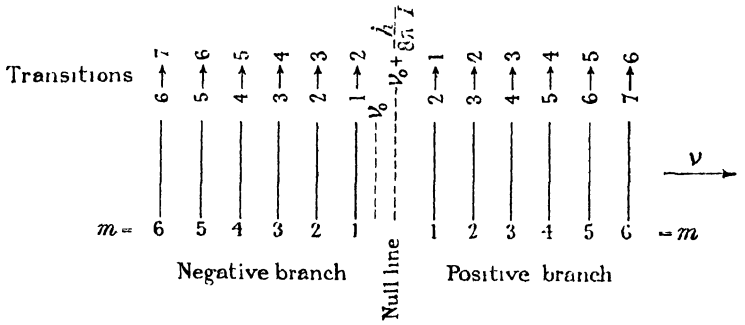


FIG. 29.

Its position on the scale can be determined from equation (13); because if $\nu=\nu_0$ in that expression, then

$$\frac{h}{8\pi^2 I}(\pm 2m+1)=0 \quad . \quad . \quad . \quad . \quad (15)$$

a condition which is fulfilled only by making $m=\frac{1}{2}$. The wave-number ν_0 is therefore situated at the abscissa $m=\frac{1}{2}$, as shown in the figure.

The absence of the null line from these rotation-vibration spectra raises a problem. The simplest solution would be to assume that no molecule ever reaches the rotationless state indicated by $m=0$. But this answer cannot be accepted, since lines are actually observed which correspond to the transitions from the state $m=0$ to the state $m=1$, and from the state $m=1$ to the state $m=0$, which is fair evidence for the existence of the state $m=0$.

In the foregoing, it has been assumed that the molecule behaves as an harmonic oscillator; but if the oscillation of

the nuclei be taken as non-harmonic, then the limitation that only unitary changes in the value of n are permissible is no longer tenable; and transitions such as $4 \rightarrow 2$ or $6 \rightarrow 3$ may be expected, which would add considerably to the complexity of the spectrum.

In actual practice, molecules have not been found to behave exactly like harmonic oscillators; and the rotation-vibration spectra observed in the near infra-red can be correlated with values for $(n_1 - n_2)$, which may be 1, 2, 3 . . . etc. Further, the factor ν_0 requires a slight correction if the results of experiment are to concord with the theory. If we give ν_0 the form $\nu_0(1-nx)$, better agreement is attained. Here x is a small constant involving factors such as the masses of the nuclei and the forces acting between them.

6. *Electronic Bands*

In the last two sections, consideration has been focussed on two types of spectra: those produced in the far infra-red by the rotation of a molecule as a whole; and those in the near infra-red which are generated by a combination of this rotatory motion with an intramolecular vibration of the nuclei. In both cases the influence of electrons within the molecule was left out of account; but this factor must now be introduced, in order to round off the whole subject.

The type of emission with which we are about to deal is the result of three contributory causes: a factor depending on molecular spin, which we may term ν_m; a second factor governed by nuclear vibrations, which may be indicated by ν_n; and, finally, a factor originating in the electronic system of the molecule, to which we may assign the symbol ν_e. If ν be the wave-number of the emitted light, then the quadruple relationship can be expressed in general terms by

$$\nu = \nu_e + \nu_n + \nu_m \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It has been pointed out in Chapter II that orbital leaps of valency electrons lead to the emission of light in the visible and ultra-violet regions of the spectrum; and since the factor ν_e depends upon such electronic rearrangements, it is to be anticipated that the spectra now under consideration will make their appearance in the visible or the ultra-violet tract.

Hitherto it has been convenient to regard the molecule as a purely mechanical system in which electrical conditions remain constant throughout. Now, however, with the introduction of the electronic factor, we are unable to neglect the electrical moment of the molecular system. Suppose that an electron leaps from one orbit to another within the molecule. So far as purely mechanical factors go, the alteration in the system is very slight, in view of the minute mass of the electron. But such an electronic transfer might have marked influence upon the electrical moment of inertia of the system, since the tiny electron carries a charge numerically equal to that of a proton, though opposite in sign. Consequently, the inertia of the molecular system will be considerably altered by a shift in the position of an electron; and a correction for this will have to be introduced into our calculations.

Let us assume that the moment of inertia of the molecular system is initially I' and that it becomes I'' in its final state. At the same time, the rotation alters from a state corresponding to the quantum number m_1 to the final state corresponding to the quantum number m_2. The kinetic energies in the initial and the final states can be expressed as below, in accordance with the equation (5) which we have already derived :

$$\text{Initial kinetic energy of system} = \frac{h^2 m_1^2}{8\pi^2 I'}$$

$$\text{Final kinetic energy of system} = \frac{h^2 m_2^2}{8\pi^2 I''}$$

The energy emitted during the change from the initial to the final state will be given by equation (17), if the energy is radiated at the wave-number ν_m :

$$h\nu_m = \frac{h^2 m_1^2}{8\pi^2 I'} - \frac{h^2 m_2^2}{8\pi^2 I''} \quad . \quad . \quad . \quad . \quad (17)$$

Whence

$$\nu_m = \frac{h m_1^2}{8\pi^2 I'} - \frac{h m_2^2}{8\pi^2 I''} \quad . \quad . \quad . \quad . \quad (18)$$

We have already seen that the Principle of Selection limits the transition to a leap of one unit in the value of m; so that (18) may be written as in (19), since $m_1 = (m_2 \pm 1)$:

$$\nu_m = \frac{h(m \pm 1)^2}{8\pi^2 I'} - \frac{h m^2}{8\pi^2 I''} \quad . \quad . \quad . \quad . \quad (19)$$

This expression can be rearranged into the following form

$$\nu_m = \frac{h}{8\pi^2 I'} \pm 2\frac{h}{8\pi^2 I'}m + \frac{h}{8\pi^2}\left(\frac{1}{I'} - \frac{1}{I''}\right)m_2 \quad . \quad (20)$$

If this value for ν_m be introduced into equation (16), we find

$$\nu = \left[\nu_e + \nu_n + \frac{h}{8\pi^2 I'}\right] \pm 2\left[\frac{h}{8\pi^2 I'}\right]m + \left[\frac{h}{8\pi^2}\left(\frac{1}{I'} - \frac{1}{I''}\right)\right]m^2 \quad (21)$$

But this is simply one of the Deslandres' formulæ for the band systems

$$\nu = A \pm 2Bm + Cm_2 \quad . \quad . \quad . \quad . \quad (22)$$

wherein

$$A = \nu_e + \nu_n + \frac{h}{8\pi^2 I'} \quad . \quad . \quad . \quad . \quad (23)$$

$$B = \frac{h}{8\pi^2 I'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$C = \frac{h}{8\pi^2}\left(\frac{1}{I'} - \frac{1}{I''}\right) \quad . \quad . \quad . \quad . \quad (25)$$

This reasoning, as is obvious, has given us a physical meaning which we can attach to the constants obtained purely empirically by Deslandres.

A graphical representation of these results is due to Fortrat.[1] If on rectangular axes the values of m are plotted as ordinates and the corresponding wave-numbers as abscissæ, the equation:

$$\nu = A \pm 2Bm + Cm^2$$

yields the tracing of two parabolic branches: a *positive branch* (generally termed the R-branch), and a *negative branch* (usually referred to as the P-branch). The positive branch represents points corresponding to $(A + 2Bm + Cm^2)$; whilst the negative branch contains the points represented by $(A - 2Bm + Cm^2)$. A purely illustrative graph is shown in Fig. 30.

Since the quantum numbers m have only integral values, the points where the ordinates 1, 2, 3 . . . cut the curve are indications of the positions of the various lines in the spectrum. This is shown in the graph of the P-branch lines at the foot of the figure; and the closing-in of the lines towards the head of the band can be seen at a glance.

In actual practice, the equation for the R-branch is not

[1] Fortrat, *Thèse* (Paris, 1914).

identical with that for the P-branch, though the difference between the two expressions is usually slight, as has already been pointed out.

The Fortrat method of plotting brings out clearly the line-grouping which leads to the *head of the band.* Examination of the spectral arrangement of the lines in the P-branch at the

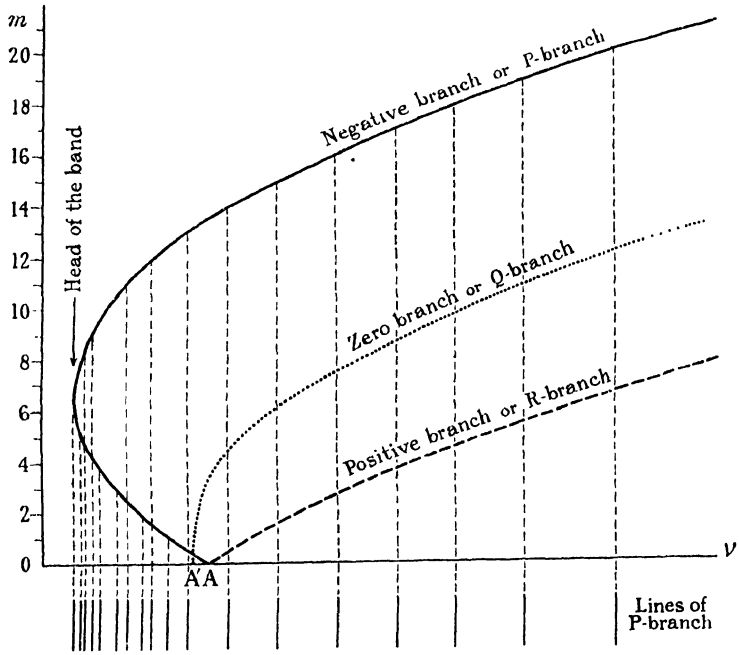


FIG. 30.

top of the figure shows at once that this series is converging upon a limit; and it is obvious that this limit is the vertex of the parabola. In order to find the position of the head of the band from the equation, since the vertex of the parabola lies at the minimum value of ν, we simply differentiate

$$\nu = A - 2Bm + Cm^2$$

with respect to m, and equate the differential coefficient to zero in the usual way.

$$\frac{d\nu}{dm} = -2B + 2Cm = 0$$

Whence it is obvious that the head of the band will lie at

$$m=\frac{B}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

If B/C is fractional, m must be taken as the nearest integer.

With regard to the convergence of the lines in the band towards this head, one point must be noted. This convergence is not like that which is seen in a geometrical progression such as $\nu=1+\frac{1}{2}+\frac{1}{4}+\frac{1}{8}$ . . . in which we are dealing with an *infinite* series converging by smaller and smaller steps upon a limit of 2. In the case of the lines in the band spectrum, we are dealing with a *finite* number of lines, as the Fortrat plotting shows; and the convergence is due merely to the shape of the parabolic curve, in which the negative branch bends back again after reaching the vertex and in which the jump from m to $(m+1)$ corresponds to greater and greater increments of ν as m increases in value. The band head is thus merely an " accidental " accumulation of lines, conditioned by the form of the curve and the scale of the wave-numbers.[1] It is obviously in a category quite different from that of the limit in atomic line spectra wherein, for example, the value of λ in Balmer's formula

$$\lambda=3645{\cdot}6\times\frac{m^2}{m^2-2}$$

can be made to approach more and more closely to 3645·6 with every increase in the value of m.

Since the head of the band is thus a more or less " accidental " position, it is necessary to look elsewhere for a fixed point of reference. If in the equation

$$\nu=A+2Bm+Cm^2$$

we put $m=0$, then $\nu=A$. Inspection of Fig. 30 will show that A is the point of intersection of the R and P branches of the graph. It will be noticed that in the figure, the line corresponding to $\nu=A$ is dotted. This line evidently corresponds to the null line or zero point in rotation-vibration spectra; and like that line, the line $\nu=A$ is not found in observed spectra, though it should theoretically exist.

We must now examine a fresh aspect of the electronic bands.

[1] Thiele, *Astrophys. J.*, 1897, 6, 65.

The original expression (16) contained three factors defining the value of the frequency of the emitted radiation:

$$\nu=\nu_e+\nu_n+\nu_m$$

and in (18) it was shown that the factor ν_m is represented by

$$\nu_m=\frac{hm_1^2}{8\pi^2I'}-\frac{hm_2^2}{8\pi^2I''}$$

This expression pre-supposes that the rotating molecule simultaneously changes *both* its speed of rotation (represented by the change of m_1 to m_2) and its inertia (represented by the substitution of I'' for I'). Assume, however, that the speed of the molecule's rotation remains unaltered—*i.e.* that $m_1=m_2=m$. The expression for ν_m then becomes

$$\nu_m=\frac{hm^2}{8\pi^2}\left(\frac{1}{I'}-\frac{1}{I''}\right) \quad . \quad . \quad . \quad . \quad (27)$$

By (25), the right-hand side of (27) is simply Cm^2; so that the general expression (16) now takes the form

$$\nu=\nu_e+\nu_n+Cm^2 \quad . \quad . \quad . \quad . \quad (28)$$

or, by substituting for $(\nu_e+\nu_n)$ the value $(A-h/8\pi^2I')$ obtained from (23), it becomes

$$\nu=\left(A-\frac{h}{8\pi^2I'}\right)+Cm^2 \quad . \quad . \quad . \quad . \quad (29)$$

The expression (29) is obviously a variant of the usual parabolic equation

$$y^2=4ax$$

and on the Fortrat method of plotting, it is represented by a fresh parabola, which is marked as the *zero-branch* or *Q-branch* in Fig. 30.

Putting $m=0$ in the expression (29) we obtain

$$\nu=A-\frac{h}{8\pi^2I'}=A' \quad . \quad . \quad . \quad . \quad (30)$$

as the abscissa at which this new parabola cuts the ν-axis of the graph. This point is not coincident with the point of intersection of the other two branches. The difference $h/8\pi^2I'$ is a small factor*; and this implies that when lines belonging to

* In the diagram, Fig. 30, it is taken as two units for illustrative purposes, so that the curves lie clear of each other.

the Q-branch make their appearance in spectra they form close doublets with some of the other lines belonging to the R- or P-branches.

It is now advisable to see what physical interpretation can be placed upon lines attributed to the Q-branch. If (29) be written in the form

$$\nu = A' + Cm^2 \quad . \quad . \quad . \quad . \quad . \quad (31)$$

it is evident that each line in the Q-branch is associated with a single value of m; and thus the Q-branch lines differ from those of normal rotation spectra or rotation-vibration spectra in which, it will be remembered, each line was associated with the difference between two values of m. The physical meaning of this appears plain enough at first sight: the molecule is emitting rotational energy without changing its rotational quantum number.

This may seem a contradiction in terms, but a little thought will show that it is perfectly possible. As was shown in (5), the kinetic energy of the molecule is represented by $I\omega^2/2$; so that a change in kinetic energy may be produced by altering I, or ω^2, or both factors together. Now if m, the rotational quantum number, be kept constant, then ω^2 is constant also; and a change in kinetic energy must be due to an alteration in the value of I.

How can such a change in the value of I be brought about? Obviously, since the molecule may suffer a rearrangement of its electrons, there may be a change in the *electrical* moment of inertia, whilst the rotational conditions remain unaltered. If in its initial arrangement, the moment of inertia is I' and if in the final stage, after electronic rearrangement, this becomes I'', then we have the case represented by (27) where

$$\nu = \frac{hm^2}{8\pi^2}\left(\frac{1}{I'} - \frac{1}{I''}\right)$$

Thus if the electrons in a molecule shift from one position to another and in so doing they change the total moment of inertia from I' to I'', the molecule will radiate or absorb energy at the frequency ν, even though the rotational conditions remain constant throughout. This yields the required physical interpretation of the lines belonging to the Q-branch.

Another point is brought out clearly by the Fortrat method

of plotting. For the sake of simplicity, let us confine our attention to the Q-branch of the graph. A glance at Fig. 30 will show that the Q-branch, corresponding as it does to the equation $\nu=A'+Cm^2$, is a parabola with its vertex at $m=0$, $\nu=A'$. As m increases step by step, the parabola becomes projected further and further towards the region of high wave-numbers and the ordinates for successive values of m spread further and further apart. The spectrum corresponding to this arrangement will have a head at the red side of the band and will be degraded towards the ultra-violet. On the other hand, if the factor C be a negative one, the equation becomes $\nu=A'-Cm^2$. This represents a parabola with its vertex at the same point as before ($m=0$, $\nu=A'$); but in this second case an increase in the values of m carries us in the opposite direction; and the curve represents a band with its head at $\nu=A'$, degraded towards the infra-red end of the spectrum.

Recurring to (27), we see that the factor C in

$$\nu_m=\frac{hm^2}{8\pi^2}\left(\frac{1}{I'}-\frac{1}{I''}\right)=Cm^2$$

will be positive or negative according to the sign of the expression within the bracket. If I' is less than I'', the expression takes the positive sign; and physically this corresponds to the molecule increasing its moment of inertia by electronic rearrangement as it passes from the state I' to the state I''. Conversely, if I' is greater than I'', the expression within the bracket takes the negative sign; and this is physically interpreted as the passage of a molecule from a state of high inertia to one of low inertia.

Correlate this with what has been said above with regard to the direction in which bands are degraded, and we get a clear idea of the implications of the two possible types of degradation. A band system degraded towards the infra-red is an indication that the factor C is negative in sign, which means that I' is greater than I''; and this might show that the molecule was shrinking in size as it passed from the initial to the final state. On the other hand, a band system degraded towards the ultra-violet corresponds to a positive value of C, implying that I'' is greater than I'; and this might indicate that the molecule increases in size as it passes from its initial to its final state.

Hitherto we have assumed that the quantum numbers are

always integers. In some recent theories,[1] half-quantum numbers are demanded. Suppose that in addition to the nuclear momentum $mh/2\pi$, a molecule has also an electronic angular momentum which can be designated by $\epsilon h/2\pi$. This fresh factor may be either added to or subtracted from the nuclear momentum, and the results will be

$$(m \pm \epsilon) \frac{h}{2\pi}$$

This introduces the conception of the *total quantum number*, j, which is simply the value of $(m \pm \epsilon)$. The resultant angular momentum is then obviously $jh/2\pi$. In practice, ϵ is a fraction close to $\frac{1}{2}$; so that when it is subtracted from m, half-quantum numbers come into our expressions. At the same time it should be noticed that in such cases it is j that is quantised and not m.

Further extensions of these ideas do not concern us here; but experimental evidence in favour of half-quantum numbers will appear in the next section.

7. *The Isotope Effect*

Earlier in this chapter, reference was made to the absorption spectrum of hydrogen chloride in the infra-red. This spectrum, it will be remembered, consisted of a series of lines evenly spaced along the wave-number scale. In describing his results, Imes [2] pointed out that in the "first harmonic" band ($n_1=2$, $n_2=0$), each structure "line" is quite definitely recognisable as a doublet composed of a strong line with a weak companion on the long-wave side.

At the time, this phenomenon was not understood; but shortly after, the explanation was given independently by Loomis and Kratzer,[3] who suggested that these doublets should be ascribed to the existence of the two isotopic forms of chlorine.

Aston has shown that chlorine contains the two isotopes Cl^{35} and Cl^{37}, and that ordinary chlorine is a mixture of 3·5 parts of Cl^{35} with 1·0 part of Cl^{37}. Now according to modern theory, the heavier isotope should yield a line of lower wave-

[1] Heisenberg, *Z. Physik*, 1925, **33**, 879; Born and Jordan, *ibid.*, 1925, **34**, 858; Kratzer, *ibid.*, 1920, **3**, 289.

[2] Imes, *Astrophys. J.*, 1919, **50**, 251.

[3] Loomis, *Nature*, 1920, **106**, 179; *Astrophys. J.*, 1920, **52**, 248; Kratzer, *Z. Physik*, 1920, **3**, 460; 1921, **4**, 476.

number than its congener; so that we may infer that the fainter of the two absorption lines in the HCl spectrum is due to HCl^{37}; and this opinion is confirmed by the fact that the relative intensities of the two lines are approximately 3·5 : 1.

A consideration of the theory of the isotope effect would occupy too much space in this chapter; but the original papers may be consulted for the details.[1] It will suffice here to summarise the results which have been obtained.

As was mentioned in Chapter VII, the difference between the emission line spectra of two isotopes is very small; and from this it may be inferred that the electronic factor plays little part in differentiating the spectra of two isotopes. Any pronounced difference produced in molecular spectra by the influence of isotopy can therefore be ascribed to the rotational and vibrational factors which affect the energies of molecules. Further evidence in favour of this view is to be found in the experimentally established fact that the origins of the band systems of two isotopes coincide with each other; for at the origin of a band system the rotational and vibrational terms vanish from the equation, and this would lead to coincidence if the electronic difference (the only remaining factor) is negligible. Again, since in the case of a problem involving two particles, the masses of the particles M′ and M″ enter the equation only in the form of the "effective mass" μ, where

$$\mu = \frac{M'M''}{M'+M''}$$

it is clear that μ will be very small in the case where M′ is the mass of an electron and M″ is the mass of an atom: and hence in such a case the "effective mass" factor would be negligible for practical purposes in comparison with other factors in the problem.

The isotope effect in spectra is measured by the so-called isotopic displacement $\nu_1 - \nu_2$. This is the difference in wave-number between analogous lines in the spectra of two isotopes or of two compounds of identical molecular character, one of

[1] In addition to the papers of Loomis and Kratzer, the following may be consulted: Mulliken, *Science*, 1923, **58**, 164; *Nature*, 1924, **114**, 349, 423, 489; 1925, **116**, 14; *Physical Rev.*, 1925, **25**, 119, 259; **26**, 1, 319; Watson, *Nature*, 1926, **117**, 692; Watson and Rudnick, *Astrophys. J.*, 1926, **63**, 20. A short account will be found in Loomis's contribution to *Molecular Spectra in Gases*.

which contains one isotopic form of an element whilst the second compound is built up from another isotope, as in the case of hydrogen chloride which may be HCl^{35} or HCl^{37}. It is usual to use the suffix 1 to denote the more abundant isotope in a mixture —*i.e.* the material which gives the stronger set of lines due to the element under consideration.*

Without going into details, it is sufficient to say that the vibrational contribution to the isotope effect can be expressed as

$$\nu_1^n - \nu_2^n = \left(\sqrt{\frac{\mu_1}{\mu_2}} - 1\right)\nu_1^n$$

where ν_1^n is the wave-number corresponding to the vibrational quantum number n in the case of the more abundant isotope, while μ_1 and μ_2 are the effective masses of the two molecules containing respectively the two isotopic atoms, such as Cl^{35} and Cl^{37}. Similarly the contribution to the isotope effect which is made by the rotational movement of the molecule can be shown to be

$$\nu_1^m - \nu_2^m = \left(\frac{\mu_1}{\mu_2} - 1\right)\nu_1^n$$

where m is the quantum number corresponding to the state of rotation of the molecule containing the more abundant isotope.

It can also be shown that the vibrational contribution to the isotopic displacement can be measured by the fraction

$$\frac{1}{2}\left(\frac{\mu_1}{\mu_2} - 1\right) = \frac{M'(M_1 - M_2)}{2M_2(M_1 + M')}$$

The example of hydrogen chloride will make the matter clear. Here M′ is the mass of the hydrogen atom (1·008); M_1 is the mass of the more abundant chlorine isotope (35), and M_2 is the mass of the other chlorine isotope (37). The fraction thus becomes

$$\frac{1{\cdot}008(35-37)}{2\times 37\times(35+1{\cdot}008)} = -0{\cdot}000749$$

Suppose that we wish to apply this to the case of the infra-red band at 1·76μ. The wave-number of this band is the reciprocal of 1·76, *i.e.* 5682. We therefore multiply the value of the fraction by 5682 and obtain as a result −4·26 cm.$^{-1}$. This gives

* This would be HCl^{35} in the case we have chosen for example, since ordinary HCl contains HCl^{35} and HCl^{37} in the proportions of about 3·5 to 1.

the distance of the band of the second isotope from the main band at 1·76μ.

As to the influence of vibrational factors on the isotope effect, it has already been pointed out that at the origin of the band system the isotopic displacement will be zero. Further, if the factor $\left(\sqrt{\frac{\mu_1}{\mu_2}}-1\right)$ is positive, the displacement will be positive on the high wave-number side of the origin and negative on the other side. Again, the corresponding band systems of two isotopes will be identical in pattern, but the scale of the pattern will be different in each case.* The lighter isotope has the larger pattern, so that each band of the lighter isotope lies further from the origin than the corresponding band of the heavier isotope. If the positions of the bands be plotted on a wave-number scale, the distances between the origins of corresponding bands of two isotopes ($\nu_2''-\nu_1''$), increase approximately linearly with the distance, ν'', in either direction from the origin.

The molecular rotational factor in the problem also leads to similar patterns for two isotopes; but the spacing is greater for the lighter isotope in the ratio $\mu_1 : \mu_2$.

Further spectroscopic evidence for the isotopy of chlorine has been detected by Henri [1] in his examination of the absorption spectrum of gaseous chlorobenzene. Here there is a close doublet, one component of which is found experimentally to lie at 1·4 cm.$^{-1}$ from the other. According to the theory which was outlined above, calculation shows that the distance between the two bands should be 1·48 cm.$^{-1}$; so that the agreement between theory and practice is very good indeed.

One or two other cases in this field are of interest. In 1915, Jevons [2] published an account of a spectrum which he attributed to boron nitride, BN. Five years later, Aston [3] proved that boron contains the isotopes B^{10} and B^{11}. Mulliken,[4] having rephotographed the spectrum in question under improved conditions, found that the results could best [5] be accounted for

* The ratio of the scales is given by the ratio of μ_1 to μ_2.

[1] Henri, *Structure des molécules*, p. 113 (1925).

[2] Jevons, *Proc. Roy. Soc.*, 1915, (A), **91**, 120.

[3] Aston, *Nature*, 1920, **105**, 547.

[4] Mulliken, *Nature*, 1924, **114**, 349; *Physical Rev.*, 1925, **25**, 259.

[5] See further Mulliken, *Nature*, 1924, **113**, 489; **114**, 349; but compare Jevons, *ibid.*, **113**, 744, 785; *Proc. Roy. Soc.*, 1924, (A), **106**, 174.

by assuming that the emitter is the boron monoxide molecule, BO, and by attributing the pattern of weak lines to $B^{10}O$ and the pattern of stronger lines to $B^{11}O$ (since the boron isotopes are mingled in the ratio of 4·6 parts of B^{11} to 1 part of B^{10}).

Copper consists of the two isotopes Cu^{63} and Cu^{65}. Frerichs [1] traced a system in the copper bands which he attributed to copper hydride, CuH, on account of the large spacing of the lines which indicated a small moment of inertia in the emitter. This has been confirmed by Mulliken,[2] who found that the separations of the doublets agreed with the predicted isotopic displacements for $Cu^{63}H$ and $Cu^{65}H$. Further evidence has been adduced by Mulliken [2] from the spectrum of copper iodide, where a complete agreement was found between theory and experiment.

In the case of magnesium hydride, a point of considerable theoretical interest arises. Watson and Rudnick [3] measured isotopic displacements (due to the occurrence of Mg^{24}, Mg^{25}, and Mg^{26}) for the MgH band occurring at $\lambda=5211$. This band was then given the quantum numbers (0,0). Later, however, Watson [4] pointed out that the data agree much better with the numbering $(\frac{1}{2}, \frac{1}{2})$; and this fits well with the theories of Heisenberg,[5] Born and Jordan,[6] which demand the introduction of half-quantum numbers in the equations for band spectra.

Jevons has obtained evidence for an isotope effect in the band spectrum emitted by stannic chloride vapour under electrical excitation.[7] An examination of silicon with the mass-spectrograph established the existence of Si^{28} and Si^{29}; but though the presence of Si^{30} seemed also to be indicated, Aston [8] suggested that the evidence might not be entirely trustworthy owing to the possibility of hydrogen compounds of silicon being registered on the plate. Mulliken,[9] on photographing the spectrum of silicon nitride, found that each principal band head (in those

[1] Frerichs, *Ann. Physik*, 1924, **71**, 102; compare Mulliken, *Nature*, 1924, **113**, 489.

[2] Mulliken, *Physical Rev.*, 1925, **26**, 1.

[3] Watson and Rudnick, *Astrophys. J.*, 1926, **63**, 20.

[4] Watson, *Nature*, 1926, **117**, 692.

[5] Heisenberg, *Z. Physik*, 1925, **33**, 879.

[6] Born and Jordan, *Z. Physik*, 1925, **34**, 858.

[7] Jevons, *Proc. Roy. Soc.*, 1926, [A], **110**, 365.

[8] Aston, *Isotopes*, p. 77 (1924).

[9] Mulliken, *Nature*, 1924, **113**, 423; 1925, **116**, 14; *Physical Rev.*, 1925, **26**, 319.

regions where resolution is possible) was accompanied by two fainter heads. Calculation shows that the principal heads arise from the emitter $Si^{28}N$, whilst the two fainter series are produced respectively by $Si^{29}N$ and $Si^{30}N$. This result was later confirmed by means of the mass-spectrograph.[1]

Later work along similar lines has led to the announcement that both oxygen and carbon possess isotopes. According to the discoverers, in addition to the atoms of mass 16, oxygen possesses a second isotope [2] of mass 18, and a third one [3] with a mass of 17. The discovery of an isotope of carbon [4] with mass 13, has been claimed on the strength of calculations based on the Swan spectrum and spectra of CO and CN.

8. *Conclusion*

In the foregoing brief account of band spectra, many points have perforce been left untouched. The physicists' ideas of molecular models, the Zeeman effect, the Stark effect, the whole field of fluorescence and phosphorescence: these examples are sufficient to show that much more might have been written if space had been sufficient. Those who wish for further information on matters such as these are referred to Baly's *Spectroscopy*, Griffith and McKeown's *Photoprocesses in Gaseous and Liquid Systems*, and to *Molecular Spectra in Gases*.

From the purely chemical point of view, band spectra appear to be entering a stage more interesting than before. As has already been pointed out, these spectra are now beginning to suggest to the chemist the possibility of atomic groupings which cannot be isolated in molecular form under laboratory conditions. The hydride of copper, for example, has not been obtained by ordinary chemical means; but as has been shown in the last section, there is now some spectroscopic evidence in favour of its existence under fresh conditions. If the subject progresses rapidly, as it seems likely to do, we shall perhaps find in it an extension of our knowledge of chemical affinity which may be of considerable service to our theories.

[1] Aston, *Nature*, 1924, **114**, 273.

[2] Giuaque and Johnston, *Nature*, 1929, **123**, 318; *J. Amer. Chem. Soc.*, 1929, **51**, 1436.

[3] *Ibid.*, 1929, **123**, 831.

[4] King and Birge, *Nature*, 1929, **124**, 182; and a later communication to *Nature*.

At the same time, it should be borne in mind that physical evidence interpreted by physicists does not always satisfy chemical jurymen, who have their own criteria by which they judge a case. What is important is that chemists should be ready to take from physics any assistance which will help to solve chemical problems, without swallowing uncritically everything that their neighbours unearth in their incidental incursions into the field of chemistry.

CHAPTER XXI

CONTINUOUS EMISSION SPECTRA

1. *Some Types of Continuous Emission*

In earlier chapters of this volume, line spectra and band spectra have been discussed; and it will be remembered that in both these types, the energy of the emitter is liberated at certain definite points on the wave-number scale. Between these points no emission makes its appearance. Thus so far as wave-length measurements are concerned, both line spectra and band spectra are discontinuous phenomena to which the quantum theory seems peculiarly applicable.

In the present chapter, the survey of the whole field will be completed by a very brief treatment of the so-called *continuous spectra*. When a continuous spectrum is examined, it is found to consist of a band of light extending uninterruptedly between two limits. It seems undoubted that this band of light is really continuous—*i.e.* that in it every wave-length between those of the two limits is represented in the spectrum—and that even high-dispersion apparatus would not serve to resolve it into a discontinuous system. The positions of the two limits are apparently governed by various factors involved in the production of the particular spectrum under examination.

Some idea of the character of general emission spectra may be gathered from an inspection of the Frontispiece of this volume. The emission spectrum of naphthalene (No. 2) consists of a single bright tract. In the case of the acetophenone spectrum (No. 5), the single bright tract contains three obvious maxima of emission which seem to correspond roughly to the three band heads in the benzaldehyde spectrum. The spectrum of tetrahydronaphthalene is built up from two separate tracts of emission; and in the short wave-length tract there are two maxima which lie approximately at $\lambda=2920$ and $\lambda=3180$.

It would occupy too much space if any attempt were made to give even a moderately complete account of the various methods by which continuous spectra can be generated; and it will suffice to mention a few points of interest in this region of the subject.

Many solid bodies and some liquids can be induced to radiate continuously by a mere heating; and in this case the limit of the continuous spectrum are governed by the temperature at which the experiment is made. Any one who has heated a platinum wire in a Bunsen flame must have noticed that the metal at first glows dull-red, then bright-red, and finally white. This series of phenomena obviously corresponds to an extension of the emission along the visible spectrum from the red to the violet until, when the wire is white-hot, all the wave-lengths comprised in what we call "white light" are being emitted. This makes it evident that with rise in temperature the platinum's limit of continuous emission is being steadily extended towards the ultra-violet. Not only elements but compounds also can show this phenomenon, provided that the affinity between the compound's atoms is sufficiently strong to resist the disrupting effect of high temperatures. If lime be heated with an oxy-hydrogen flame, its emission also ranges from red to white with increase in temperature; and, as the case of the now obsolete "lime-light" shows, the emission can be very powerful when the temperature is sufficiently raised.

Continuous emission may also be produced by the action of light itself; but on this point reference must be made to Baly's full description of the phenomena of fluorescence and phosphorescence, to which he has added his suggestive theory as to the origin of the radiation.[1] One example, for illustrative purposes, will be sufficient here.

The ordinary quartz mercury lamp emits a line spectrum; and by using a quartz monochromator it is possible to eliminate all the lines except one at the wave-length 2536 Å. When light of this wave-length was allowed to fall on the vapour of mercury contained in a quartz tube at ordinary temperatures, it was found by Wood [2] that the mercury vapour is stimulated by the beam and emits light which also has the wave-length 2536 Å. This is what is termed a *resonance spectrum*, since the incident

[1] Baly, *Spectroscopy*, Vol. II, Chap. 4 (1927)
[2] Wood, *Proc. Phys. Soc.*, 1914, **24**, 185.

and emitted light have the same wave-length, although the phenomenon has nothing to do with reflection.

Hartley [1] had at an earlier date observed the *fluorescence spectrum* of mercury vapour, which he obtained by subjecting mercury vapour to the light from a spark passing between tin-cadmium or lead-cadmium electrodes. As we shall see, this fluorescence spectrum differs from the resonance spectrum. An important point lies in the fact that Hartley found the fluorescence most brilliant when the mercury was boiling briskly and that it ceased when all the liquid had been converted into vapour above the boiling-point.

Following this clue, van der Lingen and Wood [2] made a fuller investigation of the matter and discovered that it is impossible to excite fluorescence in *quiescent* mercury vapour but that it can easily be obtained from vapour which is being distilled at 150° C. or higher. That is not true for the case of the resonance spectrum which was mentioned above. It is thus made evident that fluorescence is a property possessed only by mercury molecules which have just changed from the liquid to the vapour state. In other words, the capacity for fluorescence is associated with molecules which have just been wrenched from close association with their neighbours in the liquid mercury; and it is lost by these molecules after they have been for a short time in the freer gaseous state of aggregation. From the physico-chemical point of view, this state of affairs seems peculiarly suggestive.

The fluorescence spectrum of mercury vapour obtained by van der Lingen and Wood contains four structureless bands in the following positions: (1) a symmetrical band extending from the red to λ=3700 Å. with its maximum at λ=4850 Å.; (2) a similar band with a maximum at λ=3300 Å.; (3) an unsymmetrical faint band just above λ=2539 Å.; and (4) a somewhat unsymmetrical band running from λ=2349 Å. to 2100 Å. When long exposures are made, the first two bands fuse together into a single band. By exciting mercury vapour by a group of zinc lines at λ=2150 to 2000 Å., a fluorescence band appears at λ=2349 to 2100 Å. If each of these zinc lines is used separately, the region of maximum fluorescence moves along the

[1] Hartley, *Proc. Roy. Soc.*, 1905, (A), **76**, 428.
[2] Van der Lingen and Wood, *Astrophys. J.*, 1921, **54**, 149.

band. For instance, excitation by a line at 2024 Å. yields only the long-waved portion of the band, whereas excitation by the line at 2138 Å. produces only the short-waved part of the band.

These facts are sufficient to indicate the manner in which the limits of continuous emission can be varied by changing the conditions of excitation.

Turning to another method of producing continuous spectra, the case of positive rays may be mentioned. Hydrogen itself emits a continuous spectrum which begins at $\lambda=360\mu\mu$ (the limit of the Balmer Series) and extends at least as far as $\lambda=250\mu\mu$. This type of emission was observed in some stellar spectra; [1] and it has been produced experimentally by Stark,[2] who detected it in an examination of streams of positive rays in a hydrogen tube.*

The next method of exciting continuous emission has a peculiar interest, since the radiation occurs in the X-ray region of the spectrum. The so-called *impulse spectrum* is emitted when a solid is bombarded with cathode rays. This is sharply cut off on the side of the short waves.† Even some organic compounds yield this type of emission if they are cooled with liquid air during the bombardment; for example, stilbene, phthalic acid, phenol, methyl-propyl-ketone, and benzanilide, among others, radiate continuous spectra under these conditions.[3]

In the next chapter, some account will be given of the results obtained by means of yet another method of excitation—the Tesla high-tension discharge; so that at present it is unnecessary to do more than mention these Tesla-luminescence spectra.

2. *Some Hypotheses about Continuous Spectra*

From a hasty survey of the facts, it might be inferred that continuous spectra are essentially different from line and band

[1] See Hartmann, *Physikal. Z.*, 1917, **18**, 429

[2] Stark, *Ann. Physik*, 1917, **18**, 429.

* Analogous results may be expected in the case of the alkali metals, for sodium vapour shows general absorption extending beyond the series limit of the line spectrum. Since general absorption is the converse of continuous emission, it is evident that the mechanism of continuous emission is present in the sodium atom.

† Continuous absorption spectra in the Röntgen region are also known They are sharply limited on the side of the long waves, *i.e.*, they link up with the K- or L-limits on the side of the short waves.

[3] Marsh, *J.*, 1927, 125.

spectra, which have discontinuity as their hall-mark. Further reflection, aided by analogy, may put a different complexion on the matter.

Suppose a staircase to be built upward in such a way that each step is half the height of its predecessor. Before the building has been carried very far, the upper portion of it will approximate, for all practical purposes, to an inclined plane. Now imagine that a marble is allowed to roll down from the top of this plane. At first it will maintain contact with the plane throughout its path; but gradually this mode of advance will change, until at last the marble is proceeding downward by a series of jumps from step to step. By this crude analogy we can represent the merging of discontinuity into something which will approach continuity more and more closely until at last the two fuse into one another.

The atomic analogy here, in which the flight of steps would be represented by successive "stationary orbits" on the Bohr theory, has already led us in Chapter II to the Correspondence Principle, whereby Bohr harmonised quantum dynamics with the old classical theory.

Now turn to the Bohr hydrogen atom, with its central proton and its electron circulating in the stationary orbits. As the radius of the orbit is increased, the pull of the nucleus upon the electron will grown feebler; and in the end, if the electron jumps outward from orbit to outer orbit continually, a stage will be reached when the nuclear attraction is so feeble that it fails to retain the electron in the system; and thus a free electron would be produced. But the quantum theory of the atom is not applicable to a free-moving electron; so that the process which we have pictured is one in which the electron passes stage by stage from the quantum-conditioned orbits to a state in which its motion is no longer subject to the restrictions of the Bohr theory.

Bohr has applied his ideas to the case of those bands of continuous emission which have been described in the last section as linking up with the series limits in certain spectra.

Suppose that a free electron passes within capture-distance of a system capable of retaining it and that the result is the entry of the electron into the outermost quantum orbit of the system. Assume further that the free-moving electron has the

energy W_1, whilst when it drops into the outermost quantum orbit its energy can be represented by W_2. Energy will be radiated during the process of capture. Imagine that this energy makes its appearance at wave-number ν. Then, by applying Bohr's original premise, one quantum of energy, $h\nu$, will be radiated, and we have

$$h\nu = W_1 - W_2$$

or

$$\nu = \frac{W_1}{h} - \frac{W_2}{h} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The factor W_1 obviously represents the kinetic energy of the free electron; and to remind ourselves of this, we may replace W_1 by the symbol $E_{kin.}$

$$W_1 = E_{kin.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The factor W_2 represents the total energy of the electron when circulating in the outermost quantum orbit of the system. We have already (in equation (15) on p. 23) derived an expression for this quantity in the case of the hydrogen atom:

$$W_2 = -\frac{2\pi^2 me^4}{n^2h^2}$$

$$= -\frac{2\pi^2 me^4}{ch^3} \cdot \frac{ch^3}{n^2h^2}$$

$$= -R\frac{ch}{n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R is the Rydberg constant, c is the velocity of light, h is Planck's constant, and n is the quantum number of the outermost orbit.

But since Rc/n^2 represents the limit of the spectral series of the system, we can write

$$W_2 = -h \,.\, L \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which L represents the limit (Rc/n^2) to which the lines of the series are converging.

Substituting the values from (2) and (4) in (1), the expression for the wave-number of the emitted light takes the form

$$\nu = \frac{E_{kin.}}{h} + L \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Interpreting this into physical terms, it is clear that if the kinetic energy of the electron before entering the system is zero,

then ν=L, and the emission will take the form of the limiting line of the series. If the electron has any kinetic energy whatever, the emission will extend beyond the usual limit of the series and the wave-number at which it is emitted will be governed by the value of the fraction $E_{kin.}/h$. Now since the kinetic energy of the free-moving electron may have any value we choose to select, it is evident that expression (5) represents a *continuous spectrum which will link itself on to the limit of the normal series.* This, as has been explained, is exactly what is observed in practice. And since in the experimental production of any spectrum, countless electrons are entering systems under these conditions, each electron with its own kinetic energy, it is easy to see how the continuous spectrum can be produced.

Something else can be inferred from Bohr's views. It will be noticed that if they are applied to the case of hydrogen, it is the *atom* of hydrogen which yields the continuous spectrum as it passes from the ionised to the neutral state.

A converse case is worth noting. Steubing [1] observed that iodine vapour, in addition to the normal band spectrum, showed also continuous emission. Franck [2] has accounted for this by applying the octet theory. The iodine atom contains an outermost shell of seven electrons—one less than the complete octet—and it is ready to take up an extra electron which will let its outer shell revert to the octet grouping. The entry of this electron into the atom—*i.e.* the *ionisation* of the iodine—would lead to the emission of the continuous spectrum. Thus in the case of hydrogen, continuous emission may be supposed to originate in the neutralisation of an ion, whilst in the case of iodine the radiation is traced to the conversion of the neutral atom into an ion. In both cases the continuity of the emission corresponds to the continuous distribution of the kinetic energy of the adopted electrons.

In this connection, another interesting point arises. If equation (5) above be applied to this case of iodine, a little consideration will show that L, the long-wave limit of the continuous spectrum, should be a direct gauge of the electron affinity of the iodine atom, since when ν=L, the electron has no kinetic energy of its own. From measurements of ionisation

[1] Steubing, *Z. Physik*, 1921, **5**, 428.

[2] Franck, *Ann. Physique*, 1921, **64**, 693 ; see also *Z. Physik*, 1922, **9**, 259.

potential among the halogen acids, Knipping [1] calculated the electron affinity of the halogens and found values agreeing with the spectral results for iodine and bromine.*

In the examples which have just been considered, we have been dealing with free electrons entering atomic systems and remaining in the Bohr orbits. There is, however, another possibility open. What would happen if a free electron rushed into an atomic system and then, without a halt in the Bohr orbits, swept clean out of the system again? Quite obviously the electron would suffer a change in kinetic energy during its passage through the atom; and this change should manifest itself in some radiation of energy from the system.

This hypothetical case is realised in an X-ray tube when one of the electrons of the cathode stream strikes the target of the tube. In its passage from cathode to target, it is completely "free." It penetrates the outer zones of the atom; flies past the nucleus which deflects it from its path; and leaves the atom again in a hyperbolic orbit.

In this case, it is evident that it matters little whether the atomic system is charged or not—*i.e.* whether we are concerned with a neutral atom or with an ion—for here the real deflector is the heavy positive charge on the atomic nucleus which will act on the incoming electron at close quarters whether the atomic system as a whole is positive, neutral, or negative.

It will be recalled that the continuous X-ray spectrum has a sharp limit on the side of short wave-length. The position of this limit is independent of the material of the target and is governed by the voltage of the X-ray tube. It is generally agreed that this short-wave limit is produced by those electrons which possess the full initial energy of the cathode gradient of potential and which lose this energy completely in their transit through the atomic system. If the voltage of the tube is lowered, no electrons can acquire and subsequently lose the energy corresponding to the original voltage; and hence under the new conditions a fresh limit would be set to the X-ray continuous spectrum. The remainder of the continuous X-ray spectrum is assumed to be produced by electrons which fail to part with their whole energy and escape from the atom with the residue.

[1] Knipping, *Z. Physik*, 1921, **7**, 328.

* A continuous spectrum has not been detected yet in the case of chlorine.

CHAPTER XXII

TESLA-LUMINESCENCE SPECTRA

1. *The Production of Tesla-luminescence Spectra*

WHEN the discharge of an induction coil is passed through the vapours of carbon compounds, decomposition ensues; and the spectra emitted are, in nearly every case, merely those of carbon or its oxides. By choosing specially stable hydrocarbons and their derivatives, Wiedemann and Schmidt [1] succeeded in obtaining spectra of continuous emission in the case of ten compounds. They were unable to extend their investigations to other compounds; and they confined their observations to the visible region: so that their results contributed nothing of importance to our knowledge. Thus, until a short time ago, nothing was known of the emission spectra of complex compounds in general.

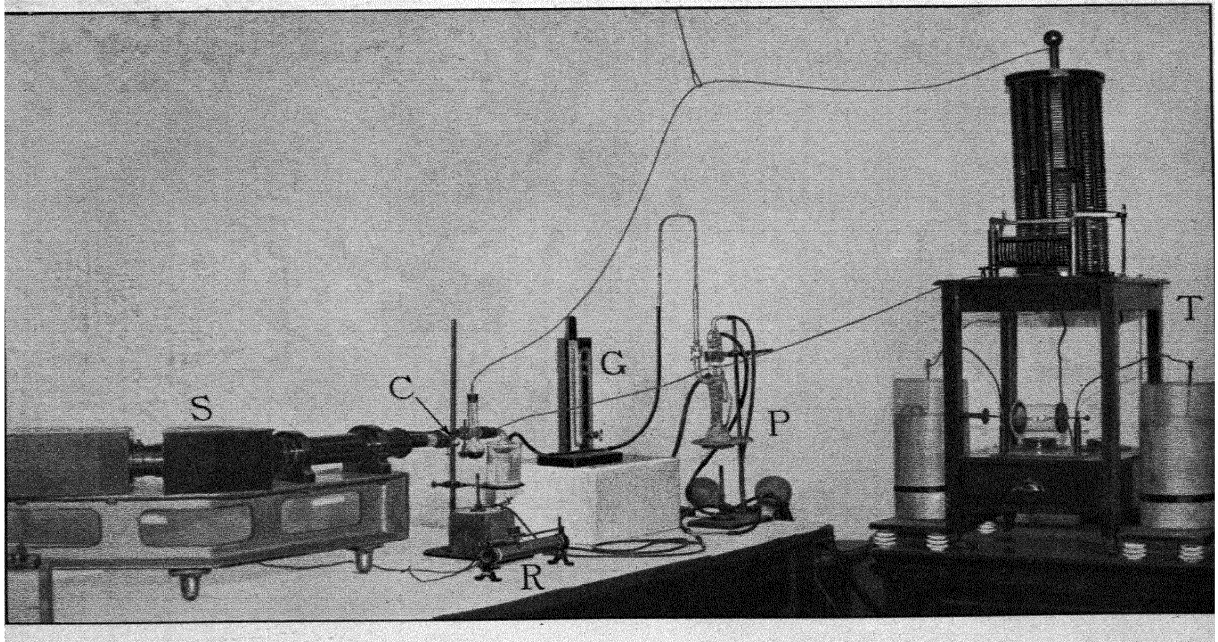
By employing a fresh method of excitation, McVicker, Marsh, and Stewart [2] obtained a series of spectra each of which is characteristic of the compound which emits it; and a new constitutional property was added to the list which already contained refractive index, magnetic rotation, absorption spectra, etc. By using the discharge from a high-tension transformer and by reducing the pressure of the vapour under examination, it is possible to obtain pure spectra even when the compounds investigated are not particularly stable; and thus a completely fresh field has been opened up in spectroscopy.

A photograph of the apparatus employed is shown in Plate V. On the left is the quartz spectrograph by means of which the

[1] Wiedemann and Schmidt, *Ann. Physik*, 1895, **56**, 29.

[2] McVicker, Marsh, and Stewart, *J.*, 1923, **123**, 642, 817; 1924, **125**, 1743; 1925, **127**, 999; *J. Amer. Chem. Soc.*, 1924, **46**, 1351; *Phil. Mag.*, 1924, **48**, 628; MacMaster, Russell, and Stewart, *J.*, 1929, 2401; Russell and Stewart, *J.*, 1929, 2407; *ibid.*, 2432; McVicker and Marsh, *J.*, 1923, **123**, 817; Marsh, *Phil. Mag.*, 1925, **49**, 971, 1206.

TESLA-LUMINESCENCE SPECTRA APPARATUS



S = Quartz Spectrograph
C = Quartz Cell
R = Resistance for Heater
G = Gauge
P = Mercury Vapour Pump
T = High Tension Transformer

spectra are photographed over the whole range of the ordinary actinic spectrum. Immediately to the right of this is the quartz cell through which the vapour is passed while the exposure is made. Below this in the picture is the resistance for regulating the heating jacket which keeps the cell at a fixed temperature when high-boiling substances are under examination. Beyond the cell is the mercury gauge and further on is the mercury vapour pump for reducing the pressure in the cell. This pump is connected with a motor-driven oil pump which is not shown in the illustration. Finally, on the extreme right, there is the high-tension transformer, actuated by a 12-inch induction coil, which furnishes the current for the discharge.

The upper part of Fig. 31 shows the outline of the wiring scheme of the apparatus. The transformer is air-insulated and its primary and secondary circuits are directly connected as shown, the primary circuit being varied by means of a sliding contact indicated by the arrow in the figure.

The design of the all-quartz cell is sketched in the lower part of Fig. 31. On the left is the plane quartz window through which the spectrum is photographed; and above this can be seen the internal electrode of the cell—a glass tube filled with mercury—which projects through an insulating stopper into the cell. Immediately below the electrode is the bulb in which the material under examination is placed. In the middle of the straight tube of the cell, on the outside, a metal foil external electrode is fixed; and, when necessary, this section of the tube can be warmed by an electric heater in an asbestos jacket. The receiver, into which the substance is distilled, lies beyond the joint, on the extreme right; and in practice it is immersed in a beaker of cooling mixture, as shown in Plate V. The exit tube of the receiver is connected with the gauge and mercury pump through traps which, for the sake of simplicity, have been eliminated from the illustrations.

Inspection will show that this system is simply a modification of the ordinary ozoniser; and by lowering the pressure within the cell a steady discharge can be passed through the vapour under examination. Spectra can be obtained with pressures up to about 60 mm.; but usually the pressure is kept at 1–2 mm. Apart from the effect of auto-absorption by the vapour itself, there is no material difference produced in the spectral character

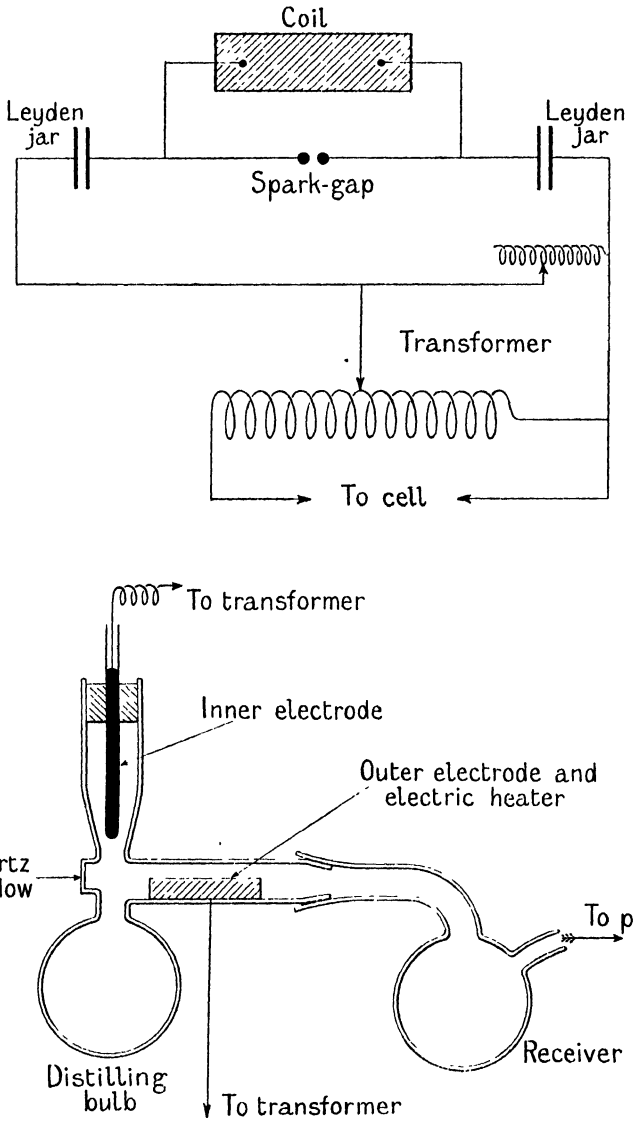


FIG. 31.

by a change of pressure within these limits; and the same is true with regard to variations of temperature.[1] The nature of

[1] McVicker and Marsh, *J.*, 1923, **123**, 817.

the transformer is also immaterial, since identical results were obtained with three independent transformers of different designs.[1]

In some cases, very faint bands have been detected in the following manner. Alcohol vapour emits no Tesla-luminescence spectrum and is completely diactinic in thicknesses equal to the length of the quartz cell employed. By simultaneously volatilising alcohol and benzene in the same cell, the pressure of the benzene in the mixed vapour corresponds to its partial pressure under the given conditions; and thus its emission spectrum can be recorded at pressures much below those obtainable with the pump alone. At these extremely low pressures, the absorptive power of the benzene is very slight; and thus some emission bands can be photographed which under 1 mm. pressure disappear from the spectrum owing to absorption.

2. *The Benzene Emission Spectrum*

When benzene vapour is examined in this apparatus, it is found to emit a spectrum of surprising regularity, part of which is reproduced in Plate I. It consists of over seventy fine bands which appear to fall into eight groups. The first two of these —termed Group H and Group G in the table below—are apparently incomplete; and it seems probable that the remaining bands of these Groups are of feeble intensity and are thus blotted out by the absorption of ultra-violet light by the benzene vapour itself. The next set, Group F, contains 12 bands; then in turn follow Group E—the most complete of all—with 18 bands, Group D with 15 bands, Group C with 12 bands, Group B with 9 bands, and Group A with 5 bands. Inspection of Plate I will reveal the manner in which the successive Groups are evenly distributed over the spectrum.

In comparing spectra, it is well known that regularities are more readily detected by using the wave-numbers instead of wave-lengths; and in the following table the former unit is used. The figures in square brackets represent bands visible only when the benzene vapour is diluted with alcohol vapour; those in round brackets represent the positions of very diffuse bands which are difficult to estimate exactly, and hence these values

[1] McVicker, Marsh, and Stewart, *J.*, 1923, **123**, 2147.

are more approximate than the others. The whole spectrum increases in brightness from the top to the bottom of the table.

THE WAVE-NUMBERS OF THE BANDS IN THE TESLA-LUMINESCENCE SPECTRUM OF BENZENE.

Group A.	Group B.	Group C.	Group D.	Group E.	Group F.	Group G.	Group H.
					3663*	3763*	[3861*]
—	(3279)*	3372*	3471·5*	3570·5*	—	—	
				3584·5			
(3194)*	(3294)*	3389*	3486·0*	3586·0*	3685·0	—	
—	—	—	3492·0	3588·5	3692·0	—	
				3597·3	3699·0		
—	—	3401·0	3500·0	3599·0	3700·5		
			3503·3				
(3211)*	(3308)*	—	3507·0*	3608·0*	3710·0*	—	
—	3319·0	3419·0	3517·0	3616·0			
(3229)*	3322·5*	3421·0*	3519·0*	3618·5*	3716·0	—	[3914]
—	—	3424·0	3523·5	3624·0	3724·0		
				3625·0			
—	3334·0	3434·0	3534·0	3632·0	3732·0	—	[3931]
(3242)*	3336·5*	3436·0	3536·0*	3635·0*	—		
—	—	3439·5	3539·0	3641·0	3740·0	[3839·0]	
				3643·0		[3843·0]	
—	3351·0	3450·5	3550·0	3649·5	3749·0		
				3651·0		[3852·0]	
(3257)*	3354·0*	3454·0*	3553·0*	3654·0*	3753·0*		
—	—	3456·0	3556·0	—	—		

Examination of the table will show the very apparent regularity of the benzene spectrum. Omitting the Groups G and H, which are incomplete, it is found that each of the remaining Groups contains bright bands (marked with asterisks in the table); and it is evident that any one of these strong bands in, say, Group D has a congener in Group C with a wave-number approximately 100 units higher. The same regularity is traceable in the case of the weak bands, though the completeness of the system is marred by the absence of certain bands from Groups B and C, these bands being probably too faint to be photographed. In Group A, the diffuseness of the bands makes it impossible to determine with exactitude whether any faint bands exist or not; and for this reason, also, the readings in this group are only approximate ones.

The benzene spectrum, then, consists of eight groups of bands; and each group in its internal structure resembles its neighbours, so that the following relationship holds good

between the wave-numbers of the corresponding bands in the various groups:

$$(F-E)=(E-D)=(D-C)=(C-B)=(B-A)$$
$$=100 \text{ units approximately}$$

Examination of the wave-numbers shows that the spectrum can be analysed into five independent series. For illustration of this, it is sufficient to take the figures in Group E of the foregoing table, since this is the most complete Group of all. The band at 3663 will be found to fit into this arrangement.

WAVE-NUMBERS OF BANDS IN GROUP E.

Series.	I.	II.	III.	IV.	V.
	3570·5	3584·5	3608	3588·5	3597·5
	3586	3599	3625	3608	3616
	—	3616	3641	3624	3635
	3618·5	3632		3643	3654
	3635	3649·5		3663	
	3651				
Average difference	16	16	16	19	19

The band at 3608 is used twice over in this table, but the probability that it is really two superposed bands seems to be supported by the fact that it is one of the bright bands of the Group.

The whole Group obviously falls into five Series, in each of which the bands are spaced evenly along the wave-number scale. In three of the Series the constant difference is 16 units; whilst in the other two Series it is 19 units. Figure 32 shows the

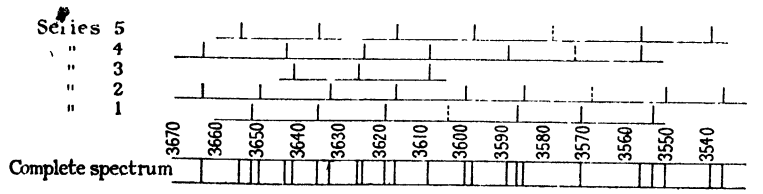


FIG. 32.

complete map of this region of the spectrum, as well as the analysis into the constituent Series. The dotted lines indicate

the positions where lines might have been expected, though they have not been detected in the photographs.*

A glance at the figure will suggest that the arrangement is one in which five rotation-vibration spectra † are superposed on one another. For instance, Series 1 might be regarded as a rotation-vibration spectrum with a null line at the position 3603, wherein $h/4\pi^2 I=16$, and the nuclear oscillation-frequency $\nu_0=3595$. It will be convenient to consider this point in a later section, when further evidence can be brought to bear on the matter.

3. *The Fraunhofer Effect*

When a luminous flame is examined by means of a spectroscope, a continuous spectrum is seen; and if some sodium be introduced into the flame, the bright sodium D-line is observed standing out sharply on the continuous background. If now between the flame and the spectroscope a cell filled with sodium vapour be introduced, the bright line vanishes; and instead of it there appears a black line occupying the same position as the D-line. This experiment proves that sodium vapour absorbs light of the same wave-length as that which is emitted by the sodium atoms excited in a flame, so that the emission and absorption spectra of the element are complementary to each other. This reversal is often termed the Fraunhofer effect.

The Fraunhofer effect has been observed mainly in the case of elements or of very simple compounds; but the discovery of the Tesla-luminescence spectra brought with it the possibility of showing that even compounds of complicated structure can exhibit the effect; and in the case of benzene a very interesting case of reversal has been detected, which is probably the most complex example known at present in the case of compounds.

Hartley [1] examined the absorption spectrum of benzene vapour at various pressures and temperatures, and embodied his results in a map on which he plotted the positions of the various absorption bands detected by him. It has already been

* Some of these positions may correspond to null lines which, of course, would not make their appearance in the observed spectrum.

† Since the spectra extend far into the ultra-violet, it is most unlikely that they are pure rotation spectra.

[1] Hartley, *Phil. Trans.*, 1908, **208**, A, 384.

pointed out that, owing to the diffuseness of certain bands in the Tesla-luminescence spectrum of benzene, absolute exactitude of measurement cannot be obtained; and the same is true in the case of absorption bands shown by benzene vapour. Allowing for this, the positions of the emission and absorption bands coincide so closely as to leave no doubt that each emission band has its counterpart in the absorption spectrum. The following table contains the wave-numbers of the absorption bands observed by Hartley and those of the emission bands detected by McVicker, Marsh, and Stewart.[1] The marks **** indicate that although Hartley did not insert absorption bands in his map at these points, his tables show that he detected absorption in the corresponding regions.

Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.	Tesla Emission Bands.	Hartley's Absorption Bands.
3763	3761	3700	3700	3643	****
3753	3754	3699	****	3641	****
3749	3749–52	3692	3691	3635	****
3740	3738	3685	3683	3632	****
3732	3734	3663	****	3625	3621
3724	3722	3654	3656	3618	3617–18
3716	3716	3651	3650	3616	****
3710	3708	3649	****		

These figures leave no doubt that the Tesla-luminescence spectrum of benzene vapour represents a reversal of the absorption spectrum; and thus for the first time it has been possible to show the existence of the Fraunhofer effect in the case of the spectra of a complex organic compound of known constitution.

4. *The Types of Tesla-luminescence Spectra*

Up to the present, the Tesla-luminescence spectra of over a hundred and fifty organic compounds have been examined; and it is now possible to trace some general relations between the chemical nature of a luminescent substance and the type of emission which it yields when excited by high-tension currents. It has been found that certain atomic groupings give rise to emission in specific portions of the spectrum, so that it is easy,

[1] McVicker, Marsh, and Stewart, *Phil. Mag.*, 1924, **48**, 628.

from an inspection of the spectrum photographs, to identify the varieties of compounds which have been used.

In the first place, there is the *Benzene Region*, which lies approximately between the wave-lengths 2500 and 3150 (see Plate I, No. 1). This type of emission is associated with the presence of a phenyl nucleus in the molecule; for it is detected in the spectra of benzene; toluene, $C_6H_5.CH_3$; ethyl-benzene, $C_6H_5.C_2H_5$; the xylenes, $C_6H_4(CH_3)_2$; as well as in those of certain more complicated phenyl derivatives.

Next may be mentioned the *Carbonyl Region*, lying roughly between the wave-lengths 3400 and 4850. This type of emission is found in the spectra of all the aliphatic ketones and aldehydes of the types R.CO.R′ and R.CHO. It appears therefore to be related to the presence of a single carbonyl radicle in the molecule, so long as the remainder of the molecular structure is saturated.

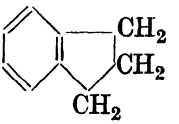
A third spectral tract of importance lies between the wave-lengths 3850 and 5000; so that it partly overlaps the Carbonyl Region. From the appearance of the spectrum when examined with the visual spectroscope, this tract has been christened the *Blue Band Region*. It is found most clearly marked in the spectrum of benzaldehyde, $C_6H_5.CHO$, which shows a very regular series of three band-groups comprising two dozen sharp bands and one further band evidently belonging to a fourth group. In the spectrum of acetophenone, $C_6H_5.CO.CH_3$, the sharp bands become merged into a series of three broader and more diffuse bands; but the family resemblance between the two spectra is unmistakable (see Plate I, Nos. 4 and 5).

A fourth characteristic spectral area lies in the visible spectrum and is known as the *Green Glow Region*.* It extends roughly from the wave-length 4550 onwards (see Plate I, No. 3); and it appears to be associated with a benzene ring carrying either two saturated hydrocarbon radicles or a second ring of non-benzenoid character. It is found in the spectra of compounds of the following types:

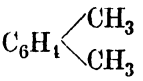
* It is of interest to note that this "Green Glow" is not observed in the vapour fluorescence spectra of the compounds, though in a modified form it has been found by Marsh in the cathodo-luminescence spectra of some substances at low temperatures.



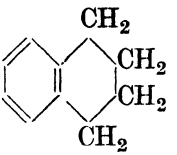
Indene.



Hydrindene.

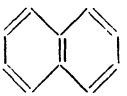


Xylenes.



Tetrahydronaphthalene

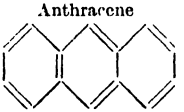
but it is not exhibited in the spectrum of naphthalene, where the second ring is of the benzenoid type :



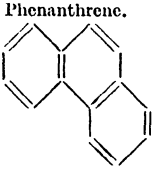
Naphthalene.

A fifth typical emission is found approximately between the wave-lengths 2900 and 4900. It is associated with the presence in the molecule of two or more benzene rings fused into a single system, as in naphthalene or phenanthrene ; and for this reason it has been termed the *Condensed Nuclei Region* (see Plate I, No. 2). The formulæ below are those of some compounds which emit this spectrum :

Anthracene

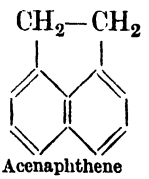


Phenanthrene.





Fluorene.

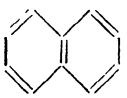


Acenaphthene

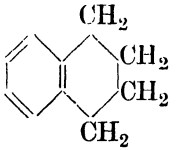
The anthracene spectrum is the most brilliant which has been observed up to the present. It lies between the wave-lengths 3240 and 5050, with an especially bright tract between 3650 and 4450. It was tested against an ordinary incandescent

mantle at the same distance from the slit of the spectrograph; and the two spectra were found to be of approximately the same intensity.

It must be pointed out that in some cases a compound may emit a spectrum embracing more than one of these regions, if its molecular structure contains two or more luminescent groups. An example of this kind is shown in Plate I, No. 3. The spectrum of naphthalene (Plate I, No. 2) lies in the *Condensed Nuclei Region*, as might be expected from the fact that the naphthalene skeleton contains two fused benzene rings, each of which, as appears from chemical evidence, is a true benzenoid structure. The reduction of one of these rings alters the character of the molecule; for now only one true benzenoid ring is present:



Naphthalene.

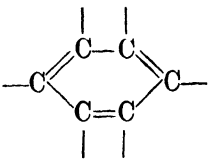


Tetrahydronaphthalene.

As a result, emission appears in the *Benzene Region*, since the single benzene ring is no longer complicated with a second unsaturated nucleus and consequently vibrates in the normal benzene period. Further, since this benzene ring has attached to it a saturated cyclic grouping, emission is found in the *Green Glow Region* also, as can be seen on inspecting the photograph in Plate I, No. 3.

5. *Tesla-luminescence Spectra and Chemical Constitution*

Up to the present, in spite of the large number of carbon compounds examined, only two systems have been discovered which are capable of emitting Tesla-luminescence: the carbonyl radicle, —CO—, and the benzenoid grouping:



The carbonyl group, when joined to saturated radicles, seems

to have the power of emitting only faint continuous spectra. When conjoined with the benzenoid system, as in benzaldehyde, C_6H_5—CH : O, it extinguishes the normal benzenoid spectrum and produces a banded spectrum in its own region (compare Plate I, Nos. 1 and 4 or 5).

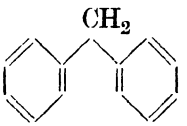
The benzenoid system is much more interesting. The fact that the luminescent power resides in this particular grouping is easily established. In the first place, the benzenoid system of double bonds is essential for the production of luminescence, since, when benzene is completely reduced to cyclohexane, C_6H_{12}, the power of light-emission is destroyed. Secondly, the hydrogen atoms of the benzene ring are not essential to the emission, since hexa-ethyl benzene, $C_6(C_2H_5)_6$, emits a spectrum, although none of the benzene hydrogen atoms remains in the structure. Finally, when one of the carbon atoms is exchanged for nitrogen atom (so that the pyridine structure results) the luminescing power disappears completely, which shows that the carbon sextet is necessary. It has already been pointed out that benzene yields a very complex and regular type of emission, which can be modified by introducing substituents into the molecule; and the results of some substitutions may now be considered.

The introduction of an amino-radicle, —NH_2, or an alkyl group into the benzene system has a marked influence in increasing the brightness of the Tesla-luminescence. As might be expected, a heavy accumulation of alkyl groups around the benzene ring leads to the reverse effect, since the loading of the ring eventually renders the true benzenoid vibration difficult. Thus while the spectra of toluene and the xylenes are brighter than those of benzene, there is a falling off with the introduction of a third methyl radicle to form mesitylene; and in hexa-ethyl benzene the luminescence is reduced to a very faint emission. From what has already been said, it is obvious that a second benzenoid ring, when fused to the benzene nucleus as in naphthalene, strengthens the luminescence (compare in Plate I, Nos. 1 and 2).

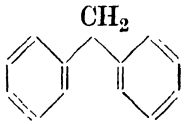
On the other hand, it has been found that the attachment to the benzene ring of groups such as —C≡N, —C≡CH, —CH_2OH, —COOEt, —$CH_2.C_6H_5$, —$NH.NH_2$, $NH.C_6H_5$, —$NH.NH.C_6H_5$, and the hydroxyl radicle leads to a dimming of the Tesla emission.

The hydroxyl group, —OH, the methoxy-radicle, —OCH_3, the cyanide group, —CN, and the amino-group, —NH_2, all tend to shift the emission region towards the red end of the spectrum when they are introduced into a molecule; whereas the opposite effect can be noted in Plate I, Nos. 4 and 5, where the change from benzaldehyde, $C_6H_5.CHO$, to acetophenone, $C_6H_5.CO.CH_3$, corresponds to a shift of the three bright bands towards the left-hand side of the photograph—*i.e.* towards the ultra-violet. Simultaneously, the sharp bands of benzaldehyde are altered to a blurred arrangement in which no individual bands can be detected.

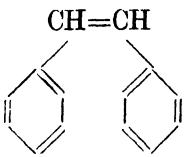
The formation of new cyclic structures within the molecule of the emitting substance has a marked influence upon the intensity of the Tesla-luminescence. Diphenyl-methane, for example, exhibits a spectrum of medium intensity; whereas fluorene emits a very intense spectrum. Inspection of the formulæ below will bring to light the fact that the only difference between them lies in the presence of an extra ring in the fluorene structure:



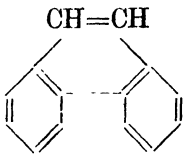
Diphenyl-methane.



Fluorene.



Stilbene.



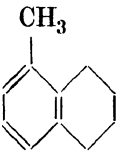
Phenanthrene.

A similar instance is found when stilbene is compared with phenanthrene; for the formation of the fresh cyclic structure in the latter compound changes the spectrum from a medium to an intense one in this case also. This effect of ring-formation appears to be a general one, as it holds in a number of other cases which have been investigated.

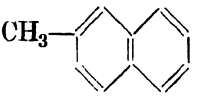
An interesting case is that of stilbene, $C_6H_5—CH : CH—C_6H_5$, and azobenzene, $C_6H_5—N : N—C_6H_5$. It is obvious that these two substances have the same general arrangements of bonds in their molecules; and the difference in molecular weight between

them is only two units. Nevertheless they differ completely in luminescent character; for stilbene yields a medium spectrum, whereas azobenzene cannot be made to emit any spectrum whatever.

The sensitiveness of the Tesla-luminescence spectra to changes in the constitution of the emitting molecule can be seen when the case of the two methyl substitution-products of naphthalene is considered:



1-Methylnaphthalene.



2-Methylnaphthalene.

Here the only difference between the two structures lies in the position of the methyl radicles; and both compounds give spectra of the same general type with an emission beginning approximately at the wave-length 3000. The continuous emission of the 1-methyl derivative stops at the wave-length 4500, however; whilst that of the 2-methyl derivative extends as far as 4700. Both compounds show faint bands in the visible region; but the heads of the bands of the 1-methyl derivative lie at 6020 and 6320, whereas those of the 2-methyl derivative are found at 5980, 6030, and 6400. Another example is to be found in the case of methyl-propyl ketone, $CH_3.CO.CH_2.CH_2.CH_3$, and methyl-isopropyl ketone, $CH_3.CO.CH(CH_3)_2$. The former shows emission between the wave-lengths 3550 and 4850; whilst the latter's spectrum extends only from 3600 to 4800, so that it is 100 units shorter than that of the normal propyl derivative. As can be seen from an inspection of the formulæ, the difference in structure between the two compounds is very small.

Turning to heterocyclic compounds, it is found that pyrrol, thiophen, and pyridine rings emit no Tesla-luminescence; and this is somewhat unexpected in view of the structural analogy between benzene and pyridine, as well as of the stability-resemblance between benzene and thiophen. But although without luminescing power in itself, the pyridine ring can act powerfully as a modifier of the benzenoid emission when it is linked with benzene nuclei. Thus quinoline, like naphthalene, gives emission in the *Condensed Nuclei Region;* and tetrahydro-

quinoline, like tetrahydronaphthalene, shows emission in the visible region of the spectrum.

Curiously enough, the Tesla-luminescence spectra furnish an exception to the general rule that conjugated double bonds (R—CH : CH—CH : CH—R) have a marked influence upon optical properties. This influence is traceable in selective absorption of light,[1] general absorptive power,[2] optical rotatory power,[3] refractivity,[4] magnetic rotatory power,[5] and other properties; but among the Tesla-luminescence spectra there appears to be no traceable relationship connecting the type of emission with the number of conjugated bonds in the molecule.

6. *The Origin of Tesla-luminescence Spectra*

It has already been pointed out that the Tesla-luminescence spectrum of benzene can be resolved into five components, each of which has the character of a rotation-vibration spectrum; and it seems interesting to consider this matter in greater detail.

It is easy to imagine a diatomic molecule rotating without perturbation; but in the case of a compound containing a ring of six carbon atoms, there must be a certain "stiffness" of the molecular fabric if a steady rotatory motion is to be possible. If the ordinary stereochemical ideas be followed, the benzene ring appears to be, to some extent, "braced" by the double bonds; and this "bracing" might serve to account for steadiness in rotational motion. Further, since this "bracing" is removed by reduction when benzene is converted into cyclohexane, the latter compound must be regarded as a much laxer arrangement of atoms than benzene is; and such a lax system would offer difficulties if an attempt was made to rotate it about an axis.

As has already been pointed out, cyclohexane emits no spectrum under the Tesla discharge; so that the facts appear in agreement with the rotation hypothesis.

When the Tesla-luminescence spectrum of benzene is examined, it is found to tail off into a faint general emission at the red end.* This implies that some of the benzene molecules are

[1] Stewart and Baly, *J.*, 1906, **89**, 489.
[2] Crymble, Stewart, Wright, Glendinning, and Rea, *J.*, 1911, **99**, 451, 1262.
[3] Hilditch, *J.*, 1908, **93**, 1388, 1618.
[4] Brühl, *Ber.*, 1907, **46**, 878, 1153.
[5] W. H. Perkin, senior, *J.*, 1906, **89**, 854; 1907, **91**, 806.

* Nothing is known about the other end, since the absorptive power of the vapour prevents investigation of the emission beyond a certain point.

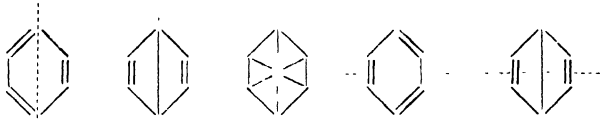
endowed with a motion which satisfies quantum conditions and gives rise to the banded portion of the spectrum, whilst other molecules are nonquantised in their emission and so produce a continuous spectrum.*

No attempt need be made to allocate the various components of the benzene spectrum to particular axes of rotation in the molecule. All that is necessary at present is to show that at least five such axes can be drawn, each different from the rest and each being an axis of symmetry through the atomic point-system of benzene.

It will be recalled that three of the five components show equal frequency-differences between the bands. If they are rotation spectra, this implies that in all three cases the system has the same moment of inertia around its axis of rotation and that the difference between the three emitters is due to differences in electronic arrangement within the molecule. The remaining two components differ from the rest in both frequency-difference and the positions of the null lines ; but since each has a frequency-difference=19, the emitters must have equal moments of inertia.

In other words, three of the five emitters under consideration must have different chemical structures but equal moments of inertia round their axes ; whilst the remaining pair must differ in structure from each other, but must have equal moments of inertia around their axes ; and, finally, the moments of inertia of the triplets and the pair must not be the same.

Collie's space formula for benzene [1] offers some help in this matter. His model provides a vibrational system of which the Kekulé, Centric, and Dewar formulæ are possible phases ; so that any one of them can be derived from another by intramolecular change. With these three formulæ at our disposal, it is a simple matter to fulfil the requirements set forth above.



(I) (II) (III) (IV) (V)

* The alternative possibility of very high quantum numbers seems hardly applicable to the case, though it cannot be excluded as impossible.

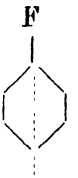
[1] Collie, *J.*, 1897, **71**, 1013 ; compare Baly, Edwards, and Stewart, *J.*, 1906, **89**, 514.

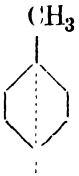
Imagine that the structures (I), (II), and (III) rotate around axes in the plane of the paper which are indicated by the dotted lines in the figures. The moments of inertia of the three systems will be identical, so far as the atomic masses are concerned; but each system will have its own electronic factor, since the bonds are differently disposed in the three formulæ, and hence the electronic distributions must be different in the three cases. The systems (I), (II), and (III), therefore, fulfil the requirements for the component Series 1, 2, and 3; though no attempt need be made to identify, say, formula (I) with the emitter of, say, Series 2.

Next imagine that the structures (IV) and (V) rotate on the axes indicated by the dotted lines. This pair will have equal moments of inertia; but these will not be the same as the moments of inertia possessed by the arrangements (I), (II), and (III).

It is thus clear that the required conditions can be fulfilled easily enough; but too much stress need not be laid on these particular illustrative models, since others, equally applicable, could readily be found. All that is required here is the fact that five different arrangements can be found, corresponding to the five components of the benzene spectrum.

Let us now turn to the problem of substitution in the benzene molecule; and here we may begin with fluorobenzene,[1] C_6H_5F, and toluene, $C_6H_5.CH_3$. On replacing one of the benzene hydrogen atoms by a substituent, the complete symmetry of the benzene ring is reduced, and only a single axis of molecular symmetry remains:





On the assumptions made above, this should lead to the disappearance from the benzene spectrum of two components, since the rotations on the axes represented in (IV) and (V) are now unlikely. Further, since the fluorine atom is compact,

[1] Russell and Stewart, *J.*, 1929, 2432.

whilst the methyl group is bulky, the latter will have a greater tendency to perturb the normal vibration of the benzene system ; and consequently the toluene spectrum should exhibit fewer bands than the spectrum of fluorobenzene and, simultaneously, there should be an increase in the general emission due to unquantised movements of the molecule.

The fluorobenzene spectrum falls into the following series of bands :

Group :	I.	II.	III.	IV.	V.	VI.	VII.
Series 1 .		3796	3699	3598	3496	3394	
,, 2 .		3791	3695	3590	—	—	3290
,, 3 .	3883	3781	3681	3577	3477	3375	
,, 4 .	3871	3771	3672	3571	—	—	
,, 5 .	3865	3768	—	—	—	—	
,, 6 .	3858	3761	3656	3554	3455	—	
,, 7 .	3852	3752	3651	3549	—	—	
,, 8 .	3839	3739	3636	3535	3433	3331	
,, 9 .	—	3727	3628	3529	—	—	
,, 10 .	3821	3721	3616	3514	3413	3309	

Examination of the figures will show that the bands, like those of benzene, fall into a set of Groups ; and the frequency-difference between a band in one Group and its congener in the next Group is about 100 units, just as is the case in the benzene spectrum. In fact, the similarity between the fluorobenzene and benzene spectra is extraordinarily close so far as the Group-relations are concerned.

A significant point comes to light when we attempt to resolve a Group into component spectra. When this is done, it is found that instead of the five component spectra of benzene, only two complete components can be found for fluorobenzene with the addition of three bands which seem to be fragments of another component or components. For example, the bands in Group II can be arranged thus :

3791

3781

3771

3761

3752

3739

3721

Here, obviously there is a common difference of approximately 20 units between a band and its neighbours in the same column —a surprisingly close approximation to the 19 units which was found analogously in the case of benzene itself.

Now let us turn to the case of toluene. The bands of its spectrum can be arranged in four groups, only one of which is nearly complete:

Group:	I.	II.	III.	IV.
		3668	3567	3465
		3662	—	—
		3647	3548	3445
		3641	—	—
	3728	3628	3528	3425
	3721	3623	—	
	3713	3606	3507	
	3697	—	—	
	3686	3590	—	
	3679	3583	3486	

Inspection will show that here again the 100-unit difference between corresponding bands in adjacent Groups is fairly maintained; but when an attempt is made to dissect Group II into its component series, the result does not yield such a satisfactory set of differences between the adjacent members of the individual series:

3668

3662

3647

3641

3628

3623

3606

3590

3583

These facts suggest that benzene can conform to quantum conditions while rotating on either of two axes, whilst fluorobenzene and toluene can rotate only on a single axis. This is precisely what a dynamical consideration of the three molecules would suggest, since the weighting of the ring by a substituent

must make any spinning on the axes represented in (IV) and (V) on p. 347 almost impossible.

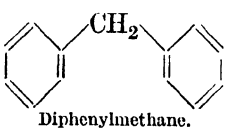
The effect of the lopsided loading of the ring can be traced in the number of bands observed in these spectra and in that of ethyl benzene :

Compound.	Bands.	Substituent's weight.
Benzene	78	H = 1
Fluorobenzene	45	F = 19
Toluene	23	CH_3 = 15
Ethylbenzene	6	C_2H_5 = 29

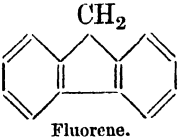
As the mass of the fluorine atom is intermediate between those of the methyl and ethyl groups, it is evident that the mere mass of the substituent alone cannot account for the decrease in the number of bands as we go down the table. If, however, stereochemical ideas be brought into the problem, it is clear that the methyl group is a less rigid system than the fluorine atom, whilst the ethyl radicle is even less braced in comparison with its mass. Thus to the benzene ring we are adding a series of chains which are free to waver about more and more at random as their length increases ; and such chains, being free to move irregularly, will tend to prevent the benzene ring itself conforming in its rotation to quantum conditions.

If this hypothesis were correct, it might be expected that the background of continuous emission in the four spectra would become more and more intense from benzene down to ethylbenzene. Examination of the plates * proves that theory and facts go hand in hand at this stage.

We may now turn to the case of those compounds in which two or more benzene rings are fused together. It has already been pointed out that internal ring-formation increases the brightness of the Tesla-luminescence, so that while diphenylmethane gives a poor emission, fluorene shows an extremely brilliant luminescence.



Diphenylmethane.

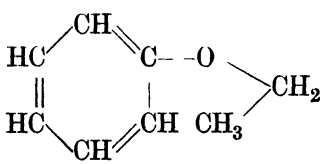


Fluorene.

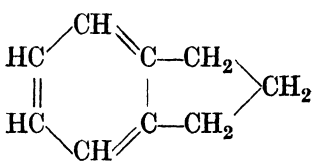
* A crude reproduction of the spectra of benzene and ethylbenzene is to be found in a paper by McVicker, Marsh, and Stewart, *J.*, 1923, **123**, 2147. It is clear enough to illustrate the point under consideration.

In the case of diphenylmethane, we have the two emitting centres (the benzene rings) spinning independently and yet hampered by being pivoted at the —CH_2— group ; whereas in fluorene we have a rigid system which can rotate as a whole. At the same time, the structure of fluorene is such that a uniform rotation is possible only about an axis bisecting the five-membered central ring of the molecule ; and the chance of the molecule happening to spin on this particular axis is small as compared with the chance that the system will simply whirl at random. Thus in molecules of this type, quantised emission of energy is not to be expected and continuous emission is much more probable. In practice, no bands have been detected in the fluorene spectrum, which is simply a brilliant tract of continuous emission. Naphthalene, anthracene, and phenanthrene also possess " braced " structures of a complex kind ; and their spectra are similar to that of fluorene. The spectrum of naphthalene is reproduced in the Frontispiece to this volume (No. 2).

From the stereochemical point of view, an interesting point arises when the spectra of hydrindene and benzyl ethyl ether are compared.[1] In both cases there is a tract of continuous emission in the ultra-violet extending roughly between the wave-lengths 2700 and 3500. In the visible region, hydrindene emits a continuous spectrum in the Green Glow tract, whilst benzyl ethyl ether yields the Blue Bands with very little continuous background. Except for this slight difference, the two spectra are extraordinarily alike in general type. Now on the face of things, there is no chemical resemblance between the two compounds ; but if the current stereochemical views on the configuration of carbon chains be taken into account it is possible to see a marked general resemblance between the two substances as the following formulæ will show :



Benzyl ethyl ether.



Hydrindene.

Obviously, regarded simply as a pair of atomic groupings the

[1] Russell and Stewart, *J.*, 1929, 2401.

two systems resemble each other markedly; and possibly the similarity in their spectra may find its explanation in this.

When we turn to the effects of various substituents in the benzene nucleus, the facts are as follows. *No emission at all* has been detected when the following groups are attached to the benzene ring: —NO_2, —NO, —N : N—. The introduction of the amino-group or an alkyl radicle, brightens the spectrum; but two or more of these substituents attached to the same ring decreases the intensity of the emission. If one of the following radicles is attached to the nucleus, the spectrum emitted is always feeble: —CN, —C≡CH, —CH_2OH, —COOEt, —$CH_2.C_6H_5$, —$NH.NH_2$, —$NH.C_6H_5$, —$NH.NH.C_6H_5$, and —OH. Some substituents shift the emission from the normal benzene position towards the red, for example: —OH, —$O.CH_3$, —CN, and —NH_2.

An examination of substituent groups in general shows that they can be divided roughly into three classes. In the first place come those which completely inhibit the process which gives rise to luminescence. The remaining set of substituents can be separated into two series: (1) those in which the atom directly attached to the benzene ring is saturated, as in the alkyl radicles; and (2) those wherein an unsaturated atom is directly linked to the benzene ring. Substituents of the first set interfere with the benzenoid vibration, but do not change its character to any great extent; for toluene, ethyl-benzene, and the xylenes all exhibit banded spectra like the parent substance itself. The direct attachment of an unsaturated atom like the tervalent nitrogen of aniline or the bivalent oxygen and sulphur atoms of phenol and thiophenol (which are capable of exhibiting higher valencies in other compounds) produce noticeable changes in the type of emission, as has already been pointed out.

It is now time to turn to the second group associated with emission, viz., the carbonyl radicle, —CO—. And here we come to some of the most puzzling facts in connection with the Tesla-luminescence spectra.

It has already been pointed out that the aliphatic ketones and aldehydes emit light in the region between the wave-lengths 3400 and 4850. This emission is feeble and continuous, with no trace of bands in it; which is what might be expected in view of the extremely lax architecture of the aliphatic compounds.

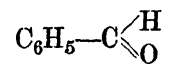
If, however, the aldehyde group be attached to the benzene ring, the emission increases in brilliancy and is resolved into a series of band-groups of which the following are the wave-numbers :

WAVE-NUMBERS OF THE BENZALDEHYDE BANDS

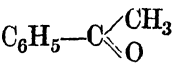
Group:	1.	2.	3.	4.	5.	Character
	—	2538	2364	2179	—	Strong bands.
	2697	2516	2344	2169	2014	Very strong bands.
	—	2494	2323	2151		Broad faint bands.
	—	2468	2299	2123		Faint bands.
	2598	2437	2262	2096		Sharp narrow bands.
	—	2415	2247	2076		,, ,, ,,
	2571	2398	2227	2061		Very faint bands.
	2553	2378				,, ,, ,,

At the same time, emission in the usual benzene region fails completely. This is not due to absorption by the benzaldehyde vapour, since no appreciable absorptive effect was observed when an arc spectrum was photographed through an equal length of benzaldehyde vapour. Evidently the attachment of the —CHO group to the benzene ring inhibits emission by the latter, while simultaneously the benzene nucleus influences the emission of the —CO— group in such a way as to resolve it into individual bands suggesting the quantumisation of the emitted energy.

When a methyl radicle replaces the hydrogen of the benzaldehyde :



Benzaldehyde.



Acetophenone

the sharp bands are broadened out and run together into a continuous spectrum, as can be seen from the reproduction in the Frontispiece (Nos. 4 and 5).

7. *Band Series and Fluorescence Spectra*

Marsh [1] has pointed out an interesting relationship between the positions of the bands in Tesla-luminescence spectra, fluorescence spectra, and the infra-red absorption spectra of organic

[1] Marsh, *Phil. Mag.*, 1925, 49, 971, 1206 ; and private communication.

compounds. Baly [1] and Henri [2] have collected evidence to show that a very general similarity exists between the frequency intervals of absorption bands in the visible or ultra-violet regions on the one hand, and the absolute frequency of important infra-red absorption bands of the same compound on the other hand. They suggest that the values for the ultra-violet bands are particular multiples of the infra-red frequencies, though it must be admitted that no absorption bands make their appearances at most of the intervening multiples.

The relationship between particular infra-red bands and the chemical constitution of the substance producing them seems to be well established, for bands due to the groups CH, OH, NH_2, etc., are easily identified. It should be noted that these particular radicles are of a stable type. Absorption in the ultra-violet, on the other hand, is associated with the presence of residual affinity, double bonds, labile groups, and, in general, with a state ascribable to the activity of valency electrons.

Ultra-violet and infra-red spectra have therefore entirely different origins; but if the mechanism giving rise to the ultra-violet spectrum (working at a frequency ν_e) is incorporated in a larger system working more slowly and giving absorption bands in the infra-red at ν_a, it is reasonable to expect that at all the frequencies $\nu_e \pm n\nu_a$, where n is a small integer, absorption or emission will be produced. Probably also there will be a distinct tendency for the rapid electronic vibration to synchronise with the slower atomic vibration by which it is of necessity influenced. Such a synchronism will result in the higher frequency ν_e being an exact multiple of the slower one ν_a—*i.e.* the relationship suggested by Baly and by Henri will be valid. Imperfect synchronism between the two sets of vibrations will result in an indefinite electronic frequency, and then no fine structure can be expected in the absorption or fluorescence spectrum.

Now energy can be either emitted or absorbed at ν_e; but emission bands are not usually found in the infra-red. If the two mechanisms of absorption mentioned above are both in action, an absorption band will be found at the frequency $\nu_e + \nu$

[1] Baly, *Phil. Mag.*, 1914, **27**, 632; 1915, **29**, 223; **30**, 510. Baly and Tryhorn, *J.*, 1915, **107**, 1121.

[2] Henri, *Études de Photochimie.*

but if the mechanism working at frequency ν_e is emitting energy whilst that working at frequency ν_a is absorbing energy, then an emission band will occur at $\nu_e - \nu_a$.

Marsh finds that the general features of absorption and fluorescence spectra support this view; for when the two types of spectra given by the same compound are examined, it is found that the two spectra usually come to a more or less abrupt end at a common point, ν_e. On one side of this point the emission spectrum stretches towards the low frequencies, whilst on the other side is found the absorption spectrum extending out towards the higher frequencies; and both diminish in intensity as they recede from the central point.

Now Marsh [1] has shown that the fluorescence and Tesla-luminescence spectra of benzene vapour have exactly the same character; so whatever applies to the fluorescence spectrum will hold good for the Tesla-luminescence spectrum also. Both the fluorescence and absorption spectra of benzene vapour consist of five or six large groups of bands lying on either side of the wave-number 3749 and differing in frequency by about $95 \times 3 \times 10^8$ units. This is the value of the frequency of a strong infra-red band in the benzene spectrum, which has been recognised as characteristic of the ethylenic grouping and which constitutes the chief infra-red band in the spectrum of ethylene, $CH_2 : CH_2$, itself. In a similar manner, Marsh finds another set of bands at frequency intervals of $16 \times 3 \times 10^8$ units in the fluorescence spectrum of benzene which may be traced to the complex CH as an origin. In the absorption spectrum of benzene, Henri has observed the same kind of small irregularities as are detected in the infra-red spectrum and has attributed them to the mutual effects of molecular and sub-molecular rotations and vibrations.

On this basis, ultra-violet spectra can be classified according to the atomic group which plays the main part in their production. In the spectrum of benzene vapour, bands are found which can be attributed to the groups CH and C : C; but the finer structure due to the former complex disappears when the spectrum of a benzene solution is examined. The spectra of naphthalene and anthracene also exhibit a predominant C : C complex at work; but methyl substituents in the benzene nucleus tend to produce an ultra-violet interval of $80 \times 3 \times 10^8$ units, which corresponds

[1] Marsh, *J.*, 1923, **123**, 3315.

to the deep bands of CH origin found in the infra-red at about 13μ. Marsh suggests that the Green Glow region in the Tesla-luminescence spectra is also due to the action of the CH complex. It should, however, be pointed out that a single influence may in different environments produce different band intervals in a manner which is not yet understood. Thus the C : C complex of benzene is associated with a frequency of about $95\times3\times10^8$; when it occurs in the naphthalene structure this value is halved, and in anthracene it is raised by 50 per cent. Again, the CH interval of benzene is $16\times3\times10^8$ in the ultra-violet, and for the methyl derivatives it is $80\times3\times10^8$ in the ultra-violet and $160\times3\times10^8$ in the visible region.

The spectra of benzaldehyde, Marsh finds, belong to an entirely different type; and by similar reasoning he attributes them to the carbonyl group. The chief infra-red band lies at $5{\cdot}8\mu$, and the frequency intervals in the ultra-violet or visible region are $172\times3\times10^8$ units, or multiples thereof.

8. *Conclusion*

From the facts described in the foregoing sections of this chapter, it is evident that an interesting field has been opened up by the discovery of the Tesla-luminescence spectra; and it is obvious that considerably greater advances may be looked for when more time has been spent on the work. The main lines are already roughed out; but clearly much more ground has to be covered before our knowledge of the field approaches completeness.

Even at the present time, however, it is possible to indicate some of the important developments which may come from further research. The mathematical treatment of spectra has perforce been confined in the past to the spectra of chemical elements and a few very simple compounds such as carbon dioxide, water, hydrogen chloride, and the like. In the Tesla-luminescence spectra a means is provided for extending this work into the region of the benzene series, and thus a mathematical treatment of the problem of the molecule has become possible. It is perhaps looking rather far forward if we anticipate the coming of a new Bohr who will do for the benzene molecule what has already been done for the system of the hydrogen atom; but when atomic dynamics has developed sufficiently to attack the

molecule, it is evident that the Tesla-luminescence spectra will furnish one of the lines of advance. The great regularity of the benzene Tesla-luminescence spectrum seems to suggest that the key is a fairly simple one if it can only be recognised.

Another, more practical, advantage is suggested by the great sensitiveness of the Tesla-luminescence spectra. In the course of the investigations, it was found that this spectral method is capable of detecting the presence of certain impurities in quantities which would escape the most refined analysis; so that possibly the Tesla-luminescence spectra may prove to be a valuable criterion of purity in compounds under examination.

From the purely chemical point of view, the results already obtained are sufficient to prove that a new weapon has been forged which will enable us to distinguish between the various effects produced upon the fine vibrational structure of the benzene ring by different substituents; and an increase in our knowledge of this field would undoubtedly react markedly on our practical processes.

CHAPTER XXIII

CONCLUSION

In the foregoing chapters many of the recent additions to our knowledge of the atom have been described ; but owing to the necessities of presentation, the chronological development of the subject could not be followed. Before concluding this volume, it seems advisable to indicate, at least in outline, the sequence of discoveries by which our contemporary knowledge has been reached ; for only in this way is it possible to appreciate the multifarious factors which have gone to build up our modern ideas on the structure of matter. It is no exaggeration to say that a full study of the atomic theory's history would be in itself a wide education—much wider, indeed, than most chemists have time to attain.

It is useless to search for the original atomist. Leucippus and Democritus, in the fifth century B.C., hazarded guesses at the truth ; but whether they originated the ideas themselves or merely repeated earlier suggestions which sprang from Indian sources, is a problem upon which it is fruitless to speculate. It any case, the fundamental features of the Hellenic atomism seem to have been set down by Lucretius in his *De Rerum Naturæ*, which dates from the first century B.C. The modern scientific reader of this poem finds in it evidence of acute speculation, mingled with some guesses which were not quite so successful; and the general impression left by it is a certain surprise that no thought of experiment seems to have entered the minds of these thinkers.

It is unnecessary to follow the development of this line of speculation in detail through the centuries, since until the coming of experimental methods, all such suggestions were a mere matter to conjecture, devoid of any real basis. They are recalled at the present day only because they happen to coincide with our modern views.

Coming to the seventeenth century, the essence of our theory of chemical combination between atoms is found in Boyle's *Sceptical Chymist.* The vocabulary is not that of the present day, yet the substitution of current terms for Boyle's " particles " and " corpuscles " would convert his text into a very fair description of a metathetic reaction.

The true founder of the modern theory was Dalton,[1] whose thesis may be summed up in two sentences. According to him, every element is composed of homogeneous atoms, the weight of which is constant. Chemical compounds are formed by the union of atoms of different elements in simple numerical proportions. As has already been shown in earlier pages, the former of these two propositions cannot now be upheld, since it is known that two atoms belonging to the element lead may differ from each other in atomic weight and also in stability.

The next step is due to Faraday,[2] who demonstrated the coincidence of the chemical and electrochemical equivalents of elements and thus established a numerical relationship between matter and electricity.

Twenty years later, a great advance in the theory of the subject was made by Frankland,[3] when he formulated our modern ideas on the valency of the elements and thus brought out clearly the relationship between the chemical equivalent and the atomic weight. On the basis thus provided, there grew up the modern views on the linking of atoms which find expression in our present-day graphic formulæ for the carbon compounds.

Another decade passed without contributing anything which calls for our attention. The periodic arrangement of the elements now known as the Telluric Helix made no impression on the scientific public of the day; and de Chancourtois' paper[4] was not even published by the French Academy, to which he submitted it in 1862. Almost contemporaneously, Newlands[5] suffered an even worse fate in England, where his sketch of the Periodic System was received by eminent chemists with ill-

[1] Dalton, *A New System of Chemical Philosophy* (1808).

[2] Faraday, *Phil. Trans.*, 1833, **123**, 23; 1834, **124**, 77.

[3] Frankland, *Phil. Trans.*, 1853, **143**, 417.

[4] A translation of de Chancourtois' paper of 1862, is to be found in *Nature*, 1889, 41, 186; see also *Compt. rend.*, 1891, **112**, 77.

[5] Newlands, *Chem. News*, 1863, **7**, 70.

mannered jeers. Thus neither of these pioneers exerted any influence upon chemical thought at that period.

It was not until after the publication of Mendeléef's views [1] in 1869 and those of Lothar Meyer [2] in 1870, that any real interest was taken in the new ideas; and only when Mendeléef's predictions of 1871 had been fulfilled by the discovery of scandium, gallium, and germanium, did the chemical world as a whole accept the Periodic System as the true method of arranging the elements.

Meanwhile, in 1879, a new field was opened by Crookes' investigations of the passage of electricity through highly-evacuated tubes,[3] which led him to the discovery of the cathode rays and thus initiated the line of research culminating in the detection of the electron.

After this, discovery followed discovery, though at the time it seemed that the various investigations dealt with almost entirely unrelated subjects. In 1885, Balmer [4] published his formula for the lines in the hydrogen spectrum, and thus laid the foundation upon which, much later, Bohr was to build. In 1886, Goldstein [5] discovered the positive rays or Kanalstrahlen, and so paved the way for the later investigations of Thomson and Aston. The year 1887 is marked by the appearance of Arrhenius' paper [6] laying down the fundamentals of the ionic theory of dilute solutions, out of which arose our ideas of ions in general. Three years later, Rydberg [7] brought out his formula for spectral series containing the Rydberg constant, the calculation of which eventually furnished the most satisfactory evidence in favour of Bohr's ideas. In 1891, Stoney [8] gave the name *electron* to the quantity of electricity which is associated in the chemical atom with each bond and which passes in electrolysis for each chemical bond that is ruptured.

A new chapter in the history of the Periodic Table was opened in 1894 by Rayleigh and Ramsay's discovery of argon,[9] the

[1] Mendeléef, *J. Russ. Phys. Chem. Soc.*, 1869, **1**, 71, 229.
[2] Lothar Meyer, *Annalen (Suppl.)*, 1870, **7**, 358.
[3] Crookes, *Phil. Trans.*, 1879, **170**, 135, 641.
[4] Balmer, *Ann. Physik*, 1885, **25**, 80.
[5] Goldstein, *Sitzungsber. K. Akad. Berlin*, 1886, 691.
[6] Arrhenius, *Z. physikal. Chem.*, 1887, **1**, 631.
[7] Rydberg, *Phil. Mag.*, 1890, **29**, 331.
[8] Stoney, *Trans. Roy. Dublin Soc.*, 1891, **4**, 563.
[9] Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, A, 187

first of the inert gases; and in 1895 Ramsay isolated helium,[1] which was eventually to play so great a part in our knowledge of atomic disintegration. Röntgen[2] in the same year detected the X-rays, which also came to be associated intimately with our knowledge of radioactivity and which proved in the hands of Moseley to be the key to the order of the elements. And in 1896, Becquerel[3] discovered the phenomena of radioactivity.

These three years, 1894–6, must stand out as some of the most remarkable in the history of physics and chemistry; and it seems worth while to emphasise the magnitude and unexpectedness of the discoveries which they brought with them. In the first place, the inert gases of the atmosphere had a double importance: they not only gave to the Periodic Table a symmetry which it previously lacked, but in addition they disclosed an absolutely novel form of matter which had no chemical properties. In the physical field, the X-rays also furnished an example of the unexpected; for up to that time no one could have foretold that a radiation was possible which would pass undeflected through solid matter opaque to normal light. And the discovery of radioactivity was so surprising to the normal scientific mind that it was received in some quarters with more than a tinge of suspicion. Thus on all sides the older ideas were perforce being modified and a fresh atmosphere was gradually forming. At that time, however, no one could have foreseen how intimately these three discoveries were eventually to be associated in history; for on the face of things they gave no particular promise of the unifying process which was soon to become clear.

In 1897, yet another fresh line of research was opened. Thomson[4] and Wiechert[5] independently determined that the ratio of charge to mass for the negative ion in Crookes tubes was about 1800 times the ratio of charge to mass in the case of the hydrogen ion; and from this it was inferred that the mass of the electron must be only about 1/1800 of the mass of a hydrogen atom. Thus for the first time, experimental evidence was furnished to prove the existence of something which was many times smaller than the tiniest known atom; and with that

[1] Ramsay, *J.*, 1895, **67**, 1107.
[2] Röntgen, *Wurzberg. Ber.*, 1895, p. 137.
[3] Becquerel, *Compt. rend.*, 1896, **122**, 420, 501, 559, 689, 762, 1086.
[4] Thomson, *Phil. Mag.*, 1897, **44**, 298.
[5] Wiechert, *Verh. phys.-okon. Ges. Konigsberg*, 1897.

discovery, science broke into the sub-atomic field. The invention of " dust-counter " by C. T. R. Wilson [1] was another of the achievements of 1897. A year later, the positive ions in Crookes tubes came under examination [2]; and the measurement of the ratio between charge and mass in their case opened up the new road which led to the mass-spectrograph and the establishment of Aston's Whole Number Rule.

At this stage, the centre of interest was transferred for a time to the novel science of radioactivity. In 1899, the Curies [3] discovered the then mysterious phenomenon of induced activity, which is now known to be due to the disintegration products of radioactive matter; and thus the initial impetus was given to the researches which ended in the unravelling of the whole complex system of the radioactive series. In 1899, too, Giesel [4] discovered the β-rays and proved their analogy with the cathode rays of the Crookes tube; whilst in the same year, Rutherford [5] found that uranium preparations emitted the less penetrating α-rays as well as the β-rays.

The year 1900 was equally fruitful. Following on the work of Owens,[6] Rutherford [7] discovered the first radioactive gas: the emanation of thorium. Crookes [8] published his investigations of uranium and uranium-X, which gave a definite clue to the rationale of radioactive processes. And Mme. Curie,[9] from her investigations on polonium, was led to the suggestion that the α-rays were stream of particles which lost energy in their transit through material bodies.

In a lecture at the end of the same year, Planck first brought forward the theory associated with his name.[10] He assumed that oscillating electrons absorb or emit energy in a discontinuous manner such that the gain or loss of energy by the particle is proportional to the frequency of the particle's vibration; and, further, that the energy can be absorbed or emitted only in

[1] Wilson, *Phil. Trans.*, 1897, **189**, A, 265.
[2] Wien, *Ann. Physik*, 1898, **65**, 440.
[3] P. and Mme. Curie, *Compt. rend.*, 1899, **129**, 714.
[4] Giesel, *Ann. Physik*, 1899, **69**, 834.
[5] Rutherford, *Phil. Mag.*, 1899, **47**, 116.
[6] Owens, *Phil. Mag.*, 1899, **48**, 360.
[7] Rutherford, *Phil. Mag.*, 1900, **49**, 1.
[8] Crookes, *Proc. Roy. Soc.*, 1900, **66**, 409.
[9] Mme. Curie, *Compt. rend.*, 1900, **130**, 76.
[10] Planck, *Ann. Physik*, 1901, **4**, 553.

integral multiples of a "quantum." These ideas lead to the assumption that there is a natural constant—Planck's Constant of Action, h—which when multiplied by the frequency of the electron under consideration, gives a product expressing the value of the energy which can be absorbed or emitted by that electron at one operation. This work of Planck furnished part of the basis upon which Bohr erected his hypothesis of atomic structure.

A year later, Strutt [1] put forward the modern conception that the α-ray consists of a stream of positively-charged particles akin to the positive rays of the Crookes tube; while Villard [2] established the presence of a third constituent of the Becquerel rays—the γ-rays—and showed that this type was analogous to the X-rays. Thus within three years a complete parallelism has been traced between the phenomena of radioactivity on the one hand and the behaviour of Crookes tubes on the other; and two lines of investigation merged into common ground and drew help from each other.

From this point onward, almost every year brought at least one important discovery. In 1903, Crookes [3] found that the impact of α-rays upon a zinc sulphide screen produced a series of isolated scintillations instead of a general glow. At the time of its publication, this discovery showed no promise of the wonderful applications which it was to find later in the hands of Rutherford, and for a while its chief interest was found in its use in the Crookes spinthariscope, which was regarded as a mere scientific curiosity. The main event of 1903 was the publication of the Disintegration Theory of Rutherford and Soddy,[4] which was put forward as a result of their detailed study of the radioactivities of thorium, radium, and uranium. Within seven years of the initiation of radioactive research, the key to the problem had been found. And in the same year came also the clinching proof of the theory, which was yielded by Ramsay and Soddy's discovery [5] that helium was produced by the disintegration of radon.

Measurements of the ranges of α-particles in various media

[1] Strutt, *Phil. Trans.*, 1901, **196**, A, 507.
[2] Villard, *Compt. rend.*, 1900, **130**, 1010, 1178.
[3] Crookes, *Proc. Roy. Soc.*, 1903, **71**, A, 405.
[4] Rutherford and Soddy, *Phil. Mag.*, 1903, **5**, 576.
[5] Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, A, 204.

were made by Bragg and Kleeman [1] in 1905; while in 1906 Rutherford [2] detected the scattering effect which occurs when α-particles are shot into a material body, and thus inaugurated a line of research which in his own hands was eventually to lead to the controlled disintegration of the elements.

In 1907, the field of radioactivity again provided the important discoveries. Boltwood [3] detected the new radio-element ionium and showed that it was the parent of radium; and in this way the first step was taken in clearing up the relations between radium and uranium. Another research of the same year was even more fundamental in its eventual results. McCoy and Ross [4] observed that thorium and radiothorium were chemically inseparable, a fact which eventually furnished the basis of the theory of isotopes.

In the succeeding twelvemonth, the centre of interest shifts back to the more purely physical field. Regener [5] was the first experimenter to count the scintillations produced by the impact of α-particles; whilst Rutherford and Geiger devised the electrical method of counting the number of particles, and were thus able to prove that each scintillation was produced by the impact of a single α-particle. This led to the calculation of the charge carried by the α-particle,[6] which was found to be $9{\cdot}3\times10^{-12}$ units, *i.e.* numerically equal to twice the charge on the electron, though of opposite sign.

The year 1908 was marked by one of the most important discoveries of recent years, for Barkla and Sadler [7] detected the existence of the characteristic X-rays which, in the hands of Moseley, were eventually to prove the key to the ordinal numbers of the chemical elements.

With 1909 came the proof by Rutherford and Royds [8] that the α-particle was a helium atom; so in this year our knowledge of the nature of that mysterious entity was completed and it was shown to be a helium atom carrying two positive charges.

[1] Bragg and Kleeman, *Phil. Mag.*, 1905, **10**, 318.
[2] Rutherford, *Phil. Mag.*, 1906, **11**, 166.
[3] Boltwood, *Amer. J. Sci.*, 1906, **22**, 537; 1907, **24**, 370.
[4] McCoy and Ross, *J. Amer. Chem. Soc.*, 1907, **29**, 1709.
[5] Regener, *Verh. deutsch. Phys. Ges.*, 1908, **19**, 78, 351.
[6] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, **81**, A, 162.
[7] Barkla and Sadler, *Phil. Mag.*, 1908, **16**, 550.
[8] Rutherford and Royds, *Phil. Mag.*, 1909, **17**, 281.

In 1911, the honours of discovery were fairly shared between the fields of physics and radioactivity. Soddy [1] recognised the existence of isotopic forms of matter, and thus brought to light the possibilities involved in the case of a chemically homogeneous material made up of physically heterogeneous atoms. At the same time he [2] gave the true interpretation to the effect of an α-ray change in a radio-element, and thus laid the foundation of the greater generalisation which was to follow soon after. On the experimental side, C. T. R. Wilson [3] invented his apparatus for photographing the track of α-particles through gases, an instrument which in later years has actually produced pictures of the atomic disintegration process.

On the purely physical side, 1911 was marked by the publication of Thomson's early results in the analysis of positive rays [4] which showed that a new analytical method of extreme refinement had been placed in the hands of investigators. On the theoretical side, physics contributed the idea of the atomic nucleus which was put forward by Rutherford [5] in order to account for the phenomena observed during the scattering of α-particles in their passage through matter.

By 1912, the idea of isotopy had gained a firm footing; and the proof given by Russell and Rossi [6] that the spectra of ionium and thorium were identical, furnished strong support to the theory. In the same year came the experiments of Friedrich, Knipping, and Laue [7] on the diffraction of X-rays by crystals, which paved the way for the fundamental discoveries of Moseley.

And now the pace of discovery was quickening to a speed which has seldom been surpassed in the whole history of science. Almost every month brought fresh light upon the nature of the elements and the atom; and at times it became difficult even to co-ordinate the various branches of research, so rapidly did one new thing follow upon another. The years immediately preceding the war stand out in retrospect as a period when an almost

[1] Soddy, *Chemistry of the Radio-elements*, 1911, p. 29.
[2] Soddy, *ibid.*, 1911, p. 30.
[3] C. T. R. Wilson, *Proc. Roy. Soc.*, 1911, **85**, A, 285.
[4] Thomson, *Phil. Mag.*, 1911, **21**, 225; see also *Nature*, 1911, **86**, 466.
[5] Rutherford, *Phil. Mag.*, 1911, **21**, 669.
[6] Russell and Rossi, *Proc. Roy. Soc.*, 1912, **87**, A, 478.
[7] Friedrich, Knipping, and Laue, *Sitzungsber. bayr. Akad. Wiss.*, 1912, p. 303.

convulsive effort was being made to clear up the mysteries which had puzzled the brains of humanity for over twenty centuries. And the success attendant upon the effort was commensurable with the labour. Whatever may be said about the deficiencies of the pre-war world, the scientific branch has no reason to be ashamed of the work achieved just before the wrench came which diverted its energies into unexpected channels.

It is doubtful if any parallel can be found to the events of 1913. In that year, Fleck's investigations [1] led to the identification of the chemical character of the individual radio-elements; and thus the whole complicated series of disintegration products was separated into its proper grouping in the Periodic Table. Almost immediately, the meaning of the β-ray change was brought to light simultaneously and independently by four investigators [2]; and this, supplemented by Soddy's earlier discovery of the meaning of the α-ray change, and the isotopes, gave the clue to the rationale of the whole process of atomic disintegration. At a single stroke, the complex tangle of the radio-elements was unravelled; and the inherent simplicity of the radioactive series was at last made clear.

The speculations of van den Broek [3] led to the conception of ordinal numbers for the elements corresponding to their positions in the Periodic Table; and the suggestion that these numbers represented the totals of the electrons circulating about the atomic nucleus has proved one of the most fruitful ideas in the history of atomic structure.

The publication of Moseley's investigations [4] of the characteristic X-rays of the elements, which were rendered possible by the earlier work of Bragg on X-ray wave-lengths, supplied an experimental basis for van den Broek's ideas. The relationship traced by Moseley between the X-ray spectra and the atomic numbers of the elements, placed the Periodic Table upon a fresh basis. The atomic weights disappeared from their old position of pre-eminence in the problem of elemental classification;

[1] Fleck, *J.*, 1913, **103**, 351, 1052.

[2] Hevesy, *Physikal. Z.*, 1913, **14**, 49; Russell, *Chem. News*, 1913 **107**, 49; Soddy, *ibid.*, 97; Fajans, *Physikal Z.*, 1913, **14**, 131, 146.

[3] Van den Broek, *Physikal Z.*, 1913, **14**, 33.

[4] Moseley, *Phil. Mag.*, 1913, **26**, 1024.

and a new criterion, hitherto undreamed of, took their place without opposition.

Further, 1913 saw the publication of Bohr's theory of spectra,[1] which, whether it be true or not, has certainly exercised a weighty influence upon the minds of physicists and which, in any case, has demonstrated that the mysterious Rydberg constant can be calculated with great accuracy on certain assumptions.

Finally, the same year brought the publication of Thomson's investigations [2] on certain gases by the positive ray method.[1] The isotope of neon was detected and the triatomic form of hydrogen was also discovered. Thus at a stroke, two new things came into view. On the one hand, the idea of isotopy ceased to be limited to the field of the radio-elements and grew into a generalisation extending over the whole of the known elements. On the other hand, the keystone seemed to be removed from the older ideas of valency; since if H_3 existed, then the fundamental monovalent element could no longer be regarded as having only a single valency.

In 1913, Soddy [3] predicted from radioactivity considerations that the atomic weight of lead found in uranium minerals would differ from that of lead derived from thorium minerals; and in 1914, he and Hyman [4] showed that this was the case. Other workers later confirmed this result; and no doubt was left in the question. Thus the last prop was knocked away from the old conception that the chemical atomic weight was a physical constant; and the atomic numbers were left as the true guide in the ordinal grouping of the elements. Soddy's prophecy was almost as bold as that made by Mendeléef in the case of undiscovered elements; and its theoretical importance was much greater than that attached to the Russian's prediction.

The final justification of Soddy's theory of isotopy was also given in 1914 by the discovery, made by Rutherford and Andrade,[5] that two istopes had identical X-ray spectra; for experimental proof was thus furnished from the physical side that their atomic numbers were the same.

The year 1914 saw also the opening of a fresh line of research

[1] Bohr, *Phil. Mag.*, 1913, **26**, 1, 476, 857.
[2] Thomson, *Proc. Roy. Soc.*, 1913, **89**, A, 1.
[3] Soddy, *Ann. Report*, 1913, **10**, 269.
[4] Soddy and Hyman, *J.*, 1914, **105**, 1402.
[5] Rutherford and Andrade, *Phil. Mag.*, 1914, **27**, 854.

which was to culminate in the experimental proof of controlled atomic disintegration. By bombarding hydrogen with α-particles, Marsden,[1] following the theoretical reasoning of Rutherford,[2] detected the existence of recoiling hydrogen atoms which had been struck by the α-particles.

At this point, the survey reaches the opening of the war period; and for four years the British workers had to turn their energy into channels remote from pure research. The result is to be seen in the almost complete sterility of the subject during the duration of hostilities. Only in the undisturbed atmosphere of the United States was it possible for purely scientific problems to be considered at leisure.

In 1916, G. N. Lewis [3] put forward his cubical atom theory with its concomitant view that the valency bond could best be represented by a pair of electrons held in common by two united atomic systems. This paper at first passed almost unnoticed in the stress of the war period and only came to its own with the return of peace conditions.

In 1918, the recognition of the isobares by Stewart [4] furnished a complement to Soddy's identification of the isotopes; and in 1919 Soddy [5] fused the two conceptions into a system which permits the complete classification of all the different types of atom known to exist at present.

In 1919, also, Langmuir,[6] using the ideas of G. N. Lewis as a basis, developed upon them an extended theory of atomic structure, which in its turn was modified by Bury [7] in 1921.

On the experimental side, 1919 was marked by the advent of Aston's mass spectrograph, which opened up a new line of research culminating in the final downfall of the "chemical atomic weight," which was now proved to be merely an average value with no fundamental importance.

Finally, 1919 saw the opening of Rutherford's investigations [8] on the controlled disintegration of the elements, which have led

[1] Marsden, *Phil. Mag.*, 1914, **27**, 824.
[2] Rutherford, *Phil. Mag.*, 1914, **27**, 488.
[3] G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.
[4] A. W. Stewart, *Phil. Mag.*, 1918, **36**, 326.
[5] Soddy, *J.*, 1919, **115**, 1.
[6] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 868.
[7] Bury, *J. Amer. Chem. Soc.*, 1921, **43**, 1602.
[8] Rutherford, *Phil. Mag.*, 1919, **37**, 571.

to an extension of our knowledge of the constituents of the atomic nucleus.

Before closing this chapter, it seems of interest to direct attention to one or two questions which still await a solution.

The Periodic Table, despite the great advance in our knowledge of the factors which underlie it, still presents a number of peculiarities for which no explanation is available. In the first place, it furnished no obvious reason for the abnormality of boron, which is trivalent in its halogen compounds, but quadrivalent in its hydrogen derivatives. The magnetic model atom of Marsh and Stewart * offers a suggestion that the nuclear constructions of boron and carbon may be analogous to each other in certain respects; and possibly this factor may play some part in the problem: but at present nothing definite is known with regard to the origin of the boron peculiarities.

Again, the behaviour of glucinum and magnesium seems to require an explanation. With the exception of the Zero Group and Group VIII, the families of the Periodic Table are subdivided into two sections, to one of which the pair of elements in the first two series can be attached without too much difficulty; by Group II is split up into three sections: glucinum and magnesium; the alkaline earth metals; and the zinc-cadmium-mercury triplet. For example, although all the alkaline earth metals form hydrides, no such derivatives of glucinum and magnesium have been obtained; on the other hand, both these metals yield alkyl derivatives. This behaviour suggests a resemblance to the zinc-cadmium-mercury triplet; but when an attempt is made to trace this alliance further into the chemical properties of the substances, it fails owing to the marked differences which come to light at once, as any text-book of analytical chemistry will show.

The formation of hydrides and of alkyl derivatives exhibits peculiarities of some interest. Calcium, for example, in Group IIA forms the hydride CaH_2, but yields no alkyl derivative; whereas zinc, like the rest of Group IIB, has no known hydride, but gives rise to zinc methyl, $Zn(CH_3)_2$. The members of the complementary Group VIB, on the other hand, form both hydrides and alkyl derivatives with ease; whilst members of Group VIA form neither hydrides nor alkyl derivatives.

* See p. 157.

The halogen group presents an unsolved puzzle when the combination between its members and oxygen is examined. Why do fluorine and bromine yield no oxides, while chlorine and iodine each gives rise to more than one oxide? Fluorine and bromine belong to the first short and first long series respectively, whilst chlorine and iodine are members of the corresponding second series; and possibly this may have some connection with these chemical peculiarities; but the point is still obscure. A somewhat similar case seems to be that in which, as in the case of titanium, the chloride is known, but the fluoride has not yet been obtained.

Thallium is one of the greatest troubles in the Periodic System, owing to the similarities in behaviour which it displays with regard to elements situated far away from it in the tabular scheme.[1] It has apparent analogies with copper, the alkali metals, silver, and gold; yet none of these is justified by its place in the Table.

An interesting problem presents itself when the Table is looked at in a broader manner. The main characteristic of the Periodic Table is, to state a truism, that it is a periodic arrangement. Now the sequence of the atomic numbers is simply the sequence of a series of successive integers, and this, of course, shows no sign of periodicity. The family relationships of the Periodic Table, then, have no direct connection with the atomic number—*i.e.* with the atomic nucleus. Therefore the origin of the periodicity must lie in the outer sphere of the atom, as is assumed in the modern atomic theories. But atomic volume is a periodic property, as can be seen from the ordinary Lothar Meyer curve of atomic volumes. Therefore the atomic volume must be controlled by the nature of the outer sphere of the atom. This is an inference of no little interest, since the atomic volume variations correspond to the variations in many physical properties of the elements. The fact that the atomic volume seems to be a natural constant—since it is the same for all isotopic atoms—suggests that some thought expended upon this matter might yield results of interest. Unfortunately the determinations of the atomic volumes have not yet been made at corresponding temperatures, so that with the available data only the roughest results can be expected.

[1] See Stewart, *Some Physico-chemical Themes*, p. 348.

When we turn from the Table to the atom, a number of other unsolved problems suggest themselves at once. As Aston has pointed out, certain masses do not appear in the atomic series * and there must obviously be some underlying reason for this peculiarity. Again, no explanation has been offered for the fact that lead forms the end-point upon which all the radioactive series converge. The element lead is not the upper limit of atomic stability, since bismuth has a higher atomic weight and yet is perfectly stable; nor is lead the lowest element in the radioactive group, for radioactive isotopes of thallium are known. There must be some reason for No. 82 being, so to speak, the dumping-ground for the residues of radioactive change; but, so far, the cause of the phenomenon has escaped us.

Then again, whilst the isotopes are numerous, the isobares are comparatively rare; and no explanation of this has been suggested. Possibly a large number of isobaric isotopes exist among the non-radioactive atoms, since none of the present methods would suffice to detect their existence. Or again, as Aston has suggested, there may be a limit to the complexity of the atomic nucleus which would prevent the stable existence of more than a few forms.

The inter-relationship between surplus nuclear charge, the system of outer electrons, and the chemical properties of atoms appears to be a subject which will repay consideration in the future, for already it is possible to note a number of interesting points which await solution. The influence of the surplus nuclear charge can be seen by considering cases of systems which may be designated as iso-electronic, since they contain equal numbers of electrons. For example, the isobaric atoms of argon, A^{40}, and calcium, Ca^{40}, both contain a total of 40 electrons; but since they differ in chemical individuality, it is clear that the chemical nature of the atom does not correspond to the total number of electrons in the atom. Further, the argon atom A^{40} and the calcium ion derived from Ca^{40} both contain 18 electrons in the outer sphere; and yet they differ in chemical individuality: so that evidently chemical individuality does not reside in the outer zone of the atom. This leaves only the nucleus as the origin of chemical nature. But chemical individuality and X-ray spectra are believed to go hand in hand; and yet the X-ray

* See p. 143.

spectra are supposed to take their rise in the outer sphere of the atom. It has been pointed out in an earlier chapter that the ordinary emission spectrum of hydrogen is apparently the same as the X-ray spectrum of the element; and if Bohr's views be adopted, this spectrum must have its origin in the single electron of the hydrogen atom. But this electron is obviously an "outer sphere" electron, since it is removed from the atom on ionisation. Thus there seems no escape from the inference that chemical individuality and X-ray spectra go hand in hand and yet originate in different parts of the atomic structure.

Again, the ions of quadrivalent uranium and of thorium show a well-marked similarity in some of their chemical properties although the atomic numbers of the elements are different. It seems possible that this resemblance might be traced to the outer zones of the two systems. Zinc and divalent germanium offer another example of the same type, for although the elements themselves lie in different columns of the Periodic Table, the zinc and germanous derivatives show quite distinct similarities in some respects.

The development of stereochemical ideas has now brought us to a space-formula for the atom and has led to the utilisation of solid figures in our symbolism. There are only five regular solids: the tetrahedron, the cube, the octahedron, the dodecahedron, and the icosahedron. The tetrahedron was used by van 't Hoff and Le Bel to account for the optical activity of compounds containing asymmetric carbon atoms; the cube has been employed by G. N. Lewis in his valency theory; the octahedron has been pressed into service by Collie for his benzene space-formula and by Werner in his explanation of the isomerism of complex salts. Thus three out of the five regular solids have already proved to be keys to chemical problems; and it seems not unlikely that the remaining two may yet find a place among our symbols when further advances are made. Certainly it will be well to bear their properties in mind when more complex enigmas of chemistry come before us.

In closing this chapter, a few words may be devoted to the elements, not with any idea of supplying a complete and concise definition of elementary matter, but rather with the object of showing some of the difficulties which beset any one who attempts to deal with the problem.

At the outset we are faced with the obvious difference between a chemical element on the one hand and homogeneous matter on the other hand. Let us consider the second of these ideas to begin with, and see whether our present knowledge and experimental methods offer any hope of a definition which will be of practical service. Since matter is atomic, it is evident that homogeneous matter must be composed of a set of atoms absolutely identical with each other in all respects; and for the sake of simplicity we may term such a sample of matter an "element." This "element," clearly, is not the same as one of our chemical elements, since it may include materials of the most varied descriptions. For example, the chemical element No. 90 includes no less than six forms of matter the atoms of which differ from each other in stability, mass, and mode of disintegration. If an "element" is to be homogeneous, then thorium, radio-actinium, radiothorium, ionium, uranium-Y, and uranium-X_1 must each be regarded as a single "element." Thus the initial simplicity of the chemical elements becomes lost in a mass of subdivisions; and although we gain in exactitude of classification, we pay a price for it in a loss in clarity.

Nor is this the only difficulty, for on going further we reach the case of the isobaric isotopes which suggest fresh problems. Here we have to deal with two sets of atoms which have identical chemical properties and identical atomic weights. In the case of radium-D and radium-Ω', it is simple enough to prove that there is no complete identity, since, radium-D ejects electrons, whereas radium-Ω' is stable. But suppose that we examine thorium-Ω' and thorium-Ω'' in order to determine whether they are identical or not. Here there are no radioactive properties to guide us; and it is impossible to say whether the atom of thorium-Ω' is or is not identical with the atom of thorium-Ω''. It seems probable that they differ from each other; but our experimental methods have not reached the stage of refinement which will enable us to settle the problem. Thus if we attempt to push our mental analysis to its limits in this field, we find that we cannot even classify the forms of matter with which we are acquainted; and therefore at the present day the attempt to recognise the "element" is fruitless. It is easy enough to define homogeneous matter in terms of the atomic theory as now understood; but of what value is the definition when it cannot

be used in practice? More, we do not even know how many of these chemically identical isobares exist; for our present methods of separation, whether physical or chemical, fail to isolate them from each other. For all we can tell, they may abound among the ordinary chemical elements.

These examples are sufficient to prove that the definition of completely homogeneous matter is at present a pure academic exercise, since we have no means of determining whether a given sample of matter is homogeneous or not. In some cases it can be shown to be heterogeneous; but even after all our tests have been applied, we cannot assure ourselves of its complete homogeneity.

Turning back to the chemical element, we meet with a conception much more fruitful than that of homogeneous matter. It provides the basis of the great generalisation embodied in the Periodic Table; and it segregates matter into groups which appear to have more in common than the mere chemical properties of the members. It is rather surprising to note that at the very time when Rutherford's work has destroyed the claim of certain chemical elements to the very name of element under Boyle's original definition, our ideas of the chemical element have survived and even become more definite than before. We have been forced to recognise that the limit of separation established by chemical means constitutes a real frontier in the classification of matter, and is not merely a halting-line which may be overstepped with an advance in our practical knowledge. The ninety-two different chemical elements are fundamental realities and not simply provisional congeries which might ultimately require further sorting out.

It is this disappearance of the "provisional" factor in the conception of the chemical element that distinguishes our modern views from those which have gone before. We may not be able to put our conception into simple and concise language, but none the less we have gained an idea of the chemical elements which pictures them as divided from each other as sharply as the vertebrates are divided from the invertebrates or the mammals from the non-mammals. And just as within the vertebrate class there are fishes, reptiles, birds, and mammals, so within the scope of the chemical element lie the groups of isotopic atoms differing from each other while still retaining the general

chemical identity. In these mysterious ninety-two groups of atoms there is something manifest which, even amid the incessant transformations of radioactive decay, remains permanent and fundamental.

The present generation has seen a wonderful change in the face of chemistry. Dogma after comfortable dogma has been overset; most of the old foundations have proved rather sandy when the spade went deep enough: but on the older ruins a new edifice of theory has been erected, so well designed and securely buttressed by experiment that it seems destined to stand for our time at least. Yet in that very completeness there lurks the possibility of a recurrence of the old danger; and it is to be hoped that when the time of decay eventually arrives, these present-day ideas will not be regarded as infallible. Dogmas have no proper place in the scientific field; and when they are allowed to flourish, their only result is the stifling of that spirit of inquiry which is the fundamental quality of the scientific mind.

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